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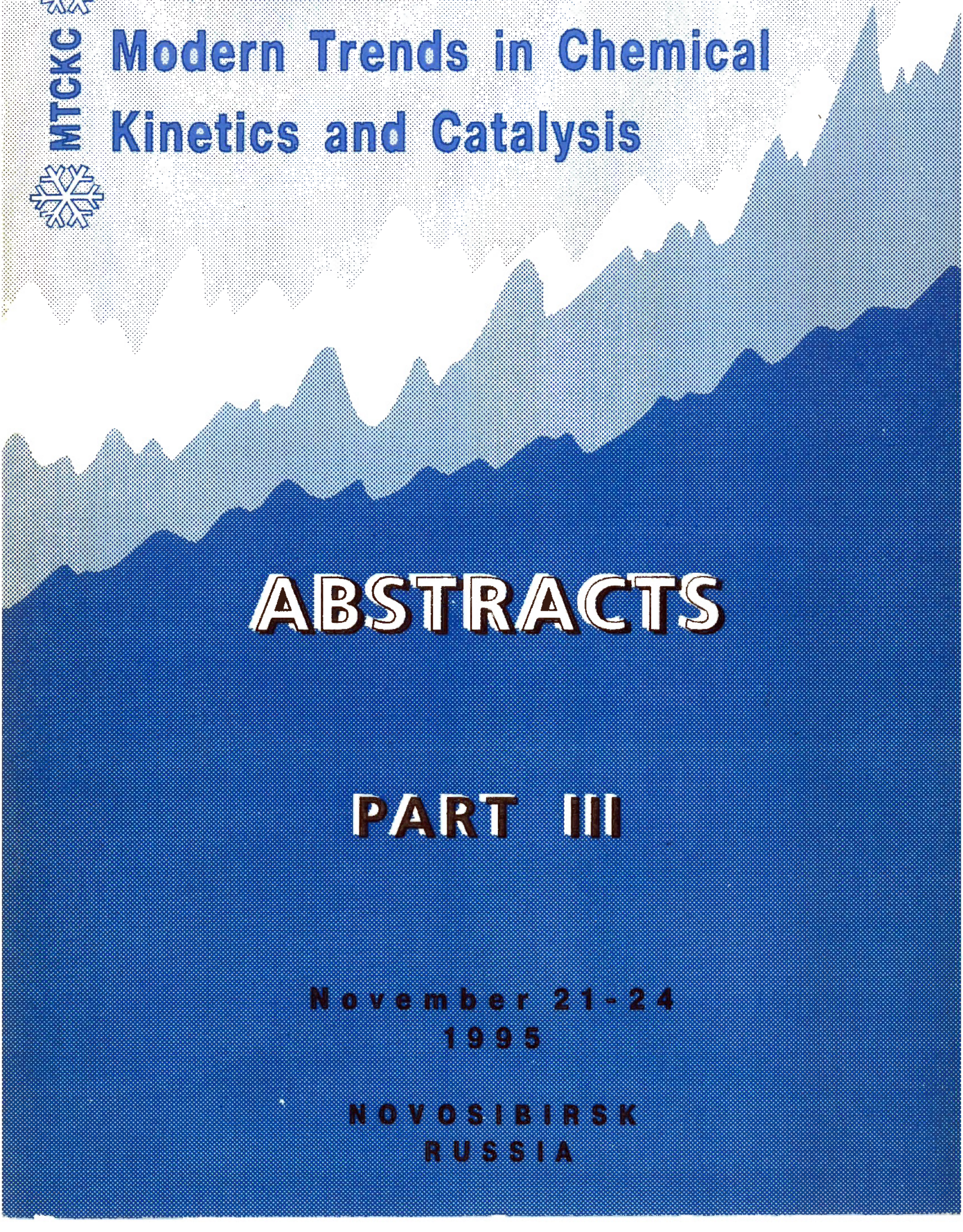

ABSTRACTS

PART III

November 21-24
1995

NOVOSIBIRSK
RUSSIA

SIBERIAN BRANCH OF THE RUSSSIAN ACADEMY OF SCIENCES

BORESKOV INSTITUTE OF CATALYSIS

INSTITUTE OF CHEMICAL KINETICS AND COMBUSTION

SCIENTIFIC COUNCIL ON CATALYSIS AND ITS INDUSTRIAL
APPLICATION OF RAS AND MINISTRY OF SCIENCE OF THE RUSSIAN
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SCIENTIFIC BOARD ON CHEMICAL KINETICS AND STRUCTURE, RAS

The Second Conference
"Modern trends in chemical kinetics and catalysis"

ABSTRACTS

PART III

Novosibirsk - 1995

УДК 66.097.3
542.97
541.124

The Organizes express their gratitude to the sponsors for financial support:

International Association for the Promotion of Cooperation with Scientists from the Independent States of the Former Soviet Union (INTAS)
Russian Foundation for Basic Research (RFBR)
Soros International Science Foundation (ISF)

KINETICS

POSTERS

Water exchange on Mn^{2+} adsorbed on SiO_2 (Aerosil 300)

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The water exchange on Mn^{2+} adsorbed on SiO_2 (Aerosil 300) was studied in situ by the temperature dependence of the ^{17}O relaxation of the solvent H_2O. The relaxation rate of ^{17}O in H_2O is strongly influenced by the exchange of H_2O in the coordination sphere of Mn^{2+} in solution. This relaxation and its temperature dependence changes strongly, if Mn^{2+} is adsorbed on SiO_2. The number of exchanging H_2O decreases from 6 to 4 per Mn^{2+} and exchange rate is accelerated by a factor of 2 to 3. No trans effect of the surface oxygen is observed. The four H_2O in the coordination sphere exchange with the same rate. Interpretation of the results by the method of Swift and Connick (1) yields the following activation parameters (values for Mn^{2+} in solution (2) in brackets) k_{298} 7.3(2.1) 10^7 s^{-1}, ΔH^* 22(35.9) $kJmol^{-1}$, ΔS^* -20(5.7) $Jmol^{-1}$, T_{1e}^{-1} 5(80) 10^6 s^{-1}. The effect increases with increasing surface coverage however not proportional to the Mn^{2+} adsorbed. The analyses of the deviation from linearity shows, that the latter is caused by a change in the electronic relaxation time of Mn^{2+}, which is due to a fast movement of the Mn^{2+} at the surface or a heterogeneous distribution of the adsorbed Mn^{2+}. The measurements indicate in addition, that the relaxation behaviour of the ^{17}O is a very sensitive probe for any changes of the surface structure of SiO_2.

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This work was supported by COST Action D5, project 00002 92

PPK-2

TWO-STAGE OXIDATION OF MONOGERMANE BY OXYGEN

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Decenerate-branched chain character was suggested for the gas phase reaction of monogermane (GeH_4) with O_2 in [1].However later experimental data were obtained which are characteristic for branching-chain processes [2].This reaction exhibits a number of features which don't agree with the conceptions commanly accepted until recently in the theories of chain processes and heterogeneous reactions.

In the present thesises experimental data are presented on observation and investigation of two-fold selfignition of GeH_4 with O_2 in confined volumes.The investigation was carried out on a static vacuum set-up. A gived portion of the reacting mixture was rapidly admitted into the thermostated and evacuated quarz vessel (diameter 4,0cm lenth 20cm)

It is seen in Fig.1,that in certain region of initial pressures (Po) the raction proceeds in two stages. The reaction rate and luminescence intensity smothly decrease the Po being lowered to zero.Meanwhile, the dependences of reaction rate and luminescence intensity on Po demonstrate the sharp crytical character in second ignition.

Below 3,6 Torr, only one stage may be observed. If Po is above this pressure, also the second selfignithon is detected. Its induction period increases the initial pressure being rised in the region of 4,5-6,1 Torr. The further rise of Po leeds to the abrupt drop of the induction period,and at the pressures above 7 Torr the two stages practically merge to one. A the same time the value of reaction rate in second ignition increases the pressure being rised in all range of its values.

The two-fold selfignithon regime is observed only at temperatures of 340-360°C for the mixtures of abovementioned composition, if the reactor is treated by the reaction at 300-360°C.In freshly washed reactor the reaction follows as one stage and practically without any induction period.These features are similar to those of silane oxidation [3].

The kinetic investigations of the pressure changes and the reaction components by gase chromatography in one-stage regime (the second stage is absent) show that the reacton occures by selfacceleration until 10% conversion is attvined and then ceases at convertions less then 30%.The induction period of hydrogen formation (10s) is significantly greater than that of pressure drop (1-2s).

The fact of two-fold selfignition and the dependence of the phenomenon on the initial conditions point to significaut change of main elementary reactions in course of the process.

The inwestigation was supported by RFFI N.93-03-18047 and ISF NL5000.

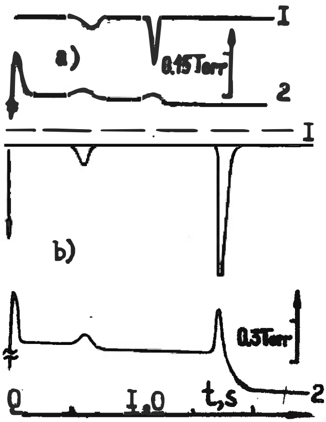

Fig.1

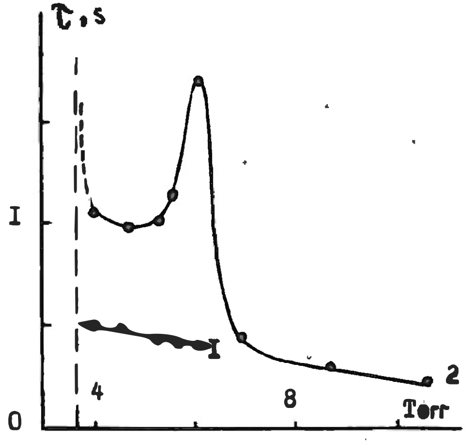

Fig.2

Fig.1. The oscillograms of chemiluminescence (1) and pressure (2) at initial pressures (Torr): a-4.6; b-6.1

Fig.2.The pressure dependance of induction periods of first(1) and second(2) selfignition of the mixture:10 % GeH_4+90 % O_2

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PPK-3

MECHANISM AND KINETICS OF PHOTOCHEMICAL DECOMPOSITION OF XENON TETROXIDE. REACTION OF XENON TETROXIDE WITH HYDROGEN.

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Xenon tetroxide is thermodynamically unstable (ΔH = 153.5 kcal/mol), although the vapor of it can be handled rather safely. At its decomposition 34-152 kcal/mol is released depending on the channel of the process. That is enough, in principle, to create oxygen atoms and molecules in excited electron or vibrational states. One can wait also that due to some relative weakness of Xe-O bond conditions can be created for effective sustaining of nonequilibrium states during the macro-conversion of corresponding mixture. At the same time, as we know, no investigations of XeO_4 gas-phase reactions have been carried out yet.

The goals of the investigation were: 1) to find out the mechanism of XeO_4 photolysis under UV-radiation in 200-300 nm range; 2) to obtain the quantum yield of formation of oxygen atoms at photodissociation of XeO_4 molecules; 3) to determine quantitative characteristics of secondary processes of photolysis; 4) to study XeO_4-H_2 mixture stability, and 5) to obtain the main general rules of "dark" reaction of XeO_4 with H_2 at dilution by neutral gases.

The investigations were conducted by a spectral photometrical method. Xenon tetroxide was obtained from the reaction $Na_4XeO_4 + 2H_2SO_4 \dashrightarrow 2Na_2SO_4 + XeO_4 + 2H_2O$. To determine the quantum yield of creation of atoms of oxygen, Φ, the photolysis experiments were run in the presence of O_2 (its pressure was up to 1 atm). The essence of the experiments was to convert oxygen atoms without losses into the spectroscopically registered ozone molecules, using the reaction $O + O_2 + O_2 \dashrightarrow O_3 + O_2$. From analysis of the experiments it was revealed that $\Phi = 3.6 \mp 0.4$. It follows that from all possible channels of photodissociation of XeO_4 molecule the dominating is the channel in which four atoms of oxygen are formed. Maintaining conditions when the process $O + XeO_4 \dashrightarrow O_2 + XeO_3$ competed with the ozone creation reaction, we have estimated the rate constant of this process $k < 4.5\ 10^{-16} cm^3 s^{-1}$ which was occurred to be more an order lower than the rate constant of the similar reaction of oxygen atoms with ozone molecules. As distinct from ozone, photodissociation of which gives electronically excited atoms $O(^1D)$ within 95%, at photodecomposition of XeO_4 no marked quantity of oxygen atoms in ^1D state was observed.

The experiments on studying of XeO_4-H_2 reaction have shown that 1) it is possible to prepare the mixtures stable enough in a wide range of XeO_4 and H_2 concentration ratio; 2) the velocity of such a reaction is about two order higher the velocity of thermal decomposition of XeO_4 that testifies to the chain mechanism of the reaction; 3) it has been discovered a strong ingibitory effect of CO_2 molecules on the reaction. In our opinion it is caused by the fact that CO_2 molecules, being the effective accepters of vibrational excitation, depress the reactions involving the vibrationally exited particles.

The mechanisms of photochemical decomposition of XeO_4 and the reaction of XeO_4 with H_2 are proposed, which consistently explain the experimental results.

PPK-4

^{13}C-SNP Investigation of Benzoin Photolysis in Micellar Solution.

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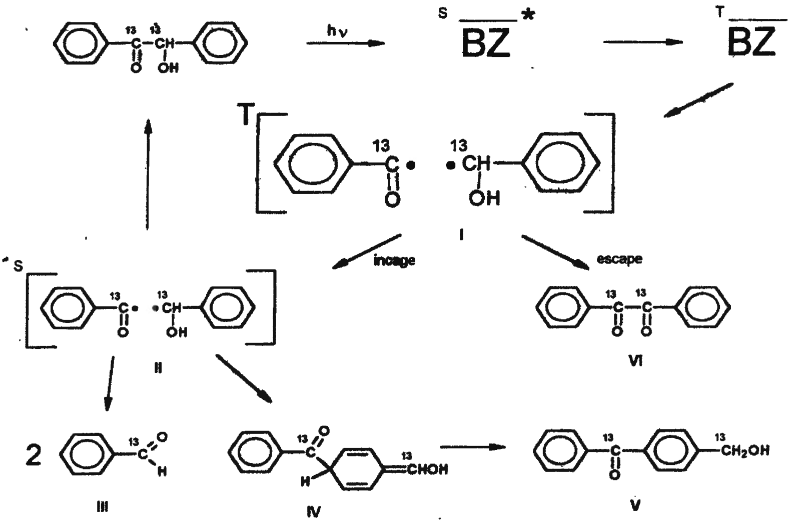
The technique of stimulated nuclear polarization (SNP) records ESR spectra of transient radical pairs (RP's) by monitoring the nuclear spin polarization in diamagnetic products, which has been formed due to the saturation of the RP's ESR transitions [1]. In the last time the SNP method has been employed to obtain parameters of these species in micelles. The analysis of SNP spectra as well as SNP kinetics obtained by time-resolved version of SNP (TR SNP) delivers precise information concerning diffusional and chemical properties as well as the spin dynamics of micellized geminate RP's [2]. In this study the SNP method has been applied to investigate the behavior of RP's formed during photolysis of ^{13}C labeled benzoin (1,2-diphenyl-2-hydroxyethanone-1,2-^{13}C) in sodium dodecylsulfate (SDS) micelles.

The reaction mechanism is shown on scheme 1.

Scheme 1.



The hfi-constants of radicals in RP **I** with ^{13}C nucleus are ≈127G in benzoyl radical and ≈50G in hydroxybenzyl radical. The SNP-spectra obtained for each recombination product of RP **I** are shown on fig.1.

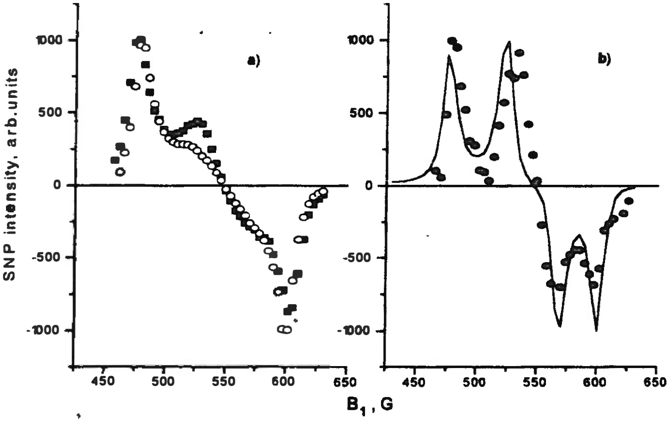


Fig.1. The SNP-spectra determined by the NMR-^{13}C signal of carbonyl group of a) benzoin (solid squares) and compound **IV** (open circles); b) of **III** (solid circles) and theoretical calculation (solid line).

The SNP-kinetics were obtained and compared with kinetics determined for benzoin with natural abundance of ^{13}C and benzaldehyde. The RP arisen by photochemical α-cleavage of the C-C bond of benzoin was shown to have different behavior from one formed during hydrogen abstraction in photolysis of benzaldehyde.

A numerical solution of stochastic Liouville equation for a microreactor model was applied to the theoretical treatment of experimental results.

This work is supported by International Science Foundation, Grant RA5300; INTAS, Grant 93-1626, and Russian Foundation of Fundamental Research (Project No.93-03-18593).

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PPK-5

^{31}P-SNP and TR ESR Investigation of Photolysis of (2,4,6-Trimethylbenzoyl)diphenylphospnine Oxide in Micelles of Different Sizes.

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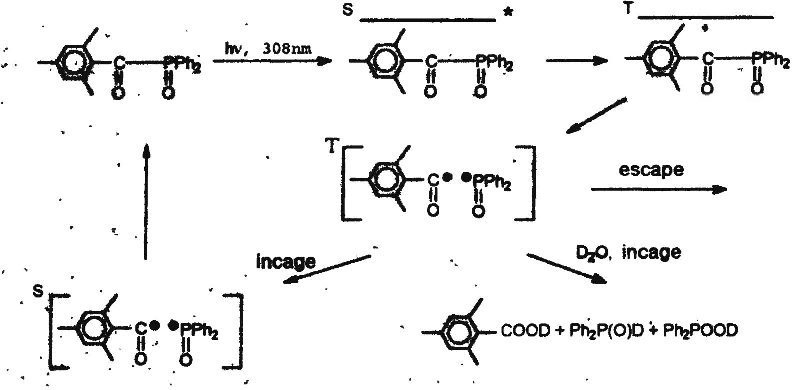
Acylphosphine oxides have currently a wide use in initiating the radical polymerization [1]. The method of stimulated nuclear polarization (SNP)[2] allows one to study the spin dynamics of radical pairs as well as the channels of radical transformation by analyzing the nuclear polarization of radical recombination products. Investigating the mechanisms of the reactions occurring in micelles of different types and sizes makes it possible to determine the reactivity and magnetic-resonance characteristics of reacting species depending on their environment.

In the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMBDPO) in sodium octyl (C-8) and dodecyl sulphate (SDS) micelles in a D_2O solution, the primary cleavage of the C-P bond in the triplet state of the molecule leads to the formation of the products in accordance with the following scheme:



The ^{31}P and ^{13}C SNP spectra show that all these products are formed inside the micelles from the diphenylphosphinoyl (HFI constant a=38,3*mT*) and 2,4,6-trimethylbenzoyl (a=13*mT*) radicals (fig. 1a).

PPK-6

STRUCTURE AND PROPERTIES OF TRIPLET STATE OF REAR-EARTH ELEMENTS COMPLEXES

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The applicability and high informativity of low-temperature phosphorescence and ODMR (optical detection of magnetic resonanses) for investigation of the properties and fine structure of the triplet state of 2,2'-bipyridine and 1,10-phenentroline complexes of transition [Ru(II), Rh(III)], non-transition [Sn(IV)] and rear-earth [Gd(III)] elements have been shown earlier [1,2]. For the first time the stationary ODMR spectra of these compounds have been obtained experimentaly ,and kinetic characteristics of triplet sublevels have been determined for more than 30 systems (monocrystals, powder, glasses) at helium temperature.

The data of spectral properties of $Gd(acac)_3phen$ in the temperature region from 1.9 to 20 K are given in this report for the first time. The vibrational analysis of high structural spectrum at 1,9 K of the compound mentioned above have been carryed out. The data of phosphorescence kinetic delay curves for the different electron-vibrational transitions have been also obtained and the spectra of complexes with common formula $Me(acac)_3bpy$, where Me=Eu, Tb, Dy have been measured. The resulting table of spectral-kinetic measurements of low-temperature phosphorescence and ODMR spectra for the f-elements complexes having different ligands is given.

It is shown that the combination of low-temperature phosphorescence and ODMR is actual for investigation of geometry and photophysical characteristics of exited states of photocatalysts applying to the solar energy utilization and the information recording process.

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Acknowledgments:

The authors thank the Russian Fund for Fundamental Investigation (94-03-08041a) for finansial support of this work.

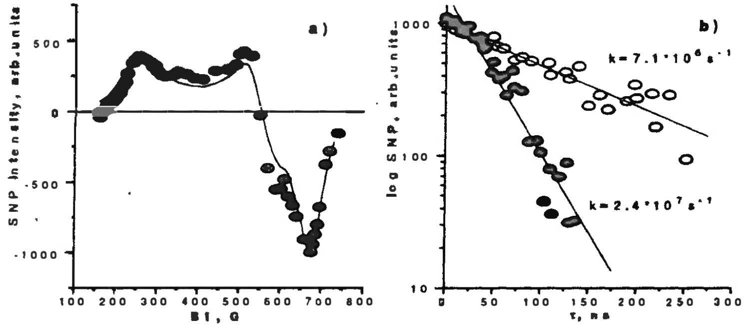

Fig. 1. a) The SNP spectrum (ω=1530MHz) in C-8 micelles of diphenylphosphinoyl radical determined by the ^{31}P NMR signal of the initial TMBDPO (solid line - theoretical calculations);
b) The SNP kinetics in SDS (open circles) and C-8 (solid circles) in the field 675G.

The participation of water molecules in the above mentioned reactions of radicals appears to be due to their coordination in the -CO-PO- fragments [3] at the boundary of the micelle or inside it. The splitting in ^{31}P-SNP spectra in SDS micelles equals to hfi-constant obtained by TR ESR. A comparison of the SNP spectra of the diphenylphosphinoyl radical in SDS and C-8 micelles shows that the hfi-constant does not decrease significantly, unlike in the photolysis of ketones [4]. This seems to be accounted for by an increased effective size of the C-8 micelles due to a high hydrophility of TMBDPO. This assumption is supported by the measured time dependences of SNP spectra (fig.1b), which exhibit the high relaxation rate of the radicals as well as the their high escape into the bulk.

The work was financially supported by International Science Foundation, Grant RA5300 and Russian Foundation of Fundamental Research (Project No.93-03-18593).

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A Switch External Magnetic Field (SEMF) Study of CIDNP Kinetics in Photolysis of Naphthalene(D_8) with 1,2-dicyanoethilene.

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Introduction.

A new method for studying the chemical and spin dynamics of short-lived radical pairs (RP) has been recently proposed [1,2]. The method is based on changing the conditions of RP recombination by instantaneously fast Switch External Magnetic Field (SEMF) B_0. The influence of SEMF on the RP recombination probability and on CIDNP has been considered. The solution of CIDNP kinetics, which was obtained by [2], implies the study of the RP kinetics at high magnetic fields. However, it has been known that at high magnetic fields, the CIDNP signals change significantly enough when the external magnetic field B_0 changes by values of the order of hundreds Gausses. Therefore, to achive the sufficient sensitivity of the method it requires to create the magnetic field changes by a value of the order of 10^2 G in nanoseconds. The last , this is a rather complex technical problem.

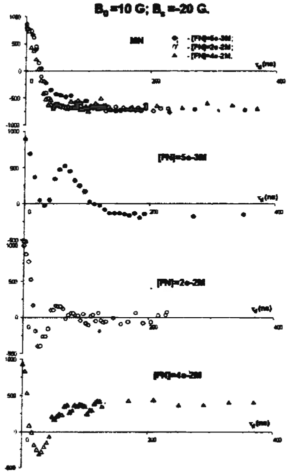
It is known that in weak magnetic fields CIDNP changes essentially with B_0 withing a few Gausses. Technically it is easy to change B_0 by tens of Gausses in nanosecond. This work reports the first results of the SEMF CIDNP studies of the the behavior of the short-lived RP and radical ions (RI) in radical-ion reactions at weak magnetic fields ($B_0 \cong$ HFI). It is shown that SEMF affects nuclear polarization of diamagnetic molecules by different mechanisms i)influence on the spin dynamics of geminate RP, ii) influence on the cross-relaxation of intermediate short-lived radical,iii) transfer of polarization from electron.

Experiment. The sample under study was irradiated by the light of an excimer laser (308 нм, 60 mJ, 10-20 Hz) in the external magnetic field B_0. A flow system was used to transfer the sample to the probe of an MSL-300 NMR spectrometer (300 MHz), wherein the NMR spectra of the diamagnetic reaction products were regisrated. The transfer time was about 1 s. An additional magnetic field B_S was induced by the Helmgoltz coils 1.5 cm in diameter. The amplitude of the magnetic field B_S was 20 G. The rise time for pulse of magnetic field is about 1 ns. The pulse duration was 800 ns. The pulse of the magnetic field was applied at a variable time delay τ_d after the laser pulse. The experimental error for τ_d was 15-20 ns. The experiments were carried out in two modes: i] $B_0 \rightarrow B_0 + B_S$; ii] $B_0 \rightarrow -B_0$

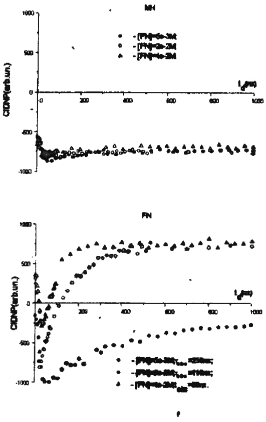
Results and discussion. The figures show the SEMF CIDNP kinetics obtained in the the photolysis of naphthalene (D_8) with fumaronitrile

PPK-7

Time dependences of SEMF CIDNP obtained during photolysis of Naph(d) with FN.
B_0=10 G; B_s=-20 G.



Time dependences of SEMF CIDNP obtaned during photolysis of Naph(D_8) with FN.
B_0=30 G; B_s=20 G.



(FN) with and without change in the direction of the magnetic field. In both i)(B_0=30G, B_s=+20G) and ii](B_0=10G, B_s=-20G), the characteristic times of change in the CIDNP signal of the in-cage product maleonitrile (MN) are within 30-40 ns and are practically independent on the electron transfer rate. This time is comparable with the experimetal error for τ_d; therefore the RP lifetime may be only estimated (t_f< 30-40 ns). At the same time, the CIDNP kinetics, which are detected by the NMR signal of fumaronitrile (FN), depend significantly on the rate of electron transfer and differ essentially for the two experimental modes i] and ii]. The CIDNP kinetics observed in the case i] are well described by the calculation, based on the influence of SEMF on the relaxation-times, formed due to degenerate electron exchange. Of most interest are the CIDNP kinetics, which are detected in the experiments with changing only direction of magnetic field. In this case SEMF does not affect the relaxation times T_1 and T_2. The amplitude of the oscillations considerably depends on the rate of charge transfer and significantly decreases with FN concentration (rate of electron transfer). Possible mechanisms of the formation of the oscillations are discussed.

The results of this work demonstrate the applicability of the new method SEMF-CIDNP to investigating the CIDNP kinetics in radical reactions and separating the contributions of geminate and escape products to the polarization at weak magnetic fields and investigation of electron polarization at weak magnetic field.

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Acknowledgments: This work was performed under auspices of International Science Foundation, Grant RA 5300, INTAS-93-1626.

PPK-8

MECHANISM OF SiH_3 + Cl REACTION: DIRECT ABSTRACTION VS. RECOMBINATION-ELIMINATION.

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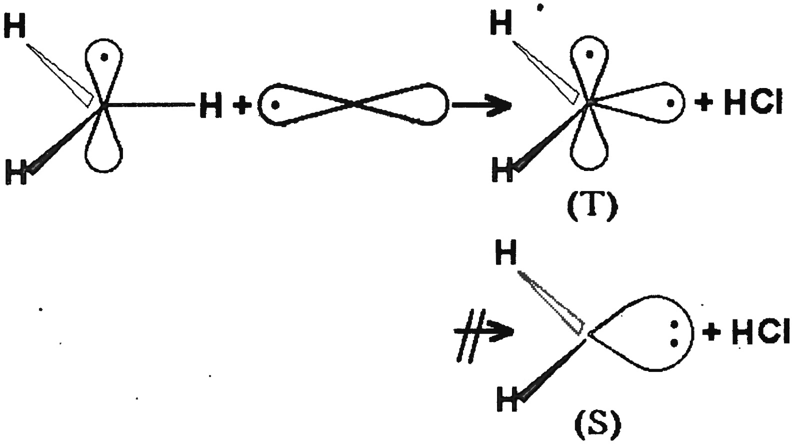
The thermochemistry of many radical–radical or radical–atom reactions allows the existence of two different mechanisms simultaneously: “direct abstraction” and “recombination-elimination” ones. The mechanism is established only for several reactions of this kind, enumerated by Sloan [1] and by Setser and co-workers [2]. The study of the reaction SiH_3 +Cl was started in our previous work [3]. In current work the mechanism of this reaction has been studied by means of a time-resolved IR-chemiluminescence technique and by product analysis applied to the SiH_4 + Cl system. The kinetics of HCl(v) luminescence has been measured and modeled by numerical solutions of a set of differential equations describing a kinetic scheme of the processes occurring in the system under study. For the reaction SiH_3 +Cl the yields of HCl(1) and of HCl(2) have been determined to be $\alpha_1=0.8^{+0.2}_{-0.3}$ and $\alpha_2 \leq 0.08$, respectively. This result has allowed us to conclude, that the SiH_3 +Cl reaction proceeds mainly via "direct H atom abstraction" mechanism with the formation of silylene biradical in triplet ($^3B_1$) state. The yield of molecular hydrogen in SiH_4 + Cl and in SiD_4 + Cl systems has been measured by mass-spectrometry. It has been concluded then that in the reactions $SiH_3+Cl\rightarrow$ and $SiD_3+Cl\rightarrow$ the contribution of the “recombination-elimination” channel giving rise to the molecular hydrogen, is no more than (0.20 ± 0.04) and (0.19 ± 0.04), respectively.

The “orbital correlation “ diagram has been considered for the abstraction mechanism of radical–atom and radical–radical reactions, in which abstracted atom is in α -position to the free electron orbital of parent radical. The idealized scheme of the abstraction mechanism (radical is planar and reaction coordinate coincides with symmetry axis of reacting system) is presented below. It is seen that the initial state of reagents in this mechanism correlates by the orbital symmetry with a triplet final state. We believe that this correlation has a general



nature independently of the details of geometry of reacting fragments provided that the abstracted atom is in α -position to the free electron orbital of parent radical (α–abstraction mechanism). As a consequence of this correlation it is possible to wait for an activation barrier of the abstraction reaction to be much lower on the triplet potential energy surface. The experimental data are in excellent agreement with this prediction. In the reactions where the direct abstraction mechanism is established (SiH_3+Cl (this work), NH_2+F [1], CH_3+F [4]), the byradical appears in triplet state. In all systems, where the triplet state is inaccessible from the point of thermochemistry, the recombination-elimination mechanism prevails.

This work was financially supported by Russian Fund of Fundamental Research (Grant No. 93-03-05018) and by International Science Foundation (Grant RBK000).

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PPK-9

FEMTOSECOND (1+2)REMPI AND NANOSECOND (1+1)REMPI APPLIED TO STUDY ALLYL IODIDE PHOTODISSOCIATION DYNAMICS.

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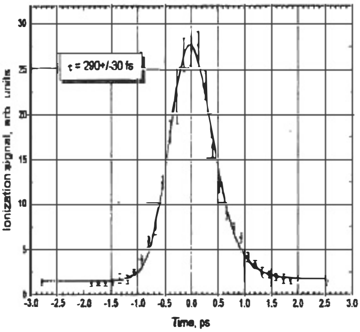
FEMTOSECOND (1+2)REMPI. Previously a photodissociation dynamics of the molecular states lying in the VUV region was probed on a femtosecond time scale with the (2+1) schemes of resonance-enhanced multiphoton ionizaton (REMPI) technique, including two-quantum excitation of a molecule [1,2]. The progress in generation of tuned VUV radiation gives the opportunity to use the (1+N) schemes of REMPI for probing the dynamics of the states excited by one quantum. It is particularly interesting because these states are just the subject of the traditional one-quantum VUV spectroscopy.

In this work femtosecond (1+2) REMPI technique has been used for time-resolved measurement of the dynamics of allyl iodide (AI), excited by VUV quantum. VUV radiation was produced by non-resonant quintapling of Ti:S femtosecond laser [3] radiation (λ =795-830 nm) in mercury vapor or xenon gas. Time delayed fundamental radiation was used for two-quantum ionization of VUV excited AI molecules. In Fig.1 there is shown the dependence of the ionization signal on the delay time between exciting (λ=159 nm) and probing (λ=795 nm) pulses. The time of life of the VUV excited state (E*=7.8 eV) of AI extracted from this time profile, was found to be (290±30) fs.



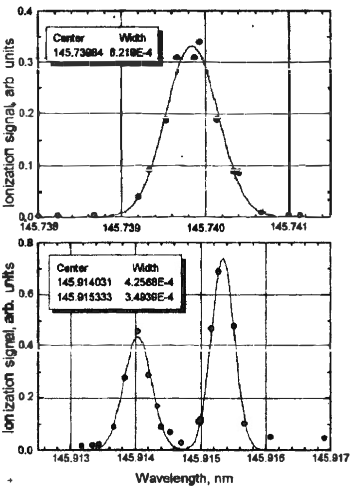
NANOSECOND (1+1)REMPI. After photodissociation of halogen containing molecules, halogen atoms are produced in the two fine states ($^2P_{1/2}$) and ($^2P_{3/2}$). Determination of the ratio of the yields of these fine states is important for clarifying the photodissociation dynamics. Such experiments have been realized for many molecules, when excited in the UV or VIS regions. At present, there are tunable but less powerful sources of radiation in the VUV region, where the Rydberg states of the molecules are situated. An increase of the sensitivity in detection of atoms would give a possibility to extend such measurements to this very interesting region. The (1+1)REMPI technique for detection of atoms used by current authors [4] gives such a possibility from the points of sensitivity as well as of spectral resolution.

In this work (1+1)REMPI technique was used for measurement of iodine I atom fine states branching ratio, arising in VUV, UV and VIS photodissociation of AI. The sequences of transitions used for detection of the I atoms are as follows

$$I(^2P_{1/2}) \xrightarrow{145.915\text{nm}} I\{(^3P_2)6d[1]_{3/2}\} \xrightarrow{437.744\text{nm}} I^+ + e^-$$

$$I(^2P_{3/2}) \xrightarrow{145.740\text{nm}} I\{(^3P_2)5d[0]_{1/2}\} \xrightarrow{437.220\text{nm}} I^+ + e^-$$

The VUV radiation used has been obtained by non-resonant frequency tripling in xenon of visible dye laser radiation, which has also been used for ionization of VUV excited atoms. The REMPI spectra of $I(^2P_{1/2})$ and $I(^2P_{3/2})$ arising in the photodissociation of allyl iodide at 355 nm are shown in Fig.2. The measured signals were compared with those measured for known concentrations of I atoms in both fine states, resulted from well studied photodissociation of diiodomethane at 308 nm. So the ratio $I(^2P_{1/2})/I(^2P_{3/2})$ was determined under photodissociation of AI at different λ values in the VIS (437 nm), UV (308, 355 nm) and VUV (145 nm) regions.



This work was financially supported in part by Russian Fund of Fundamental Research (Grant No. 93-03-05018) and by Swedish Natural Science Research Council.

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CRYOCHEMISTRY OF HYDROGEN CYANIDE.

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The molecular formation of HCN is very abundant in cosmic space: comets, protoplanet clouds and interstellar dust. In general, the HCN molecule is commonly considered to be the base of prebiological chemical evolution. It is of interest to steady the chemical behaviour of this simple molecule under conditions similar to those in outer space (low temperatures and radiation) and its role in the "cold"chemical evolution of the Universe.

When hydrogen cyanide is cooled to 77 K, it transforms to the crystalline state. During its heating, a phase transition of the crystal-crystal type (248 K) and melting at 260 K ($\Delta H = 8{,}4 \pm 4$ kJ/mol) occur. Calorimetric measurements carried out directly in the irradiation field at 77 K have shown that there is no noticeable heat evolution associated with chain polymerization. When HCN radiolised at 77 K is warmed to melting point, the formation of polymer occurs. The thermal effect of the polymerization HCN is recorded before and in the melting region. The heat evolution was registered at more and more low temperature with increasing the dose irradiation.

The analysis of the IR absorption spectrum of the freshly prepared polymer has shown that, along with the absorption bands due to C≡N stretching vibration (2100-2200 cm^{-1}), which had also been observed in the spectrum of the monomer, HCN, this spectrum exhibits additional bands at 1600-1700 cm^{-1} and 1200-1250 cm^{-1}, which are apparent caused by the stretching vibration of C=N and C-N bonds, respectively.

The polymer exhibits a singlet ESR spectrum characteristic of polyconjugated systems. The electric conductivity of this polymer is typical of most of dielectrics. Besides the polymerization of HCN the arising the crystals of 1,2-diaminomaleinodinitrile (tetramer) is takes place.

An X-ray structural investigation of crystals taken from the residue of the above-described sublimation has shown that these crystals are of monoclinic syngony [13]. Bond lengths and angles are conventional. The molecule is planar and has an own symmetry plan, C≡N triple bonds and C=N double bonds are localised. There are no shortened intermolecular contacts or other specific interactions in the crystal. These crystals are produced by the recombination of biradicals of the aminocyanocarbene type, which are stabilised by the low-temperature radiolysis of matrix. The radiation yield of tetramer is $G \approx 2$. The fact that 1,2-diaminomaleinodinitrile is formed under conditions close to those in outer space (low temperatures and radiation) seems to be considerable importance, since this compound might have played a key role in the prebiological organic synthesis, because hydrolysis of 1,2-diaminomaleinodinitrile directly leads to an amino acid.

Polymerization of the closest analogue of HCN, dicyane $(CN)_2$ and BrCN is of no less interest from the viewpoint of cold chemical evolution of metter in outer space and formation of complex polymeric molecules.

There is the copolymerization acetaldehyde with HCN in solid phase. This copolymerization was spread as mechanochemical autowave.

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Laser-induced subpicosecond thermoemission of nonequilibrium electron gas from metal into electrolyte solution.

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The characteristics of new type emission arising on metal electrolyte interface has been considered. Subpicosecond laser pulses with peak intensity I~100GW/cm^2 induce the heating of electron gas up to several thousand Kelvin. Nonequilibrium temperature of the electron gas in good metals originates from the rapid electron-electron relaxation (in the time scale of 10^{-16} s) and delayed electron-phonon exchange (in the time scale of 10^{-11} s). The specific heat of electron gas is 1-2 orders of magnitude smaller than that of lattice, so that the described above overheating of the electron gas is followed by only insignificant growth of equilibrium temperature T of metal [1,2].

Thermoelectron emission results from electron gas heating. Since the universal work function from metal into electrolyte solution decreases by 1.5-3.0 eV with respect to that for emission in vacuum, the emitted charge is measurable at intensities below the boundary of fracture. Two mechanisms of thermoemission were considered: electron transition into the medium conduction band and one-electron reduction of molecules adsorbed on the electrode. The found dependences of the emitted charge Q on I and electrode potential E are described by a Richardson-like formula in which T_e depends on I, pulse duration, rate of cooling and thermal difusivity of electron gas, while the work function depends on surface barrier height and E. Since $T_e \gg T$, the special mechanism of the electrode reaction which is not connected with medium reorganisation is realized.

The theoretical model was tested for mercury and silver electrodes in water electrolyte solutions. When the duration of laser pulses is 0.3 ps (λ 616 nm) the charge emitted from Hg electrode grows from 10^{-9} to 10^{-5} C/cm^2 in I range from 4 to 30 GW/cm^2. The emission origin of photoresponce is confirmed by an increase in Q under introducing electron acceptors into the solution and by appearance of a delayed component of photoresponce due to slow reduction of intermediates forming upon electron capture by acceptor. At I≥6 GW/cm^2, Q exceeds the charge of one-photon emission induced by subpicosecond pulses λ 308 nm. The current density of thermoemission approaches 10^7 A/cm^2. The described above super linear emission disappears upon illumination of Hg electrode with 6 ps long laser pulses with the same energy, but retains for Ag electrode.

The results of measurements agree with theoretically expected for the thermoemission of nonequilibrium electron gas.

The perspectives of application of the novel emission phenomena to the generation of intermediate species and studies of fast electrode reactions are discussed.

Two of us, V.A.B. and A.G.K., thank Russian Fund of Fundamental Investigations (Grant No. 94-03-08862) for the financial support.

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PPK-11a

ALTERNATING COPOLYMERISATION OF ETHYLENE AND CARBON MONOXIDE IN METHANOL:KINETIC STUDIES

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Recent advances in the copolymerization of carbon monoxide and olefins (ethylene and propylene) have resulted in the discovery of efficient palladium catalysts for the preparation of perfectlyalternating CO-olefins copolymers, so-called olefin polyketones (POK) [1-6].

POK are of considerable interest from at least four different stand points: -copolymers have a good adhesium to the surface of inorganic materials and metals, possesses good fibre properties; -the presence of reactive carbonyl groups in the backbone confers photodegrability to the copolymers, when compared with the corresponding polyolefins; -POK are excellent starting materials for obtaining other classes of functionalized polymers; -as a monomer, carbon monoxide is particularly inexpensive and saving on other comonomers may reach 50%.

In this paper, some peculiar aspects the influence conditions on kinetic reaction of the copolymerization of ethylene and carbon monoxide with catalytic systeme PdR_2-diphosphine-CF_3COOH has been studied.

This work was supported by Russin Foundation Fundamenta Investigations (RFFI grant N 95-03-09436)

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PPK-12

Spin-orbit quenching and ESR transitions broadening of the F($^2P_{1/2}$) and Cl($^2P_{1/2}$) atoms.

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The ESR transitions broadening cross-sections of the F($^2P_{1/2}$) atoms were measured for the He, Ne, Ar, and Kr atoms and also for the N_2, F_2, and O_2 molecules. For the Cl($^2P_{1/2}$) aroms upper estimates were obtained for their ESR transitions broadening cross-sections for the He and Ar atoms.

The technique used was the high-resolution superheterodyne ESR spectrometer with pulse-repetitive UV photolisys of F_2 and Cl_2 molecules by an excimer laser as the source of F and Cl atoms.

Data obtained is shown in Table1.

Table 1. ESR transitions broadening coefficients of the F($^2P_{1/2}$) and Cl($^2P_{1/2}$) atoms and the corresponding rate constants and cross-sections.

Reagents	$\frac{d(\Delta H_{1/2})}{dp}$, Oe/Torr	k, cm^3/s	σ, Å^2
F - He	0.125±0.018	$(4.30\pm0.62)\cdot10^{-12}$	0.31±0.045
F - Ne	< 0.015	$< 5.15\cdot10^{-13}$	< 0.064
F - Ar	0.013±0.002	$(4.57\pm0.76)10^{-13}$	0.065±0.011
F - Kr	0.015±0.003	$(5.12\pm0.82)10^{-13}$	0.080±0.013
F - N_2	0.110±0.017	$(3.78\pm0.58)10^{-12}$	0.506±0.077
F - F_2	0.40 ± 0.03	$(1.37\pm0.10)10^{-11}$	1.94 ± 0.14
F - O_2	1.21 ± 0.43	$(4.16\pm1.48)10^{-11}$	5.72 ± 2.03
Cl- He	< 0.003	$< 2.7\cdot10^{-13}$	< 0.020
Cl- Ar	< 0.002	$< 1.8\cdot10^{-13}$	< 0.031

A comparison of data with the results of theoretical calulations [1,2] revealed the fact the F($^2P_{1/2}$) ESR line broadening crossection for He atoms σ = 0.31 Å^2 within 20% accuracy interval coincides with the F($^2P_{1/2}$) spin-oprbit quenching cross-section for He atoms.

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PPK-13

Time-resolved Electric Field Effects in Recombination Fluorescence.

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The technique of measuring electric field effects in recombination fluorescence in nanosecond time scale was developed. The variation of electric field strength E is possible from 0 to 50 $\text{kV} \cdot \text{cm}^{-1}$. The X-ray pulse about 2 nanoseconds was used as radiation source. The single photon counting technique was used for registration of kinetics of recombination fluorescence $I(E,t)$ at different values E. The time dependence of electric field effect $Q(E,t) = 1 - I(E,t)/I(0,t)$ was obtained.

The time dependence of electric field effect $Q(E,t)$ was also calculated for different conditions by Monte Carlo method. It was shown that $Q(E,t)$ does not depend on spatial distribution parameters and spur density but strongly depends on concentration of acceptors and viscosity of solvent. These dependencies were proved in experiments.

The nature of concentration dependence of $Q(E,t)$ is due to variation of mobility of charges during recombination. Using this fact the method of study of precursors of ions was proposed. It is especially interesting to study the precursors of cations — the primary holes.

PPK-13 a

Existence of Fast Holes in Liquid Irradiated Hydrocarbons is the Rule but not the Exception.

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In 1973 two groups of researchers (Yakovlev and coworkers in Chernogolovka and Warman and coworkers in Delft) discovered the high mobile holes in irradiated cyclohexane. Later the high mobility of positive charge was found also in methilcyclohexane and trans-decalin. This mobility was found about 20 times higher than mobility of molecular ions. The fast holes were not found for other hydrocarbons. Warman with coworckers used the microwave absorption method with time resolution about 50 ns. So if lifetime of fast holes is shorter they could not observe them.

In present work we used the timeresolved electric field effects in recombination fluorescence that let to get information about fast holes even if their lifetimes are in picosecond time scale. The idea of using this method is based on dependence of kinetics of electric field effect on mobility of precursors of recombining ions. One precursor is an electron, another is a hole. To eliminate the electrons we used 0.1M C_6F_6 and than we studied the electric field effect kinetics at different concentration of hole acceptors for different hydrocarbon solvents. We studied cyclohexane, octane, isooctane, nonane, decane and we observed fast holes in all cases. The values of mobilities were got by simulation using Monte Carlo method.

PPK-14

$Cl(^2P_{1/2})$ in the products of reactions $O(^1D)$+HCl, Cl_2 and $COCl_2$: LMR experiment and dynamics modeling.

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(1). The method of time-resolved laser magnetic resonance (LMR) was used to detect chlorine atoms arising in the reactions:

$$\begin{array}{llll}
O^* + HCl & \rightarrow OH + Cl(Cl^*), & \Delta H_0^0 = -44.4\ \mathrm{kcal/mol} & (1) \\
O^* + Cl_2 & \rightarrow ClO + Cl(Cl^*), & \Delta H_0^0 = -51.6\ \mathrm{kcal/mol} & (2) \\
O^* + COCl_2 & \rightarrow ClO + CO + Cl(Cl^*), & \Delta H_0^0 = -25.5\ \mathrm{kcal/mol} & (3a) \\
 & \rightarrow CO_2 + 2Cl(Cl^*), & \Delta H_0^0 = -88.9\ \mathrm{kcal/mol} & (3b) \\
 & \rightarrow CO_2 + Cl_2, & \Delta H_0^0 = -146.1\ \mathrm{kcal/mol} & (3c)
\end{array}$$

at room temperature, $Cl^* \equiv Cl(^2P_{1/2})$, $O^* \equiv O(^1D)$. It has been established that the yields of spin-orbit excited Cl atoms resulting from these reactions are (0.10±0.04), <0.10, <0.05, respectively. Measurements of Cl atoms appearance times (Fig.1) have shown, that the rate constants of $O(^1D)$ reactive and nonreactive deactivation are (2.6±0.7), (2.5±0.7) and $(1.5\pm0.4)\times10^{-10}$ cm^3/s for $COCl_2$, Cl_2 and HCl, respectively. It has also been determined from Cl atoms signal analysis (Fig.2), that $k_{3a} + k_{3b}/2 = (2.4\pm0.4)\times10^{-10}$ cm^3/s.

(2) $R \rightarrow E$ energy transfer due to long-range multipole interaction between OH(OD,HF) and Cl is proposed as a mechanism of Cl^* formation in

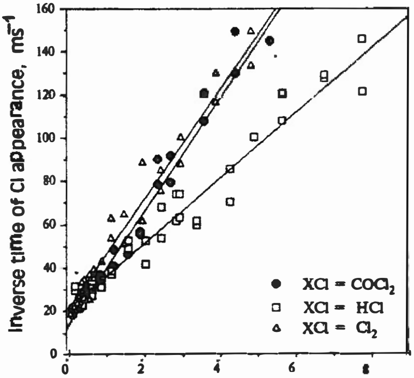

Fig.1 [XCl], 10^{14} cm^{-3}

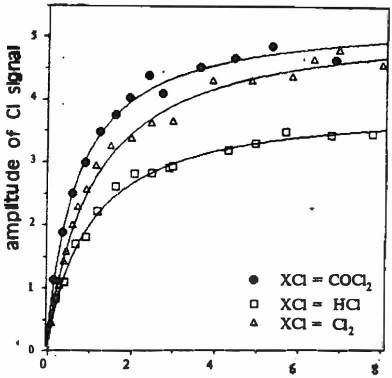

Fig.2 [XCl], 10^{14}, cm^{-3}

the $O(^1D)+HCl(DCl)$, F+HCl reactions. Probabilities of Cl* formation were estimated with Sharma-Brau-Ewing model, reasonably good agreement with experimental results was obtained.

(3) It is known from literature, that the reactions (1-2) proceed via long-lived complexes, but the energy distribution of products can not be described by statistical theory. Completely adiabatic dynamical model of HOCl complex dissociation is proposed in the present study. The energy transfer from HOCl bending to O-Cl stretching vibrational modes in HOCl complex is assumed to be caused by repulsive interaction between rapidly moving H atom and Cl atom. Modeling of this kind of energy transfer is based on the quantisation rule of Bohr-Sommerfeld. The result of calculations is shown in Fig.3.

This model was employed to explain qualitatively nearly equal yield of Cl* atoms in $O(^1D)+HCl$ and $O(^1D)+DCl$ reactions, the fact, which is surprising for $R \rightarrow E$ energy transfer mechanism of Cl excitation. Fig.4 illustrate the main idea of the explanation: while spin-orbit splitting in Cl atom is assumed to be constant, the rotational constant of OH(OD) radical increases when Cl atom approaches (this is a principal consequence of the model), and at some O-Cl distance R there is a curve-crossing, where defect of resonance for $E - R$ exchange process is zero. Curve-crossings for OD+Cl system occur at smaller distance R, then for OH+Cl system. According to Landau-Zinner approach, in the former case this fact leads to the higher probability P of Cl excitation, because interaction between OH and Cl grows when R decreases. For example, $P \sim 1/R^8$ for dipole-quadrupole interaction, this interaction seems to be the most important in the case.

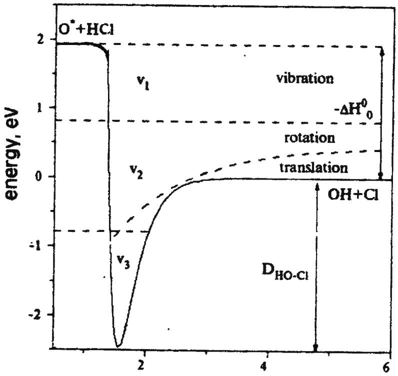

Fig.3 R(HO-Cl), angstrems

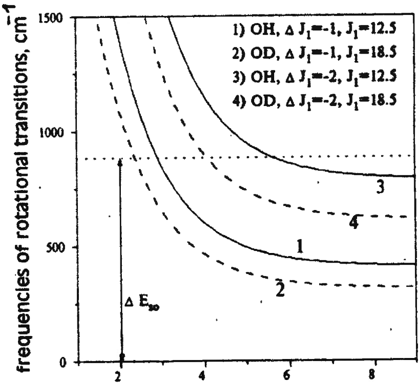

Fig.4 R(O-Cl), angstrems

PPK-15

Structure-Reactivity Relationships for Peroxo Vanadium Complexes.

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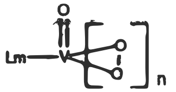
The number and the nature of peroxo vanadium species:



L = heteroligand or solvent molecule

which can be formed in acidic solution by addition of hydrogen peroxide to suitable V(v) precursors, largely depend on the concentration of metal, of hydrogen peroxide, of acid and, when present, also of heteroligands. Accordingly, depending on the numbers of peroxo groups and on the number of ligands, cationic, neutral and anionic species are formed, at constant acid concentration.

^{51}V-NMR technique has been widely used as a tool for the identification and characterization of vanadium species and more recently it has been also applied to the speciation and characterization of peroxo vanadium derivatives.

Spectroscopic parameters, when properly analyzed, can be useful in understanding the factors governing the reactivity of peroxo metal species. In this paper we shall discuss the dependence of the ^{51}V-NMR chemical shifts of a number of peroxo vanadium complexes on the electron donating ability of the coordination sphere. In addition, a Ramsey type correlation between the ^{51}V-NMR chemical shifts and the maximum of absorption, in the visible region, for various peroxo vanadium complexes has been observed. Such a correlation allows to estimate the difference in energy between the frontiers molecular orbitals of the complexes as a function of the nature of the ligands. Moreover, we shall present a study on the effect of the solvent on the chemical shifts of some mono- and di-peroxo vanadium species. As expected, a large difference is observed in passing from neutral to charged species. Worthy of mention is the fact that these experiments provide useful hints on both the coordination sphere and the solvation sphere of peroxo vanadium complexes in solution together with information on the rate of exchange and on the values of the equilibrium constants of exchange of solvent both in the coordination sphere and in the first solvation sphere.

Even more interesting is the evidence that correlations between chemical shifts and reactivity in a given solvent may be found.

PPK-16

COMPETITIVE MECHANISMS OF FREE RADICAL HALOGENATION. KINETICS AND SELECTIVITY

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Free radical halogenation processes carry out by two competitive mechanisms in the most part:

$$\mathrm{RH + Hal\cdot} \xrightarrow{k_{11}} \mathrm{R^1\cdot + HHal} \qquad \mathrm{RH + X\cdot} \xrightarrow{k_{21}} \mathrm{R^1\cdot + HX}$$

$$\mathrm{RH + Hal\cdot} \xrightarrow{k_{12}} \mathrm{R^2\cdot + HHal} \qquad \mathrm{RH + X\cdot} \xrightarrow{k_{22}} \mathrm{R^2\cdot + HX}$$

$$\mathrm{XHal + Hal\cdot} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{X\cdot + Hal_2}$$

$$\mathrm{R^1\cdot + Hal_2} \xrightarrow{k_{15}} \mathrm{R^1Hal + Hal\cdot} \qquad \mathrm{R^1\cdot + XHal} \xrightarrow{k_{25}} \mathrm{R^1Hal + X\cdot}$$

$$\mathrm{R^2\cdot + Hal_2} \xrightarrow{k_{16}} \mathrm{R^2Hal + Hal\cdot} \qquad \mathrm{R^2\cdot + XHal} \xrightarrow{k_{26}} \mathrm{R^2Hal + X\cdot}$$

Experimental selectivity is a function of two free radicals stationary concentrations:

$$\frac{k_1}{k_2} = \frac{k_{11}[\mathrm{Hal\cdot}] + k_{21}[\mathrm{X\cdot}]}{k_{12}[\mathrm{Hal\cdot}] + k_{22}[\mathrm{X\cdot}]}$$

It was demonstrated by computer simulation that hyperbolic dependence exists between experimental selectivity and two reagents concentration ratio:

$$\frac{k_1}{k_2} = \frac{\dfrac{k_{11}}{k_{12}} + \dfrac{k_{21}\,k_{22}}{k_{22}\,k_{12}}\,\Psi\,\dfrac{[XHal]}{[Hal_2]}}{1 + \dfrac{k_{22}}{k_{12}}\,\Psi\,\dfrac{[XHal]}{[Hal_2]}}$$

It was found that Ψ value is constant over a wide range of elementary stages constants variation. Selectivity characteristics for individual radicals X• may be calculated from this dependence and relative contribution of two mechanisms for hydrogen atom transfer may be estimated for individual C-H bond. Hyperbolic dependencies were found for halogenation reactions with dichloro- and dibromomonoxides, tert-butyl hypochloride and hypobromide and with wide set of N-halogensulfonamides and relative rate constants and kinetic isotope effects were determined for individual radicals.

XHal	k_{sec}/k_{pr} 20°C	k_{tert}/k_{pr} 20°C	k_H/k_D 20°C
$C_6H_5SO_2NBr_2$	42.1 ± 4.4		10.3 ± 1.1
$4\text{-}CH_3C_6H_4SO_2NCl_2$	38.6 ± 3.3	240 ± 20	11.2 ± 0.7
$C_6H_5SO_2NCl_2$	36.8 ± 1.5		8.2 ± 1.6
$4\text{-}NO_2C_6H_4SO_2NCl_2$	24.4 ± 2.7	165 ± 18	8.1 ± 0.5
N-bromosaccarine	26.9 ± 4.2	140 ± 5	2.97 ± 0.12
N-chlorosaccarine	24.8 ± 3.8	137 ± 4	3.06 ± 0.14
$(C_6H_5SO_2)_2NBr$	21.3 ± 1.8		3.28 ± 0.16
$(C_6H_5SO_2)_2NCl$	19.0 ± 3.0		2.53 ± 0.12
$(CH_3SO_2)_2NCl$	13.9 ± 2.4		1.81 ± 0.17
$(CH_3)_3COBr$	12.2 ± 1.1		
$(CH_3)_3COCl$	13.6 ± 2.9		
Br_2O	16.8 ± 3.0		
Cl_2O	19.6 ± 3.5	61 ± 11	
Cl_2	2.2 ± 0.1		1.13 ± 0.05

The same methodology was used for interpretation of solvent influence on selectivity in free radical chlorination by molecular chlorine. It was demonstrated that haloalkane influence on selectivity is in a good agreement with supposition about chlorine atom complex occurence:

$Cl\bullet + RHal \rightarrow RHal \text{---} Cl\bullet$

Selectivity characteristics for these complexes were determined (k_{sec}/k_{pr} for i-PrCl ---Cl• complex is 6.2 ±. 0.2, and for EtBr---Cl• complex is 20.2 ± 0.9).

This work was supported by Russian Foundation for Fundamental Research and *"Russian Universities"* Foundation.

CATION MIGRATION OVER THE SURFACES OF DIOXIDES HAVING RUTILE STRUCTURE.

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The purpose of this study was quantum-chemical calculations of the migration of H^+, Li^+ and Na^+ over the surface and through the bulk of nonhydrated and hydrated SiO_2, GeO_2, SnO_2, and PbO_2 having the rutile structure. The calculations were performed by MNDO method in the cluster approximation whose peculiarities as applied to tin dioxide were described in [1].

The calculations hold that cations migrate over the nonhydrated surface through regular channels located over the surface between oxygen atoms belonging to different metal dioxide molecules. In this case the activation energy for proton migration is high and comprises about 500 kJ/mol. The activation energy of conductivity decreases with the increase of the unit cell parameters for all studied oxides. The activation migration energy of other cations is less than that of the proton migration and is independent of unit cell size.

With hydroxyls the activation energy of the surface proton migration decreases about four times but the conductive channels remain to be unchanged. The presence of water molecules on the surface of tin dioxide causes still greater decrease in activation energy which depends on both the degree of the surface hydration and relative positions of water molecules on it.

If a migrating cation encounters a water molecule adsorbed on the surface, its migration channel must be changed. The equivalent branching which occurred on nonhydrated surface dies out. Then, the direction, in which the cation obviates the effect of positive charge (H^+) and passes to an adjacent migration channel, becomes preferential. Thus, the cation migration through a by-pass channel is much more probable than through the channel located in the proton vicinity. On the contrary, a negatively charged oxygen of the OH^- group located over the cluster surface attracts a migrating cation making the channels nonequivalent. The probability of cation location in the vicinity of OH group is then much higher than in adjacent channels less preferential in energy terms.

A cation in the vicinity of OH^- group promotes the proton abstraction. The cation therewith migrates by the OH^- group through the channels risen 0.02 nm higher than those on the dehydrated surface. However, the activation energies of cation migration in the vicinity of OH^- groups and along a nonhydrated surface are close. The migration activation energy at high degree of surface hydration can therefore be expected to be as low as that for a nonhydrated surface. At low degree of surface filling the increase in water concentration leads to the change in the rate of cation migration due to constrained by-pass of high energy regions (H^+) and delay in the low energy ones (OH^-) rather than to the change in activation energy.

The proton migration through the bulk of an oxide is also possible in nonhydrated dioxides. However the activation energy of this process is higher than that of the surface migration.

The work is supported by the Russian Fundamental Research Foundation, Grant 93-03-04637.

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Resonance Multiphoton Ionization and Dissociation of NO, O_2 and N_2 Molecules

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The processes of multiphoton ionization and dissociation of diatomic molecules under the monochromatic laser radition are investigated. The occupation of stationary or autodecaying states is occurred on the intermediate process step. It is necessary to consider in detail the field coupling of resonant discrete or quasidiscrete states and their interaction with autoionization and dissociative continua.

The analytical investigation of photoelectron and molecule photodissociation product spectrum forming mechanism is based on determining and analysis of radiation collision T-matrix. It describes the interaction of electron e^- and molecular ion XY^+ with dissociation products $X + Y$. The studying of collision is carried out under stationary representation of quasi energy harmonics. The coupling among them is due to interaction $V^f = \frac{1}{2}\mathbf{Df}$, where $\mathbf{D}$ - dipole moment, $\mathbf{f}$ - field strength amplitude.

We consider following system. The state which is populated by weak tested field with frequency Ω at transition from ground molecular state is mixed with lying higher one during reemission of strong field quantum. The two-level problem takes place when field interaction among these states is much less than distance between molecule rotation levels. We have taken for example the basic atmosphere molecules NO, O_2, N_2. For the NO molecules the process scheme is

$$X^2\Pi(J=6) \xrightarrow{\Omega} E^2\Sigma^+(s\sigma, J=7) \overset{\omega_f}{\rightleftharpoons} Y^2\Sigma^+(p\sigma, J=6) \overset{\omega_f}{\rightleftharpoons} continuum,$$

where J - total angular momentum, ω_f - strong field frequency. The total spectrum is the sum of two-peak shape curves. The resonances corresponding to the different total angular momentum projection M are not overlapped if the distinction by the value $V^f \sim (J^2 - M^2)^{\frac{1}{2}}$ for states $M, M \pm 1$ exceeds the level width. At this case the most favourable conditions is occuring to fix the rotation plane of molecular ion with respect to vector f. It is interesting for the problem of forming of ion and molecular beams with certain microscopic properties. The polarization is connected with the projection M of total angular momentum of the system $e^- + XY^+$, which is the sum of ion M^+ and electron m components of angular momenta. That is why the magnitude M^+ is fixed with some spread which is determined by possible value m for the certain process.

In the figure the photoelectron spectrum is shown. It appeares under the field effect on NO molecule in agreement with indicated scheme. For molecules O_2 и N_2 we consider next transitions:

$$X^3\Sigma_g^-(J=6) \xrightarrow{\Omega} {}^3\Sigma_u^+(p\pi, J=7) \overset{\omega_f}{\rightleftharpoons} {}^3\Sigma_g^+(d\pi, J=6) \overset{\omega_f}{\rightleftharpoons} \textit{continuum}$$

and $X^1\Sigma_g^+(J=6) \xrightarrow{\Omega} {}^1\Sigma_u^+(p\sigma, J=7) \overset{\omega_f}{\rightleftharpoons} {}^1\Sigma_g^+(s\sigma, J=6) \overset{\omega_f}{\rightleftharpoons} \textit{continuum}$, correspondingly, and obtain the similar pattern of photoelectron spectra. Note that the spectrum form is greatly depends on field strength and spectroscopic characteristics of investigated object. It gives the possibility to detect initial vibronic and rotational molecule states.

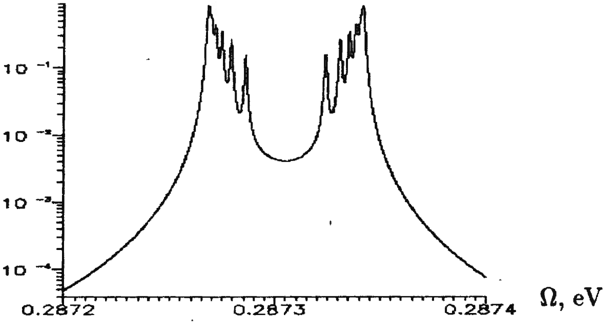

Fig.1

KINETICS OF TETRAFLUOROETHYLIDINE CFCF3 GENERATION AND TRANSFORMATION IN LASER BEAM.

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This paper is devoted to research of generation and transformations of $:CFCF_3$, reactions kinetics of which is practically unknown. For investigations we applied method of $:CFCF_3$ radicals generation such as reagent molecules decomposition under multiphoton excitation (MPE) by IR laser radiation. Hexafluoropropene oxide C_3F_6O was used as a $:CFCF_3$ source. Decomposition of C_3F_6O molecules under their MPE was carried out at 1025,3 cm^{-1} laser radiation frequency (9P42) of TEA CO_2-laser. Irradiated C_3F_6O samples were analyzed by gas chromatography and IR spectrometry. Experiments were performed at reagent pressure 0,2-20 Torr. In order to reveal reactive transient radicals a number of experiments was performed at presence of HCl (0,09-165 Torr) as a scavenger.

C_3F_6O pyrolysis is known to occur by reaction (1) producing $:CF_2$. We have found that C_3F_6O decomposition under high vibrational excitation conditions when absorbing IR laser radiation (fluence ≥ 2,6 J/cm^2) may also occur by reaction (2) producing $:CFCF_3$.

$$C_3F_6O \longrightarrow :CF_2 + CF_3CFO \qquad (1)$$

$$C_3F_6O \longrightarrow :CFCF_3 + CF_2O \qquad (2)$$

This mechanism of C_3F_6O decomposition was proved by presence of CF_3CFO, CF_2O, $CHClF_2$ and CF_3CHClF (when HCl excess was added) between final substances. On the basis of dependence of C_3F_6O decomposition products distribution on scavenger HCl pressure it was shown that processes in reaction system with participance of perfluorocarbenes $:CF_2$ и $:CFCF_3$ are as follows

$$:CF_2 + HCl \longrightarrow CHClF_2, \qquad (3)$$

$$:CFCF_3 + HCl \longrightarrow CF_3CHClF, \qquad (4)$$

$$2\ :CF_2 \longrightarrow C_2F_4, \qquad (5)$$

$$:CFCF_3 \longrightarrow C_2F_4, \qquad (6)$$

$$:CFCF_3 \longrightarrow 2\ :CF_2. \qquad (7)$$

It was found that $:CFCF_3$ forming in reaction (2) decomposes as a result of secondary photolysis on absence of stabilizing buffer gas because one may absorb IR laser radiation of itself. Due to this reason CF_3CHClF in our experiments does not appear under HCl pressure less than limit pressure 37 Torr. At the HCl pressure above limit value frequency of $:CFCF_3$ deactivation collisions with HCl molecules as a buffer gas exceed rate of $:CFCF_3$ unimolecular decomposition reaction (7). On the basis of such assumption effective rate constant of reaction (7) was estimated: $k_7 \simeq 2{,}6 \cdot 10^8\ s^{-1}$.

At HCl pressure above 100 Torr all $:CF_2$ molecules producing on reaction (1) or sequentially on reactions (2) and (7) exhaust only as a result of interaction with HCl molecules (3). This result was obtained by means of kinetic equations solution for reactions (3) and (5) rate constants of which is well known taking account of gas system heating because of relaxation of absorbed laser radiation energy. Therefore in the scavenger pressure range mentioned above C_2F_4 should be formed only on $:CFCF_3$ isomerization reaction (6). It really seemed that at HCl pressure above 100 Torr ratio of CF_3CHClF and C_2F_4 relative yields was proportional to HCl pressure. This dependence allows us to estimate rate constants ratio for reactions (4) and (6): $k_4/k_6 \simeq 320$ l/mol. Applying well known rate constant k_3 as a starting approximation for the rate constant k_4 (reaction (4) is similar to reaction (3)) it was shown that under our experimental conditions $k_6 < 7 \cdot 10^7\ s^{-1}$ and hence that $:CFCF_3$ isomerization reaction has appreciable activation barrier.

PPK-20

MODEL OF SYNERGETIC ACTIVATION FOR EXOTHERMIC PHYSICO-CHEMICAL PROCESSES UNDER CONDITIONS FAR FROM EQUILIBRIUM

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Abstract

The synergetic activation model (SA) is proposed for explication of the nature and features of superfast exotermic chemical reactions in solids caused by impact actions (shock waves or detonation) or phase transitions proceeding.

Considerations of such processes in framework of noted model exhibits that they are the activation ones but the atoms (molecules) distribution by energy in the very non-equilibrium systems in which noted processes occur is not of exponential type, but of power one:

$$P[n] = a[n]b[n](E[n]/E[0])\exp(-a)$$

where P[n] is the probability of receiving energy packet E[n] by an atom (a molecule) having average (thermal) energy E[0]; n is a quantity of intermediate energy levels between E[n] and E[0]; a[n], b[n] are factors that characterize a completion of involving the system into self-organization processes and a deepness of noted processes proceeding that depends on the value of the heat release of the reaction, consequently; a > 1 and it is determined by the structure of vibrational excitation energy levels of original substances.

Such distribution is a sequel of a self-organization of matter with dissipative structures formation and it is realized in spatiotemporal limits of noted structures. It is implemented by the best manner in the shock or detonation waves fronts, which are considered here as dissipative structures. It leads to the fact that dependences of process rate v[d] on temperature T, activation energy E[n] and chemical reaction heat release DE are expressed by more gently sloped functions that those resulting from thermodynamical approach that is in satisfactory agreement with experimental data. In the simplest case of n . 1, E[n] . DE

$$v[d] = A\,kT/(DE)\exp(1/2)(1 + DE/2E[n])$$

The synergetic activation model fits some recent experimental data and allows to do certain testable predictions.

PPK-21

STRUCTURE REARRANGEMENT DURING THE SOL-GEL PROCESS

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The method of simulating the process of formation of new crystalline phase during solid state reactions is proposed. The sol-gel process was chosen as a model system for simulating the transformation from noncrystalline state of the intermediate product ("vacancy" phase) to polycrystalline final product during the solid state reaction. Sols of some electrochemically produced hydrated oxides (original sols) and their mixtures (binary sols) are studied by SAXS method using synchrotron radiation (SR). The presence of 1-2 nm scattering entities (primary particles) is the characteristic property of the investigated sols. During gelation and concentration of the original sols the interparticle distance varies in different manner. The binary sols gelates without concentration of the system. The particles with different sizes are observed in the binary sols. It is possible to separate two sections (time intervals) on the kinetic curves of the structural parameters concerning the changes in the binary sols.

AN UNCOMMON MECHANISM OF STRUCTURE-SENSITIVE REDOX CATALYSIS

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Among the most effective processes catalyzed by metal nanoclusters, the photographic development enables billions elementary acts of electron transfer on a latent image center consisting of several silver atoms. With no competing adsorbate in developing solution, the process kinetics is determined by a constant reaction rate on every catalyst particle and the known non-catalytic behavior of developed silver. The catalytic center structure is likely stabilized by the metal-polymer interactions /1/ between the highly dispersed photolytic silver and gelatin.

Although a great many substances were capable to reduce silver halides, catalytic acceleration has been mentioned only for those with some size correspondences to the closest packed structure of (111) Ag surface /2/. The rest could not detect any image traces but formed only a silver "fog" of non-catalytic reduction.

Monatomic developers such as metal ions or neutral atoms of selectively condensing substances display the rule most clearly. During a century and a half of photography, practically all the chemical elements were tested for the developing ability under various conditions. Patents and scientific publications have been thoroughly studied in order to detect all particles mentioned to develop a silver image. With no exception, their crystallographic radii on the Shannon scale allowing for interionic electron-density minima /3/ were close to the regular spaces between interatomic hollows of (111) Ag. When hitting in the neighboring hollows, the particles have to get closely packed.

All the 18 monatomic developers fall into the three groups of their radii: 0.084±0.009, 0.145±0.005 and 0.162±0.002 nm that correspond 1) to 0.166 nm space between the nearest hollows, 2) to 0.288 nm between each second (like Ag atoms pack) and 3) to 0.333 nm between each third. Among several reducing ions of a metal, those of other radii do not react catalytically: U(V), Mn(II) and Ti(III) develop images whereas U(III), U(IV), Mn(III) and Ti(II) do not. Sn(II) ion sometimes suspected to develop but having another size has never detected any image traces in our experiments. Therewith, Tl(I) of the third size group was found out to develop. The potential-controlling ligands in developers could not cause the catalytic selectivity since in general they did not meet the upper rule or adsorb on silver.

All the molecular developers contain bound oxygen or nitrogen atoms whose van der Waals radii belong to the second size group. Borohydride never developed any image traces though could slowly produce a fog. Highly efficient developing molecules possess at least two such atoms spaced from each other at 0.28 to 0.30 nm or multiples. Also the appropriate thickness, planarity and electron deficiency of aromatic reducing molecules amplify their mutual van der Waals attraction and contribute to close packing.

Unlike the molecular or atomic developers that may possess a chemisorption affinity with silver, specific adsorption of the developing metal ions has been never mentioned in the literature. They would hardly be capable to form a "monolayer surface alloy" with "weakened bonds inside the molecule" according to Balandin /4/ even though the highest dielectric constant of water greatly weakens the intercationic electrostatic repulsion. The energy of mobile hydrate shell is even capable to break strong ionic bonds when dissolving the salts. The 0.28 to 0.30 nm hydrogen bond length favors the oriented water dipoles to form joining close-packed counterlayers of compensating negative charges.

Pre-treatment with non-reducing cations Zn(II), Mg(II), Li(I) or Pb(II) equal in radii to the developing ions or their addition to a hydroquinon developer has little or no effect on developmen rate. So some dynamic shortly-living closely packed clusters of particles hitting randomly in neighboring hollows are likely occur rather than the very competitive adsorption phase.

A developing particle undergoes van der Waals attraction by 3 silver atoms that form a hollow. Additionally, it is attracted by adjacent particles in the cluster. So the coordination number of particle can increase from 3 up to 6 for the first and third size groups and up to 9 for the second one. During a short time of hitting contact with silver, the particle may not succeed in loss of electron. The extra attraction can retain it at the catalyst surface for a longer time and increase the reaction probability.

The rule shows the importance of general steric opportunities in heterogeneous kinetics and catalysis.

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PPK-23

High temperature phosphorescence dynamics of complexes "cyclodextrin - aromatic molecule - saturated compound"

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For a long time it was considered that phosphorescence at room temperature (RTP) of complexes of aromatic molecules (AM) with cyclodextrin (CD*) exhibits only in the presence of internal or external heavy atom [1-3]. The similarity of AM phosphorescence spectra with high resolution in solutions at 77K and in complexes with CD assumes also the similarity of these systems. However, phosphorescence in frozen solutions does not require the presence of a heavy atom. Indeed, sensitized RTP of fluorene was observed in the presence of acetone on excitation at 315 nm [4]. Hence, heavy atom is necessary for population of AM triplet in complex with CD. The behaviour of AM in complex may be similar to that in the gas phase [4].

RTP of complex " β-CD - phenanthrene - chloroform" in water has demonstrated that the phosphorescence lifetime is increased to 2.3 s with increasing of chloroform concentration. In chloroform solution of phenanthrene at 77K lifetime is equal 2.1 s. These data indicate that for appearence of RTP not heavy atom, but some molecule with saturated bonds is necessary. Indeed, intense RTP was detected by addition to complex "AM + β-CD" of cyclohexane and n-hexane [5], isooctane, decalin.

With isooctane RTP of phenanthrene was observed at 323K and at 274K with lifetimes 1.8s and 3.05s (in frozen solution 3.3s).

The necessary condition for appearence of RTP with large lifetime is the formation lightscattering polycomplexes of micron sizes containing CD, AM and molecules with saturated bonds [1,4,5].

This work is supported by RFFI, grant 94-03-09961a.

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PPK-24

PHOTOCHEMISTRY OF $IrCl_6^{2-}$ COMPLEX

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The study of the $IrCl_6^{2-}$ photochemistry is of major importance in understanding the primary processes in the photochemistry of the chloride complexes of transition metals. The $IrCl_6^{2-}$ complex is a rather stable particle existing in solutions containing no Cl^- ions.

It is generally believed that photochemical activity of the haloid transition metal complexes in organic solutions is connected with the primary process:

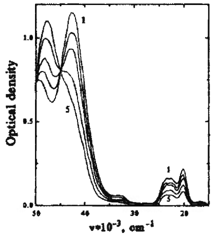
$$MeX_n^{z-} \xrightarrow{h\nu} MeX_{n-1}^{z-} + X^\bullet$$

The identical view on the $IrCl_6^{2-}$ photochemistry is in existence [1]. However, there is no direct spectroscopic or kinetic evidence for the $X^\bullet$ atom formation.

We have previously shown for several haloid complexes that the primary photochemical process is the electron transfer from the solvent to the excited complex [2]:

$$MeX_n^{z-} \xrightarrow{h\nu} (MeX_n^{z-})^* \xrightarrow{RH} MeX_n^{(z+1)-} + R^\bullet + H^+$$

and that for Cu(II) and Pt(IV) chloride complexes, $MeX_n^{(z+1)-}$ and $R^\bullet$ form the radical complexes $MeX_n^{(z+1)-}...R^\bullet$ which are stable only in frozen matrices.

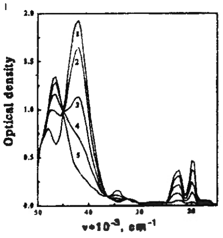


$IrCl_6^{2-}$ photolysis (308 nm) in methanol at 300 K. Change in optical spectrum ($5.4 \cdot 10^{-4}$ M, 17.5 mJ per pulse).
1 -5 - 0, 35, 70, 160, 260 laser pulses.

Figure 1

In this work we used both cw irradiation, laser flash photolysis and ESR in liquids and frozen matrices to study the $IrCl_6^{2-}$ photochemistry in alcohols. It is shown that the irradiation of $IrCl_6^{2-}$ at 308 nm leads to the formation of $IrCl_6^{3-}$ complex (see Fig.1). The quantum yield of the photolysis in oxygen free methanol and ethanol is 0.1. The forming $IrCl_6^{3-}$ complex is then slowly solvated and turned to the $IrCl_5(CH_3OH)^{2-}$ complex.

The photolysis of $IrCl_6^{2-}$ in frozen alcohol matrix (Fig.2) leads to the formation of a new absorption band with its maximum on 287 nm and appearance of the ESR signal of the alcohol radicals. The yield of radicals is equal to the quantum yield of $IrCl_6^{2-}$ disappearance (0.03). We believe that the forming absorption band belongs to the primary radical complex $IrCl_6^{3-}...R^{\bullet}$.



$IrCl_6^{2-}$ photolysis (308 nm,) in methanol at 77 K. $8.3 \bullet 10^{-3}$ M, laser energy 3 mJ per pulse, ν = 10 Hz. Curves 1 - 5 denote 0, 1, 4.5, 9, 19 min of irradiation.

Figure 2

The irradiation in the short-wave region (248 nm) in liquid phase leads to the formation of both $IrCl_6^{3-}$ and $IrCl_5(CH_3OH)^{2-}$. The yield of $IrCl_5(CH_3OH)^{2-}$ is a 30% fraction of total quantities of the disappeared $IrCl_6^{2-}$ complex.

The primary stages of $IrCl_6^{2-}$ photoreduction at 308 nm were studied by laser flash photolysis. The kinetic picture depends on the concentration of dissolved oxygen. In the absence of O_2 the instant bleaching in the initial bands is observed, which is then doubled by a first-order reaction. The rate of this reaction is linear with $IrCl_6^{2-}$ concentration. These rate constants are $3.3 \bullet 10^9$ and $2.3 \bullet 10^9$ $M^{-1}s^{-1}$ for methanol and ethanol respectively. In the presence of O_2 only initial instant bleaching is exhibited. We propose the following kinetic scheme of the photolysis at 308 nm (in methanol):

$$IrCl_6^{2-} \xrightarrow{h\nu} (IrCl_6^{2-})^*$$

$$(IrCl_6^{2-})^* + CH_3OH \longrightarrow IrCl_6^{3-} + {}^{\bullet}CH_2OH + H^+$$

$$IrCl_6^{2-} + {}^{\bullet}CH_2OH \longrightarrow IrCl_6^{3-} + CH_2O + H^+$$

In presence of O_2 the primary alcohol radical ${}^{\bullet}CH_2OH$ disappears in the reaction:

$${}^{\bullet}CH_2OH + O_2 \longrightarrow {}^{\bullet}OOCH_2OH$$

The irradiation in 248 nm leads to both the electron transfer process and the release of chlorine atom:

$$(IrCl_6^{2-})^* + CH_3OH \longrightarrow IrCl_5(CH_3OH)^{2-} + Cl^{\bullet}$$

It is also shown that the irradiation of $IrCl_6^{2-}$ in liquid acetonitrile leads to the photosolvation but not to the photoreduction with the release of a chlorine atom as believed in [1].

The financial support of Russian Foundation for Fundamental Researches is greatefully acknowledged (Research Grants N 94-03-08933).

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PPK-25

KINETICS OF DIFFUSION-INFLUENCED REVERSIBLE REACTION A+B<=> C

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In recent years much effort has been devoted to the theoretical study of liquid phase reversible diffusion-influenced reactions A+B<=> C. Such kind of reaction is quite relevant to experiment. Association-dissociation reaction is a difficult many-body problem. It has been studied by applying analytical methods of different character such as superposition approximation, stochastic approach, as well as simulation methods. The recent analytical theories give correct equilibrium concentrations at infinite time, reduce to Smoluchowski theory when the dissociation rate is zero, and become equivalent in the reaction-controlled limit. At very long times a $t^{-3/2}$ relaxation to equilibrium was derived.

The approaches differ mainly in the case of diffusion-controlled reaction. None of the approaches provides an exact result, thus one cannot say which approach is more accurate. As for $t^{-3/2}$ relaxation to equilibrium, it has been questioned in Ref.[1]. The long-time power law kinetics has been experimentally studied and the concentration-dependent power was observed.

In the present contribution we consider pseudo first order reaction with B particles in excess. Loss of generality makes it possible to investigate the problem in a rigorous fashion, verify the validity of the results derived earlier, and obtain some new results. In the model under consideration a single A particle reacts with static noninteracting reversible traps B when they come together at sufficiently close distance.

Under most general assumptions, namely: space dependent reactivity, arbitrary Markovian motion of minority species (A), the presence of the force interaction between particles, arbitrary initial conditions - the problem of the reversible reaction kinetics was reduced to the consideration of the effective irreversible reaction with time dependent reactivity and source. Thus the exact relation between two many-particle problems has been obtained.

To study the effective irreversible problem, we developed the formalism where the absence of initial bound states (C particles) was a priori assumed. By conventional procedure, we related the Green function of the effective irreversible problem to the memory operator, for which formal expansion in a multiple scattering series was obtained. The average effective reactivity is proportional to Laplace-variable s at small s, so the series convergence is better as compared to real irreversible problem. In the framework of the average t-matrix approximation (ATA) we reproduced some results derived earlier. However, as is known, for irreversible reaction ATA has a limited time interval of applicability, and needs modification.

The modified theory was developed on the basis of diagrammatic summation of the terms for the memory operator necessary for correct long time behavior. A central finding in this work is that the $t^{-3/2}$ law predicted earlier is valid, but with a different concentration-dependent amplitude.

An advantage of the modified theory is that the range of its validity is much wider as compared to other theories. Moreover, this theory made it possible to describe the intermediate times not only at infinite dilution. At intermediate times, a new power-law phase emerges that may lead to the impression of a new asymptotic behavior. Similar result was derived earlier for one-dimensional model by Brownian simulations [2].

It should also be noted that the modified theory is rather simple which allows one to obtain the basic results analytically. In the limit when the dissociation rate is zero the modified theory reproduces all binary terms of the irreversible reaction kinetics [3]. This fact points to a binary nature of the approximations made. Thus the results obtained for the given model will be interesting for the case of all moving species.

This work was supported by Russian Foundation of Fundamental Research (project 93-03-05032).

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PPK-26

STUDY OF VIBRATIONALLY EXCITED MOLECULES FORMING IN ELECTRON-EXCITED OXYGEN ATOM $O(^1D)$ REACTION WITH FORMALDEHYDE

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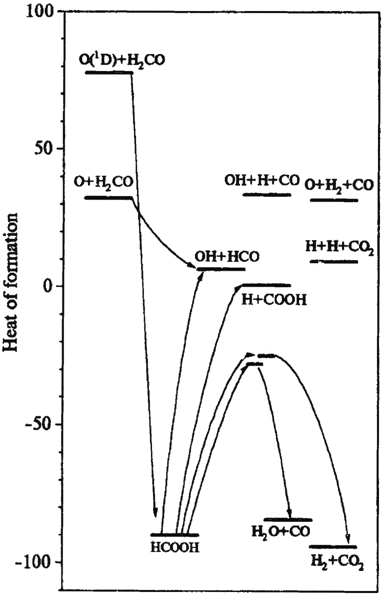
1. Both of the reagents are the particles important for atmospheric chemistry.
2. Reaction of oxygen atom in the ground state with H_2CO molecule proceeds via H atom abstraction:

$$O(^3P) + H_2CO \rightarrow OH + HCO$$

The reaction of electron excited $O(^1D)$ atom that, unlike the atom in the ground state has no spin, can follow the other channels. These can be represented as the formation and subsequent decay of formic acid molecule.

$$\begin{aligned} O(^1D) + H_2CO \rightarrow HCOOH &\rightarrow H_2 + CO_2 & -\Delta H &= 170\text{kcal/mol} \\ &\rightarrow H_2O + CO & -\Delta H &= 161\text{kcal/mol} \\ &\rightarrow H + COOH & -\Delta H &= 77\text{kcal/mol} \\ &\rightarrow OH + HCO & -\Delta H &= 64\text{kcal/mol} \end{aligned}$$



A great energy release in these processes implies the formation of vibrationally excited product molecules.

3. The paper studies the kinetics and spectral composition of IR-chemiluminescence of the products of the $O(^1D)$ + H_2CO reaction. The $O(^1D)$ atoms were obtained by photolysis of ozone by radiation of an excimer KrF laser. λ=248 nm. Experiments were carried out in a flow gas system in He atmosphere at pressure of about 5 Torr. The pressures of O_3 and H_2CO were varied in the range of 1-30 mTorr.

4. Strong IR-luminescence arising from the O_3 + H_2CO mixture was recorded after excimer laser pulse CO_2 formation was demonstrated by luminescence absorption in a gas filter filled with CO_2 . The luminescence spectrum was mainly observed in the range 4.3-4.9 µm as a wide asymmetric band. The appearance of this band was

explained by calculating the luminescence spectra of the asymmetric stretching vibration of CO_2 with large energy supply in the molecule. Calculations were performed by direct search of anharmonic vibrational levels of the molecule. Level-distribution was considered as Boltzman with temperature T_{vib}. According to calculations, as energy supply increases, the luminescence spectrum moves to the long-wave region and its width increases. Comparing the experimental spectrum observed just after the laser pulse with the calculated one, has given a fair agreement at T_{vib}= 3500 cm^{-1}.

5. The energy evolved in the reaction as asymmetric stretching vibrations of CO_2 was determined from luminescence strength. To this end, the signal amplitude was compared with that of the luminescence of CO molecules excited upon energy transfer from $O(^1D)$ atoms. It is known that 40% of the energy of electron excited atoms passes to CO vibrations. As a result the energy yield was obtained for the asymmetric stretching vibrations of CO_2 equal to 1600 cm^{-1} per one electron excited oxygen atom. Comparing this value to the calculated energy supply in the mode of asymmetric stretching vibrations at T =3500 cm^{-1} leads to the conclusion that the channel with CO_2 molecule formation is the basic one in the $O(^1D)+H_2CO$ reaction.

6. Observing the kinetics of IR-luminescence intensity decay allowed one to extract information about the peculiarities of vibrational relaxation of highly excited CO_2 molecules. The decay curve is not monoexponential. In our experiments two stages can be distinguished, i.e. the initial stage of fast relaxation with time being about 70 μs and the stage of subsequent slow relaxation with time of about 1 ms. Studying luminescence spectrum it is seen that during the first relaxation stage the vibrational temperature T_{vib} drops from 3500 cm^{-1} to 2500 cm^{-1} . The intensity of observed luminescence decreases by about 40% which coincides with the decreases of energy supply in the luminescing vibrational mode calculated for these temperatures. The coincidence testifies to the applicability of the concept of the common vibrational temperature of the molecule in the process of relaxation.

7. For low concentrations of O_3 and H_2CO one can study the stage of luminescence signal increase. As H_2CO concentration increases the stage becomes shorter. The total rate constant of all channels of the reaction of $O(^1D)$ with H_2CO molecules was measured by analysing kinetic curves in these conditions. The rate constant is $(1.3\pm0.2)\cdot 10^{-10}$ cm^3/s.

PPK-27

TUNNELING DYNAMICS AND SPECTRA OF NON-RIGID MOLECULES

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Coherent tunneling transition in polyatomic molecules and molecular complexes is a prototype of irreversible chemical reactions in a gas and solid phases. Recent progress in modern high-resolution spectroscopic techniques enabled one to measure the vibration-rotation-tunneling (VRT) or vibration-tunneling (VT) spectra of cooled non-rigid molecules in a gas phase. This made ugent the question of theoretical calculation of tunneling splittings in such objects as a function of relevant quantum numbers of the system.

Multidimensionality of the potential energy surfaces (PES) is an obstacle for applying direct quantum-mechanical methods of computing the spectra. Thus, approximate methods become indispencible for treating tunneling dynamics of these systems. Recently, we devised [1 - 3] a semiclassical method for calculating VT spectra of coherently tunneling systems, multidimensional PES of which is symmetric and has two or three equivalent minima, separated by saddle point(s). This method is capable of predicting the approximate, within the WKB accuracy, tunneling splittings of the ground, as well as the excited vibrational states along both the tunneling and non-tunneling ("transverse") modes. The method is based on the Herring's formula [4], relating tunneling splitting of a certain state to the probability density flux through the dividing surface of the D-dimensional potential. This flux is constructed with the wave function of the state in the "isolated" well. The required wave function deeply in the classically forbidden region of the potential ("the transition state wave function") is found semiclassically, that is through the solution of the Hamilton-Jacobi and transport equations, in the vicinity of the extreme tunneling path, connecting equivalent minima of the upside-down potential. Propagating the WKB solution right to the minimum, we avoid the fundamental difficulty of the traditional semiclassical approximation in multidimensional case, i.e. matching of the solutions, obtained in different areas of the configuration space, at the caustics, separating classically-accessible and forbidden regions. Tunneling WKB wave function is normalized after comparing it near minimum with the variational solution inside the "isolated" well, which describes fairly well the given state. To the exponential accuracy, tunneling splitting is determined by the action along the extreme tunneling path. Pre-exponential factor appears, if the width of tunneling channel, i.e. the uncertainty in the position of the particle near the underbarrier trajectory, is taken into account. Prefactor is given, roughly, by the ratio of the averaged over the time of motion dynamical transverse frequency at the dividing surface to the transverse frequency at the minimum.

We test the accuracy of this method by calculating the VT spectra in a set of model 2D potentials with two [1 - 3] and three equivalent minima. They differ in symmetry of the coupling between the tunneling coordinate and transverse harmonic vibration, spanning almost all possible types of their interaction in 2D. These 2D potential are relevant for desciption of intramolecular tunneling proton transfer in OH...O fragments in malonaldehyde and tropolone, interconversion (puckering) of cyclopentanone, and hindered internal rotation of one or two coupled methyl groups in organic crystals. Comparison of the semiclassical results to the available quantum-mechanical computations demonstrated the wide range of applicability of the proposed approach. WKB methods, dealing with equations of motion, are not practically limited by the dimensionality of the problem. Thus, the proposed method is generalized to the case of an arbitrary symmetric D-dimensional double-well potential. We found, that the dynamics of the transverse modes, coupled only to the tunneling coordinate, may be strongly correlated. This observation is exemplified by computing the VT spectra in a 3D symmetric potential.

Along with tunneling splittings, this semiclassical procedure enables one to figure out the transition state geometry, given by the maxima of the square of the tunneling wave function at the dividing line of the potential. This transition state is different from that, predicted by the potential function (i.e., saddle point), because tunneling trajectory for most types of coupling deviate from the minimum energy path strongly. It is also found, that the transition state geometry in multidimensional potentials changes with the growth of quantum numbers of the transverse modes. For example, plane transition state of puckered cyclopentanone molecule in the ground vibrational state changes in the vibrationally excited states to the strongly bent configuration, close to that observed for pseudorotating molecules.

Authors feel that the proposed method, in which the tunneling splitting is expressed in the closed form through the dynamical parameters of the tunneling path and parameters of PES, will find its use in the solution of a reverse spectroscopic problem - extracting multidimensional potential from the experimental VRT spectra.

We thank Russian Fund of Fundamental Investigations (Grant No. 94-3-08863) for the financial support of this work.

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PPK-27a

PHASE SHIFT OF THE QUANTUM BEATS OBSERVED IN RECOMBINATION FLUORESCENCE OF SPIN-CORRELATED ION RADICAL PAIRS.

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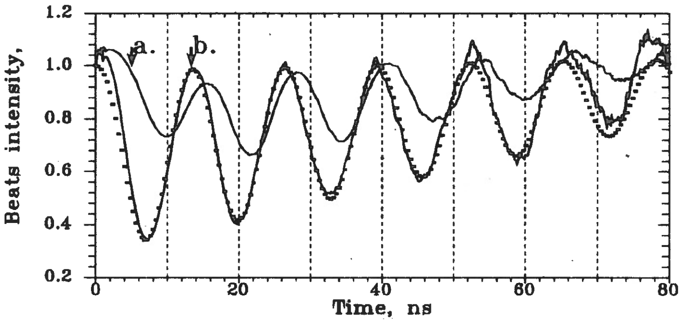
The singlet–triplet oscillations in the recombination fluorescence of the spin-correlated ion radical pairs forming under ionizing radiation could be observed in the alkane solutions containing acceptors of primary electrons and matrix holes [1]. For secondary ion radical pair (diphenylsulfide-d_{10})$^+$ / (p-terphenyl-d_{14})$^-$ the oscillations arises due to g-factors difference in pair partners. The delay time in the pair formation depending on matrix hole capture rate leads to phase shift of the oscillations (fig.1). This phenomenon allows to obtain directly a rate constant for reaction of matrix holes capture by the molecules of diphenylsulfide. The rate constant found by this way for isooctane is $(3.5 \pm 1) \times 10^{10}$ $M^{-1}s^{-1}$. The capture rate constants measured also for *cis*-decalin, *trans*-decalin and cyclohexane were found to exceed the diffusion controlled values.



Acknowledgement. This work was performed under auspices of International Science Foundation, Grant #RCE300, INTAS Grant #93–1626 and Russian Fund of Fundamental Research, Grant #93–03–5035.

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PPK-28

KINETIC STUDY OF THE REACTIONS OF THE NEW QUINOID COMPOUNDS - 1,10-ANTHRAQUINONES

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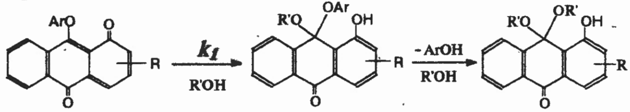
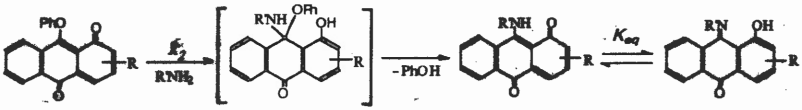
The 1,10-anthraquinone derivatives have long been unknown owing to their high reactivity [1]. The first derivative in the series of 1,10-anthraquinones has been isolated by irradiating of 1-aryloxyanthraquinone derivatives [1]. Therefore 1,10-anthraquinones are a novel class of quinoid compounds that became the subject of study only 10-15 years ago. The aim of this contribution is to study the reactions of 1,10-anthraquinones with nucleophilic agents (alcohols and aliphatic and aromatic amines).

The primary stage of the reaction between 9-aryloxy-1,10-anthraquinones and alcohols is the nucleophilic 1,4-addition



The reaction of 9-aryloxy-1,10-anthraquinones with the primary aliphatic and aromatic amines results in the formation of 9-alkyl(aryl)amino-1,10-anthraquinones that are in a tautomeric equilibrium with 1-hydroxy-9,10-anthraquinone-9-alkyl(aryl)imines. The data of quantum chemical calculations confirm the addition-elimination mechanism of the reaction



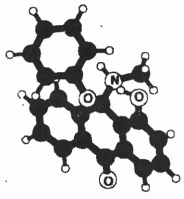


Fig. 1. A computer generated drowing of the intermediate, 9-phenoxy-9-methylamino-1-hydroxy-10-anthrone.

According to our calculations the reaction of the 1,4-addition of amines is exothermal. The minimum at the potential energy surface fits the adduct (fig. 1) of 1,10-anthraquinone with amine.

The spatial and electronic structures of amine effect on the rate constant of 1,4-addition. The rate constant decreases by more than an order of magnitude upon transition from alkyl amines to aniline (Table 1). The electron withdrawing substituents in the anthraquinone increase and the electron donor ones substantially decrease the reaction rate constant favoring the stability of photoinduced 1,10-anthraquinones (Table 2). When the electron donor substituents are introduced into aniline, the rate constant considerably increases, and after introduction of electron withdrawing substituents it decreases (Table 3, fig. 2).

PPK-28

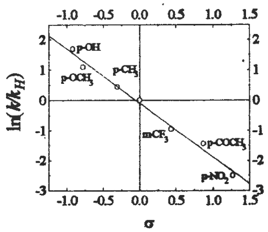


Fig. 2. Dependence of the rate constant on the nature of substituent in aniline

A substantial negative activation entropy (-28÷-34 e.u.) of the reaction between 1,10-anthraquinone derivatives and n-propylamine allows a conclusion on the high order of the transition state. The reaction proceeds easily due to fairly low activation enthalpy ($\Delta H^{\#}$= 2÷7 kcal/mol).

Table 1. Rate constants of 2-methylamino-1-phenoxy-1,10-anthraquinone with primary amines (RNH_2) in toluene at 305 K.

R	n-C_3H_7	n-C_4H_9	iso-C_3H_7	CH_2Ph	Ph
k_1, l/mol×c	24.0±0.2	19.0±1.0	4.0±0.2	21.7±0.1	0.56±0.05

Table 2. Rate constants of the reactions of 9-phenoxy-1,10-anthraquinone derivatives with methanol (k_1) and iso-propylamine (k_2) in toluene at 298 K and data of AM1 calculations.

R_1	k_2, $M^{-1}c^{-1}$	k_1, $M^{-1}c^{-1}$	q_C	ρ_{LUMO}	E_{LUMO}
2-NO_2	$(2.1\pm0.2)\cdot10^4$	4.2	0.19	0.17	-2.63
4-NO_2	$(5.8\pm0.5)\cdot10^3$	-	0.20	0.19	-2.54
H	150±10	0.3	0.16	0.17	-1.95
2-OCH_3	21±1	-	0.15	0.17	-1.85
4-OCH_3	5.4±0.5	$7\cdot10^{-3}$	0.14	0.17	-1.82
2-$NHCH_3$	4.0±0.2	$3\cdot10^{-4}$	0.14	0.18	-1.75

Table 3. Rate constants of the reactions of 9-phenoxy-1,10-anthraquinone with substituted anilines and data of AM1 calculations.

R	k_1, $M^{-1}s^{-1}$	ΔH_1, kcal/mol	q_N	ρ_{HOMO}	E_{HOMO}, eV
p-OH	$5.9\cdot10^3$	-10.1	-0.32	0.21	-8.28
p-OCH_3	$1.5\cdot10^3$	-10.2	-0.32	0.21	-8.22
p-CH_3	$3.3\cdot10^2$	-10.3	-0.33	0.23	-8.36
H	$1.2\cdot10^2$	-10.2	-0.33	0.27	-8.52
m-CF_3	$1.3\cdot10^1$	-10.1	-0.32	0.29	-9.04
p-$COCH_3$	4.4	-9.7	-0.34	0.26	-8.78
p-NO_2	0.4	-9.6	-0.38	0.29	-9.17

Acknowledgments. This work was supported by Foundation for Fundamental Study of Russia (grant 95-03-08920) and by Committee of High Education of Russia (program "Chemistry, section "Photochemistry").

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PHOTO-AFFINITY LABELING REAGENTS. PHOTOCHEMISTRY OF AZIDOETHIDIUM DERIVATIVES IN WATER.

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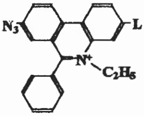
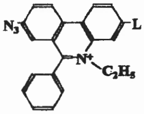
The sequence-specific chemical modification with oligonucleotide derivatives is one of the most promising approaches to influence directly the genes of living cells [1]. The photolabeling reagents are the most interesting ones according to their unique opportunity to perform modification at any desired moment of time. The recent data [2] demonstrate the high efficiency of azidoethidium derivatives of oligonucleotides (L_1 on a scheme) for sequence-specific modification of single-stranded and double stranded nucleic acid targets.



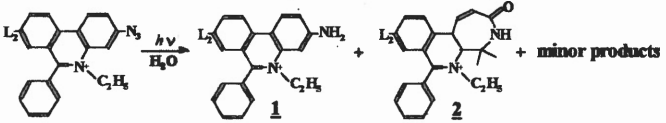


L_1=NHC(O)CH$_2$CH$_2$NH$\overset{O}{\underset{O^-}{P}}$O(oligonucleotide)

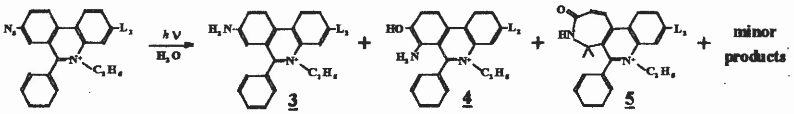
L_2=NHC(O)CH$_2$CH$_2$NHR, R=H or COCF$_3$

A knowledge of the mechanism of photochemical processes occurring in tight-specific complexes is very useful for understanding of the modification nature. This presentation is devoted to study of the photochemistry of model compounds: 2- and 7-azidoderivatives (2-AEt and 7-AEt) of ethidium dye (L_2 on a scheme).

The products of photolysis of 2-AEt and 7-AEt in water were isolated by high pressure liquid phase chromatography (HPLC). Their nature were identified by UV and NMR (^{1}H and ^{13}C) spectroscopy. Two main products were identified for 2-AEt photolysis



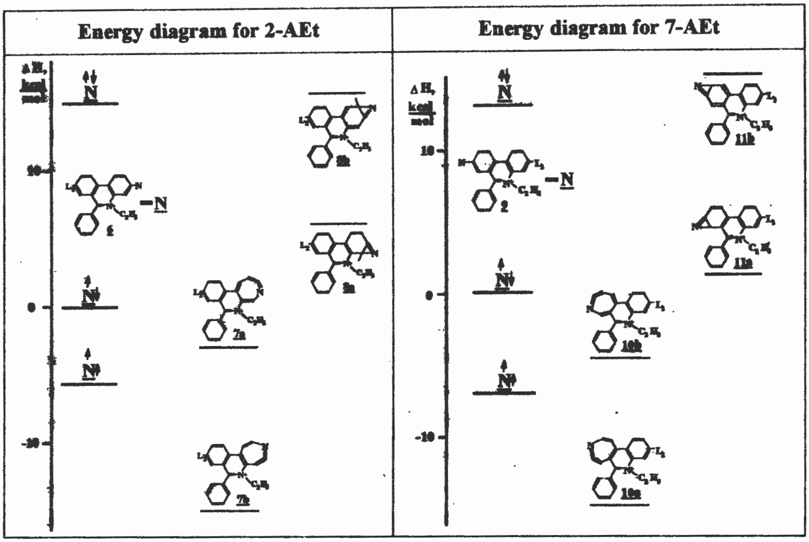
A lot of peaks (more then ten) were recorded by HPLC for 7-AEt photolysis mixture and three main products were identified.



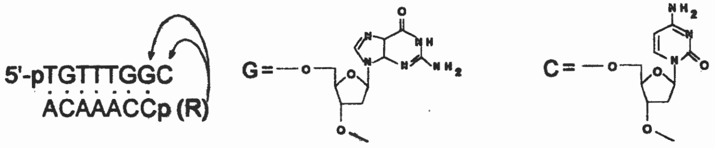
It was established that quantum yields of 2-AEt and 7-AEt photodecomposition do not depend on the presence of oxygen, excitation wavelength, concentration of azides and equal to 0.95±0.20 for 2-AEt and 0.57±0.12 for 7-AEt. The first type of products (7- and 2-N-(3-

aminopropionyl)ethidium appeared from the triplet nitren and other products from the singlet precursors.

The nature of key intermediates of aromatic azide photolysis is known from the literature, but in every particular case the different types of intermediates can participate in the reaction [3]. The difference in the behavior of 2- and 7-AEt was explained using the data of quantum chemical calculations (AM1 method) of the structure and energy of photolysis intermediates.



Experimental results (higher yield of product 1 (30%) comparing to 3 (15%); appearance of product 4) are in accordance with the data of AM1 calculations. The result obtained for model compounds (2-AEt and 7-AEt) will be used for interpretation data of sequence-specific modification by azidoethidium derivatives of oligonucleotides [2]:



Acknowledgments. The present work was supported by International Science Foundation (grant RBV000) and by Russian Foundation for Fundamental Researches (grant 95-03-08920).

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PPK-30

LASER FLASH PHOTOLYSIS AND FLASH CIDNP STUDIES OF 1-NAPHTHYL ACETATE PHOTO-FRIES REARRANGEMENT

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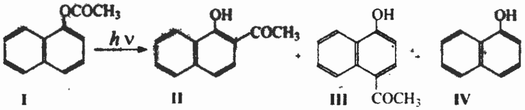
In this work, we have employed a number of experimental methods (the steady-state and time-resolved CIDNP and flash photolysis) for a detailed investigation of the phototransformation of 1-naphthyl acetate, which is a typical photo-Fries rearrangement reaction. The photo-Fries rearrangement was first discovered by Anderson and Reese [1] in 1960. Over the years this phenomenon has been extensively studied and has been observed in various aromatic compounds; however, data on the rate constants of the elementary stages are lacking. It has been known that the irradiation of 1-naphthyl acetate (**I**) in various solutions gives rise to the products typical of the photo-Fries rearrangement: 2-acetyl-1-naphthol (**II**), 4-acetyl-1-naphthol (**III**) and 1-naphthol (**IV**) [2,3] (scheme 1).

Scheme 1



This work was aimed at determining the role of the excited singlet and triplet states in the photo-Fries rearrangement of **I** as well as at establishing the nature, spectral characteristics, and reactivity of the intermediates. To make the conclusions about mechanism of photoprocesses more valid, we used different experimental methods and quantum chemical calculations (AM1, INDO, CNDO/S methods).

The analysis of the effect of piperylene on the quantum yield and on the signs of polari-zation observed in CIDNP spec-tra has validated the assumption that the decomposition of **I** to acetyl and naphthoxyl radicals through the singlet state is the main channel of the reaction (more than 90%). The major contribution to CIDNP is made by the radical pairs resulting from the decomposition of the excited triplet states of **I**. The most likely limiting stage of CIDNP formation in the products **II** and **III** is the izomeri-zation of intermediates (Fig.1).

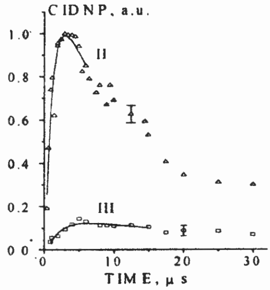


Figure 1. CIDNP kinetics obtained during the photolysis of **I** in acetonitrile-D_3. Triangles - for methyl protons of **II**, squares - for methyl protons of **III**, solid line - calculated

In the flash photolysis experiments we have detected decay kinetics (Fig.2) and the

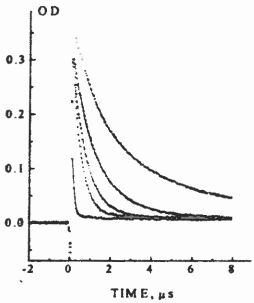
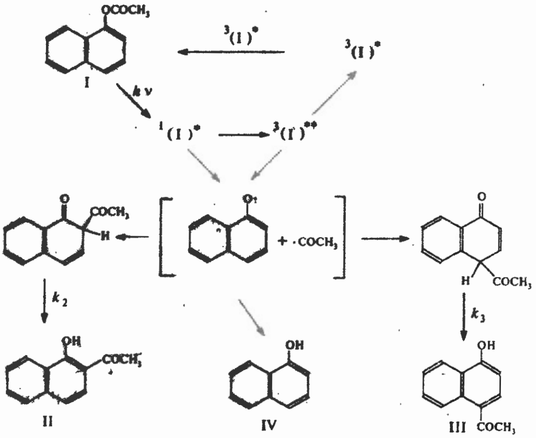


Figure 2. Transient absorption decay curves observed after excitation of a solution of 1×10^{-3} M 1-naphthyl acetate in acetonitrile in the presence of piperylene: 0 (upper trace), 2×10^{-4}, 5×10^{-4}, 1×10^{-3}, and 5×10^{-3} M (lowest trace).

absorption spectra of 1-naphthyl acetate triplet and naphthoxyl radical. It has been established that the main channel of triplet decay is the triplet–triplet annihilation. It was assumed that the different methods detect two different triplet states. In the experiments on the flash photolysis of **I** we detect the spectrum of the lower nonreactive $\pi\pi^*$ state, whose properties are similar to those of the naphthalene triplet state. In the photo-Fries rearrangement, the reactive state is the excited short-lived triplet state (probably the $n\pi^*$ triplet state) which decomposes to yield a radical pair, wherein the CIDNP effects arise.

The results obtained allow us to propose the following mechanism for the photo-Fries rearrangement of **I**

Scheme 2



This work was supported by grant of Russian Fund of Fundamental Research (projects 93-03-18593 and 95-03-08920) and International Science Foundation and Russian Government (project JJD100)

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DIPOLE-DIPOLE RELAXATION OF MICELLIZED RADICAL PAIRS. A MODEL OF MICROREACTOR WITH AN ATTRACTING WALL.

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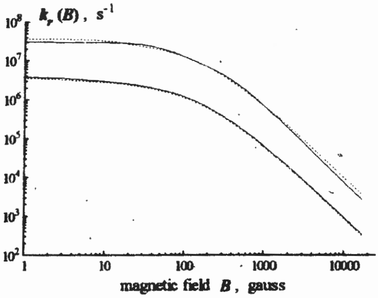
The magnetic effects that appear in the recombination reactions of radicals in micelles have been the objects of much investigation in the modern spin chemistry. In micelles, unlike in homogeneous systems, the role of inter-radical spin interactions is great. The dipole-dipole magnetic interaction between the electron spins of a radical pair (RP) is less sensitive to the radical structure than the exchange interaction and can play an important part in the relaxation of the triplet sublevels of RP at strong magnetic fields.

The model of microreactor [1], in which one radical of the RP is fixed at the center of a spherical cavity with a partly reflecting wall and the other radical freely diffuses in the bulk of the cavity (micelle), is widely employed in quantitative analysis of the magnetic effects in micelles. This paper proposes an analytical calculation of the rate of the dipole-dipole relaxation in the modified model of the microreactor. In our modification, the microreactor wall can interact with the diffusing radical via the short-range attraction potential of an arbitrary force. In the limit of weak interaction, our results show good fit to the numerical calculations of the dipole-dipole relaxation rate, which were performed by Steiner and Wu using the Monte-Carlo method [2] (see the figure). In the other limiting case (strong attraction of the radical by the wall), our results reproduce the Hayashi calculations, which



The magnetic field dependence of the rate of the dipole-dipole relaxation between the triplet sublevels $T_\pm T_0$ of the micellized RP.
Upper curves: solid line-our analytical calculation, dashed line - the Monte-Carlo numerical calculation by Steiner and Wu [2], micelle radius 20Å , radical contact radius 4Å, non-attracting wall.
Lower curves: the effect of the apparent increase in the micelle radius in the microreactor model with an attracting wall ($\xi \neq 0$); solid curve - $r_m = 35$Å, $\xi = 1$; dashed curve - $r_m = 45$Å, $\xi = 0$. ξ - is the relative probability of localization of radical on the micelle surface.

correspond to the surface diffusion of one radical in the micelle [3]. In the general case, for an arbitrary interaction intensity, it is shown that the attraction of the radical to the wall can lead to the natural effect of an apparent increase in micelle radius (see the figure). This fact should be taken into account in the experimental analysis of the magnetic effects in micelles. It is shown that if the coefficients of volume and surface diffusion are close in value, the rigorous analytical expression can be reduced to a sum of two terms, which have clear physical meaning.

The work was supported by the Russian Foundation of Fundamental Research (project № 93-03-18593).

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NON THERMAL MECHANISMS OF FRONT CHEMICAL REACTIONS IN CONDENSED MATTER

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The two different types of non stationary states of front propagation were considered. The first one is connected with variations of conversion front propagation velocity and its form, whereas the second one appears in the case when dimension of sample is less or comparable with front width (quasi front regime [1]) . It is shown that in quasi front regimes the stationary propagation of experimental mark may be observed despite the essentially non stationary character of kinetics in the sample.

The applicability of auto wave or induction models is considered as a main principle of classification of front propagation mechanisms [2].

New method of front radical polymerization of auto wave type was proposed and studied experimentally [3,4]. The essential feature of this method is the presence of polymer inhibitor incompatible with polymer produced. The analytical model was developed based on diffusion-reaction differential equation [4].

The conversion wave propagation with induction mechanism was demonstrated for radical polymerization of methyl methacrylate in the sample with gradient of strong inhibitor concentration [2]. The gradient of inhibitor concentration was adjusted as a result of preliminary reaction of inhibitor with initiator in non homogeneous temperature field.

It was shown that in the case of front photo polymerization both auto wave and induction types of mechanisms may be realized, the latter being observable in media with constant optical density [5,6]. The mechanism of auto wave type for photo polymerization [2] and the mixed one for photo oxidation [8] were studied experimentally and analyzed theoretically. In [8] full conversion profiles at different moments of time were measured by UV-spectroscopy method and compared with theory.

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A STUDY OF FLAME PROPAGATION IN DICHLOROSILANE-OXYGEN MIXTURES BY MEANS OF HIGH SPEED CINEMATOGRAPHY.

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The silanes oxidation reactions are widely used in integrated circuits processing.However, the kinetic mechanisms of these processes have not been revealed at present. Thus, the information on phenomena caused by the chain mechanism of silanes oxidation oxidation is quite valuable.

In the present work, the flame propagation phenomenon was studied by high-speed schlieren cinematography over the pressure range of 20-450 torr and the initial temperature 300K.Heated steel or quartz reactors with diameters 10 cm (spherical) or 4 cm(100 cm lengthwise) respectively had inlets for electric power supply and gas evacuation as well as optical windows. The combustible gas mixtures contained 5% SiH_2Cl_2(DCS) and 95% oxygen.

It has been shown that the visible flame velocity U is proportional $P^{-1/2}$(P is the total pressure) over P range of 15 m/s(P=60torr)-7 m/s (P=400torr). U values for the mixture containing 5% DCS+ 2% SF_6 + $O_2$are about 40% less over this range of P than for the one without SF_6 .The comparison of U data for steeland quartz reactors shows that U in quartz one decreases markedly with pressure drop at low pressures (P<30 torr). In this case the mass diffusivity at NTP of the active centers (AC) determining the flame propagation ($D > 0.7 cm^2 s^{-1}$) has been estimated on condition that the characteristic times of AC break process and the chemical reaction are equal on the flame propagation limit.

It has been shown that the flame zone consists of two areas. The fore-part of the flame is the low temperature area with maximal density gradient: the second part is the area of vigorous chemiluminescence.The fore-part has a cell structure pointing to the marked role of mass diffusion as compared with thermal one. D value estimated on the basis of this data is 2.3 cm^2s^{-1}. D values obtained above are markedly higher than thermal diffusivity and close to hydrogen atoms mass diffusivity. An inhibitory effect of SF_6 on U may be conditioned by the fast reaction $H+O_2+SF_6$ -- HO_2 +SF_6 (ΔH=-45 kcal/mole) provided that HO_2 is not active in subsequent chemical conversions. It is also possible that SF_6 interacts with charged AC revealed in our previous works, causing the chain break with charged particles participation being of significance in silanes oxidation.

On present evidence it may be argued that the flame propagation in DCS-oxygen mixtures has a chain-thermal nature; AC with high mass diffusivity being of importance in this phenomenon.

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T-MATRIX REPRESENTATION AND LONG TIME BEHAVIOR OF OBSERVABLES IN THE THEORY OF MIGRATION-INFLUENCED IRREVERSIBLE REACTIONS IN LIQUID SOLUTIONS

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The theory of migration-influenced irreversible reactions upon binary encounters of reactants in liquid solutions is for the first time consistently formulated in the terms similar to those of non-stationary scattering theory: a resolvent, free resolvent, T-matrix, etc. The approach developed has made it possible to construct the theory of irreversible chemical bimolecular reactions based on nonmodel consideration.

Free motion of a reacting pair in the configuration space is treated as random walks in three-dimensional infinite space and arbitrary Markovian motion over internal degrees of freedom. Some general properties of the free resolvent that describes the motion of reactants in liquid solutions have been established. The mixing principle for the problem under study is stated. In the case of mixing by free motion, general asymptotic properties of free resolvent describing this motion have been revealed at long distances and times. On the basis of the approach developed, the general long-time kinetic law of the attainment of steady-state values by the observables in bulk and geminate reactions has been deduced. As is shown, all literature results of long-time kinetics asymptotic studies obtained for specific simple models are particular cases of the general law established. Thermodynamically, not only the universality of their long-time dependence is important, but also the fact that the rate of attaining the steady-state values is completely determined by macroscopic quasiequilibrium observables.

ACKNOWLEDGEMENTS
The paperis supported by the Russian Foundation of Fundamental Research (project 93-03-05032).

PPK-35

Accumulation of energy at low-temperature radiolysis of molecular matrix and its influence on postradiation process.

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A series of works has been carried out to study critical phenomena and autowave processes initiated by local brittle fraction of previously γ-irradiated solid samples at 4.2-77 K. In the analysis of conversion mechanisms the radicals and ions forming under radiolysis were thought to be the only active centres of a chemical process. However, during low-temperature radiolysis the energy of incident radiation can be stored as potential energy of nonequilibrium phase states.

While studying the cryochemical reactions in the autowave regime (chlorination of hydrocarbons, hydrobromination of olefins, polymerization and copolymerization) it was shown that the role of this energy in chemical conversion was significant. In particular, there is a considerable deviation from the linear dependence between the chemical activity of systems (the rate of wave propagation in the sample) and the concentration of active centres, accumulated in matrix. The rate propagation of the polymerization autowave initiated by local brittle fracture increases linearly up to doses of 1000 kGy, while linear accumulation of active centres stops at much smaller doses (≈50 kGy). It is an evidence for accumulation of a part of the absorbed energy and using its for the act of chemical conversion.

The question connected with the most effective use of energy accumulated during radiolysis for realising autowave cryochemical processes are examined. A hypothesis of the initiation in same systems of the detonation-type autowave mechanism (self-supporting shock wave) has been suggested.

The absorption of 100 eV of γ-ray leads to generation of G=8,2±0,2 paramagnetic centres trapped in solid HCN (registered by an ESR technique). It was found out that during radiolysis the anion radicals not giving any ESR signal were stabilized as well . After photobleaching the radiolyzed HCN at 77 K the concentration of the paramagnetic centres was three times higher. Therefore, on absorbing 100eV of the γ-ray energy 24 trapped radicals were formed in 1g of solid HCN, i.e., about 50-55eV in the form of trapped radicals was accumulated per 100eV of the absorbed energy. Thus, when irradiating the solid HCN with γ-rays ^{60}Co, it accumulated only as radicals up to 50-55% of the absorbed γ-ray energy. And still the energy accumulated as ions was not taken into account here. Such an effective accumulation of γ-irradiation energy in the form of chemically active intermediates has been observed for the first time.

Quite unusual proved to be the experimental results on optical bleaching of the HCN samples radiolyzed at 77 K. The action of light with wave length of $\lambda \leq 350$ nm led to a triple increase in the total amount of the paramagnetic centres in a sample.

We assume that during radiolysis of solid HCN the arising electrons are stabilized on the forming radicals, thus making impossible to detect them with an ESR technique. Optical bleaching leads to that the electrons are thrown away from the traps and the radicals they have been stabilized on are registered with an ESR technique.

Therefore, not 8 but 24 paramagnetic centres are stabilized 1 g of solid HCN as a result of its absorbing 100 eV of γ-radiation energy at 77 K. As this system spends 4.0-4.5 eV to form one pair of radicals, then 48-54 eV are accumulated as stabilized radicals from each 100 eV of the absorbed energy. Thus, when irradiating solid HCN with γ-rays ^{60}Co, it accumulated only as radicals up to 50% of the absorbed γ-radiation energy. We haven't yet known any other system that can so effectively accumulate the energy of γ-radiation as chemically active intermediates.

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PPK-36

Catalysis of Cooperative Processes in Non-isothermal Synthesis of Oxygen from Perchlorates.

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The association accompanying the formation of compounds with the specific ratio of components leads to the abrupt change of physical properties and reactivity of liquid solutions, at such proportions of compositions which approach the stoichiometry. At solvatation of simple inorganic salts by solvents with strong hydrogen bonds, there are the stable forms containing from 1-8 to 100 and the more molecules of H_20, CH_30H for one dissociated molecule of $CuS0_4$, NaCl, $NaC10_4$, which can be detected by different methods, for example by dilatometric titration. Recently, similar processes were noticed in melts of alkali metal perchlorates. In the present report, the advent of singular points revealed at the decomposition of mixtures containing perchlorates and oxides is compared with changing the reactivity of forming melts for magnesium. DTA and TGA are simultaneously carried out at heating rate 10°C/min.

It has been found [1], despite the known evidence and explanations, the Ca0 can act as a catalyst for 0_2 evolution from perchlorates similarly to d-metal oxides, for example Ni0. The previous authors discussed the behavior of the Ca0, which contained a considerable amount of chemically bounded water. In binary system $MC10_4$-$Ca0_2$ when M = Na, K, Rb, Cs, first, the $Ca0_2$ has been decomposed, then the free water surface of the Ca0 effectively acts as a catalyst for oxygen evolving from perchlorate or its melts. The rate of weight-loss is changed abruptly at mol. ratio $Ca0/MC10_4$ about 0.12-0.16 and 0.5.

In ternary system $MC10_4$-Mg-$Ca0_2$ the particular low-temperature reaction arises which is lacking in any binary subsystems. The process takes place only in mixtures, when the count of components is over two. As a consequence, this process is cooperative.

Degree of Mg conversion at the cooperative stage depends on the relationship of the all three components. In system $KC10_4$-Mg-$Ca0_2$, the doping the binary mixtures by the peroxide from the molar ratio $CaO_2/KClO_4$ = 0.05 to 0.12 increases the part of Mg burning at 490-520°C and decreases its part self-igniting in oxygen after 590°C. At 0.11, 0.12 M CaO_2 per 1 M $KClO_4$ practically all metal burns at 490-520°C. However, the dope of the CaO_2 from 0.13 to 0.5 throws away the Mg to high temperatures. The transfer between 0.1 and 0.13 M CaO_2 vs. 1 M $KClO_4$ agrees with singular point which had been observed in binary systems of the perchlorates and oxides.

At heating the mixtures $KClO_4$-Mg-Fe_2O_3 two processes arise when active magnesium oxidation and fast O_2 evolution occur at low temperatures. The additives of Fe_2O_3 from 0.005 to 0.04 M per 1 M $KClO_4$ lead to all but complete Mg burning in range 530-540°C. At 0.05-0.07 Fe_2O_3 a considerable amount of the metal is ignited at second stage after 590°C. When mol. ratio $Fe_2O_3/KClO_4$ runs into 0.17-0.18 then Mg burns completely at 500-520°C as in the case of CaO_2. When the Fe_2O_3 more than 0.18, the Mg oxidation occurs after 590°C newly.

The data obtained in the ternary systems fit the findings that the shift of singular points in the binary mixtures of perchlorates with oxides can correlate with the content of oxygen atoms in mole of oxide. For example: 0.17 for Fe_2O_3 and 0.5 for CaO. The result can be connected with fast transfer of products arising by the interaction between oxides and chlorates and perchlorates within oxide. (Likewise to system CaO-H_2O). The isotopic exchange of O^{18} in reacting mixtures $KClO_4$-BaO_2 fits the hypothesis. In the case, at estimations of mechanisms of oxide and peroxide catalytic action for perchlorate and chlorate decomposition, account must be taken of both the surface function and the scope for the formation of solutions, that is to say, homogeneous mediums between salt melt, products of the breakdown and catalysator.

This work was carried out by financial backing of Soros International Science Foundation and Government of Russian Federation (Grants: N9K 000, N9K 300).

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PPK-37

PROTON PHOTOTRANSFER AND PHOTOINDUCED CONFORMATIONAL PROCESSES IN N-HETEROCYCLIC COMPOUNDS

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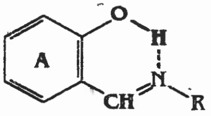
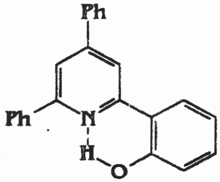
By absortion and emission spectroscopy, photochemical methods and quantum-chemical calculations with use of the structural modeling method the N-heterocyclic compounds containing the exo (I) and endo (II) cyclic H-bonded (O-H—N) C—N-groups have been studied.



R= Ar, Alk

I



II

In compounds I the Excited State Intramolecular Proton Transfer (ESIPT) occurs due to the photoinduced Intramolecular Charge Transfer from aldehyde ring (A) to the exocyclic C=N-group. ESIPT is a primary adiabatic process followed by fluorescence with Anomalous Stokes Shift (ASS) and the competing diabatic rotations around C—C- and C—N-bonds reponsible for the colored form origin.

The compound II with the endocyclic C—N-group does not undergo ESIPT in spite of H-bond in the ground state. The fluorescence (without ASS) and intensive phosphorescence corresponding to the longwavelength absorption band of the structure II are revealed.

The fast intersystem crossing (S1⤳T1) and excited state H-bond disruption due to adiabatic OH-Ph ring twist, are considered as processes succesfully competing with ESIPT.

The work is supported by Russian Fund of Fundamental Investigations (RFFI, **project N 94-03-09302).**

ACTIVATION OF PROCESSES IN SOLUTION WITH NON EQUILIBRIUM PLASMA.

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It is well known the plasma activation of the gas phase and heterogeneous processes. The "cold" plasma allows the treatment of the non thermal-resistant materials. It is natural to use the cold plasma to activate of the solution processes in the conditions of the limited possibilities of the thermal activation.

The investigations of this problem are not very numerous and the industrial applications of this method is not known for us. We have analyzed three possible versions of the cold plasma-solutionsystems:

1. The corona discharge over the solution surface.
2. The corona discharge between the electrode in the gas phase and the electrolyte.
3. The discharge in the gas-vapour cavity near the electrode immersed into the electrolyte solution.

We have considered the basic problems of the investigation and application of these plasma - solution systems. The processes of the real ion transfer between the solution and plasma were theoretically analyzed. The influence of the solvated ions state in the liquid and gas phase on the transfer process and plasma boundary conditions was taken into account. The active particle generation kinetic was estimated on the basis of the modern experimental and theoretical data concerning of the gas discharge plasma properties and plasma processes.

It was shown by experiment the acceleration of the homogeneous and heterogeneous oxidation processes in solution by use of the cold plasma, the role of the ozone generation and the possibility of the water cleaning using this method.

The research described in this publication was made possible in part by Grant № RLP300 from International Science Foundation and Russian Government.

PPK-39

Ultrafast collisional relaxation of high frequency vibrations in small polyatomic molecules

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This work presents an investigation of collisional relaxation of high vibrational levels and the role of intermolecular interactions in this process. Vibrational level v =1 of ν_1 (C-H stretch) in CHF_3 or CHF_2Cl was excited by short (~10ps) pulse of optical parametric oscillator (OPO). After a definite (variable) delay τ a population of this level was probed by another short pulse (λ=532 nm, ~5 ns duration) using spontaneous Raman scattering. It was demonstrated that high dencity of nearby "dark" vibrational states (~1 state/cm^{-1}) strongly influence vibrational energy transfer in collisions.

The measured rate constants of the energy relaxation of v =1 (ν_1) level were $k(CHF_3)=16.7(\mu sTorr)^{-1}$ and $k(CHF_2Cl)=33.3(\mu sTorr)^{-1}$. It means that only 0.7 and 0.4 of gas-kinetic collision is sufficient for relaxation that is extraordinary fast. For comparison, the relaxation of C-F stretch in CHF_2Cl needs ~18 collisions ($k=0.8\ \mu s^{-1}Torr^{-1}$).

To clarify the mechanism of ultrafast collisional relaxation we investigated this process in mixtures of CHF_2Cl and CHF_3 with various buffer gases. The obtained relaxation rates in heteromolecular collisions (see the table) for all collisional partners including noble gases are found much greater than regular rate of V-T relaxation. The process is significantly faster when a second collision partner is a particle with permanent dipole moment and practically mass-independent.

The observed effect of ultrafast collisional relaxation of high-laying vibrational states is impossible to explain on the basis of existing theories of V-V' exchange. The above experiments with noble buffer gases unambiguously show that after a collision the energy is remained in initially excited molecule. It means that the observed ultrafast relaxation is caused by energy transfer from excited "bright" states to nearby "dark" states. Thus the collision-induced intramolecular vibrational relaxation (CIVR) takes place.

Collision partner	Mass (reduced mass), *a.u.*	Permanent dypole moment, *D*	Rate constant, $(\mu s Torr)^{-1}$	Probability per hard-sphere collision
$^{(1)}$He	4 (3.8)	0	2.85±0.22	0.12
$^{(1)}$Kr	84 (42)	0	3.12±0.40	0.38
$^{(1)}$Xe	131 (52)	0	3.5±0.25	0.37
$^{(1)}N_2$	28 (21)	0	3.05±0.35	0.24
$^{(1)}SO_2$	64 (37)	1.61	11.35±1.15	1.03
$^{(1)}H_2S$	34 (24)	0.93	9.4±0.83	0.71
$^{(1)}CHF_2Cl$	86 (43)	1.41	33.3±7.5	2.6
$^{(2)}SF_6$	146 (47)	0	3.1±0.8	0.4
$^{(2)}CHF_3$	70 (35)	1.6	16.7±3.8	1.4

$^{(1)}CHF_2Cl$ is excited

$^{(2)}CHF_3$ is excited

The model of ultrafast collisional V-V' exchange is proposed. It assumes that CIVR takes place due to intermolecular rovibrational mixing influenced by electric field of the second particle. The estimations are made that approuve such a possibility.

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PPK-40

CIDNP IN PHOTOLYSIS OF COENZYMES B_{12} AND MODEL COMPOUNDS

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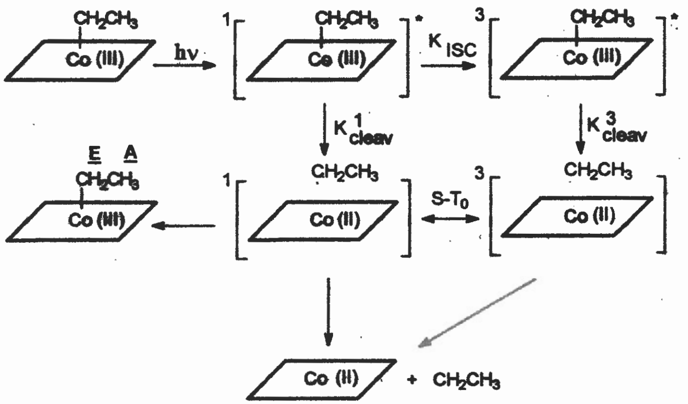
The photolysis of coenzyme B_{12} and related model compounds have been studied extensively by the optical methods of laser flash photolysis and continuous-wave photolysis [1], as well as by the spin chemistry techniques of CIDEP [2] and magnetic field effects on the rate of product formation [3]. Photolysis of the alkylcob(III)alamin leads to Co-C bond homolysis to produce a radical pair that consists of the alkyl radical and cob(II)alamin. Probes of the reaction by optical spectroscopy give information on the kinetics of product formation, but these results are ambiguous when it comes to unambiguously defining the spin state multiplicity of the radical pair precursor. The electron spin state multiplicity (singlet vs. triplet) of the initially-formed radical pair remains controversial. In continuous-wave photolysis experiments, a decrease in the escape product yield is seen as the applied DC magnetic field is increased from the geomagnetic field to 0.8 T. This suggests C-Co bond cleavage occurs from the excited singlet state. In contrast, analysis of CIDEP effects from the photolysis of aquocob(III)aloxime suggest the triplet excited state may be the precursor to C-Co bond homolysis [2]. Thus, the multiplicity of the initially-formed radical pair remains an open question.

The present study is devoted to the application of a complimentary spin chemistry probe, CIDNP. This experiment makes it possible to clarify the discrepancy between the CIDEP interpretations and the magnetic field effect studies. The photolysis of ethylCo(III)[SALEN] in CD_2Cl_2 shows polarization effects for the ethyl group of the starting material (emission, E, for CH_2; and absorption, A, for CH_3). This is consistent with C-Co bond cleavage occurring from the excited singlet state. However, the CIDNP intensity strongly depends on the oxygen concentration in the reaction mixture. Deaeration of the solution by sparging it with argon results in a dramatic decrease in the CIDNP intensity without change in the CIDNP sign. Most probably, the influence of the oxygen is to quench the excited triplet state of the EtCo(III)[SALEN]. Decreasing the oxygen concentration leads to an increase in the contribution from the triplet spin state and a net decrease in the overall CIDNP signal due to polarization with an opposite sign. The similar results have been observed for benzylaquocob(III)aloxime photolysis.

It is also possible to explain the discrepancy between the interpretations of the magnetic field effect and CIDEP studies. Taking into account the significant difference in enhancement coefficients of CIDEP formed via the radical pair mechanism (≈ 20-50) and those of electron polarization generated by means of the triplet mechanism (≈ 300), one might come to the conclusion that even a 15-20% contribution of CIDEP by the triplet mechanism may cause full annihilation of electron polarization that is formed through the radical pair mechanism. At the same time, magnetic field effects will correspond to the prevailing reaction pathway, that is, photohomolysis from the singlet excited state. CIDNP methods show that C-Co bond homolysis occurs from both states, and the rate of C-Co bond cleavage from the singlet state is greater than the rate of ISC in the molecule ($K^1_{cleav} > K_{ISC}$).



The financial support of Russian Foundation for Basic Research (grant No. 94-03-08976), International Science Foundation (grant RC7000/RC7300), and NAS of the USA (CAST program) is gratefully acknowledged.

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PPK-41

PARAMAGNETIC SPIN-CATALYSIS

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Intersystem crossing is defined as a radiationless transition of a molecule between electronic states of different multiplicity. Radiationless transitions in benzene, anracene and other large complex molecules have received much attention but very little is known either experimentally or theoretically about transitions of this type in molecules which contain a few atoms.

The double bond in ethylene can dissociate into single bond by the following way; by a transition from its singlet ground state to a triplet state. It would be expected that paramagnetic substances would catalyze above mechanism. Catalysis of some homogeneous chemical reactions by paramagnetic molecules has been reported, but the available evidence is not very conclusive. In particular, fourty years ago Evans [1] has shown that dissolved oxygen strongly induces the triplet-singlet (T-S) absorption of aromatic molecules and other unsaturated hydrocarbons (UHC). This was the first direct indication of spin-catalysis phenomena [2]: the rate of process was greatly increased by the oxygen catalizator, which assists in overcoming of spin forbiddness. Introducing the two unpaired electron spins to the collision complex, the $^3O_2$ molecule effectively lifted the spin-forbiddness of the $T_1 \longleftarrow S_0$ transition inside the UHC moiety, because both states in the complex became triplets. The nature of the $T_1 \longleftarrow S_0$ transition enchancement is then determined by small admixtures to the united triplet component of other triplet states of the complex.

The collision complex between molecular oxygen and ethylene has been studied by configuration interaction calculations, scanning the intermolecular distance, R, in C_{2V} collision symmetry . The calculation give a good explanation of the enchancement of the ethylene, $T_1 \leftarrow S_0$, observed by Evans at high oxygen pressure. A number of other oxygen and cooperative transitions are explained and predicted, considering the studied system as a general system as a general model for unsaturated hydrocarbon-O_2 interaction [3].

Besides MNDO calculations have been performed for the investigation of influence the paramagnetic molecules (O_2,NO) on the cis-trans-isomerization reaction of ethylene. The calculations carried auf both for the isolated ethylene molecule and for the catalytic collision complexes $C_2H_4...O_2$. The potential curves shows shallow minimum under the intermolecular intercation ethylene with oxygen. It is would be the evidence of the phenomena of the paramagnetic spin-catalysis II type according Minaev's classification [2].

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PPK-42

POLARIZATION SPECTROSCOPY OF ATOMIC PHOTOFRAGMENTS PRODUCED IN MOLECULAR PHOTODISSOCIATION

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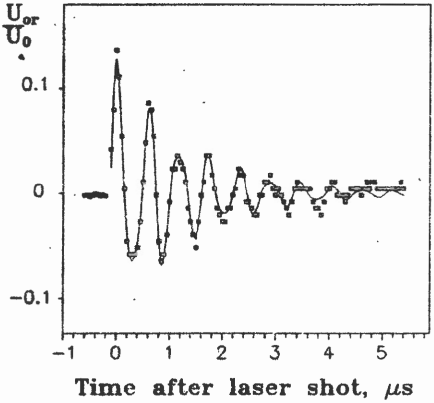
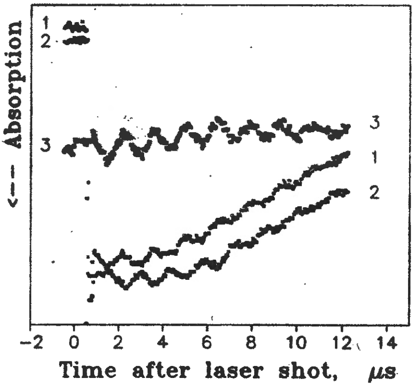
Polarization spectroscopy of photofragments (PSP) allows to obtain detailed information on photodissociation dynamics [1,2] that sometimes cannot be obtained by other methods.

We present both experimental and theoretical studies of polarized $6^2P_{1/2}$ ground state and metastable $6^2P_{3/2}$ thallium atoms and ground state $5^2S_{1/2}$ rubidium atoms produced in photodissociation of TlBr and RbI molecules respectively by polarized impulse laser radiation at 266 nm. The atomic polarization (i.e. Zeeman population differences) led to the dichroism of the atomic vapours that was detected by absorption of a probe light beam that was in resonance with the atomic transitions. In order to increase signal-to-noise ratio and to determine the polarization of different hpf atomic sublevels we used magnetic resonance technique. Figure 1 shows a typical free precession signal of mean magnetic moment of oriented metastable Tl($6^2P_{3/2}$) photofragments in an external magnetic field of H_0=1.23 Oe [3]. The dissociation light in this experiment was circularly polarized. We studied the temporary changes of the thallium orientation (M selection) and alignment (|M| selection) in various experimental conditions and determined orientation and alignment of hpf atomic sublevels. The initial electron degrees of atomic orientation and alignment at the moment of the laser pulse were also determined taking into consideration collisional depolarization of the produced atoms, hyperfine interactions in the atoms, optical thickness of the atomic vapours and hyperfine structure of the probe radiation. The initial degree of the atomic orientation and alignment just after the laser shot were found to be: P_e=(37±5)% for the Tl($6^2P_{1/2}$) atoms; P_e=(19±2)% and A_e=(17±4)% for the Tl($6^2P_{3/2}$) atoms.



Theoretical interpretation of the experimental results enabled to distinguish the channels of the photodissociation reactions under study and to determine the probabilities of radial nonadiabatic transition in the decaying molecules.

One of the typical experimental signals presenting the oriented atomic ^{87}Rb photofragments produced in RbI photodissociation is shown on Figure 2. "Step" of absorption caused by appearance of the Rb atoms after the laser shot and responsible for population; oscillations caused by the atomic momenta precession and responsible for orientation. Signals 1 and 2 correspond to left- and right-hand polarization of dissociation beam. Signal 3 is a substraction of the signals 1 and 2 and shows the orientation contribution to the experimental signal. The atomic spins orientation was studied as a function of time and the laser pulse energy. We investigated the orientation of two ground state hyperfine sublevels of Rb atoms using two different experimental geometries [4]. The hyperfine momenta $<F>_+$ and $<F>_-$ precess in an external magnetic field H_0 with the same frequency but in opposite directions that results in different contributions of two hyperfine orientations to the experimental signals in the "perpendicular" and "parallel" detection schemes. The determined hyperfine orientations were used to verify the model of RbI photodissociation via the second excited state. The initial degree of electronic spin orientation of the Rb atoms just after the laser shot was found to be $P_e=(20\pm2)\%$ that is in qualitative agreement with a simple model neglecting homogeneous and Coriolis-type nonadiabatic transitions in the decaying molecules, interference effects, and rotation of molecular axis.



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PPK-43

TIME-RESOLVED MAGNETIC FIELD EFFECTS IN REACTIONS OF ELECTRON PHOTOTRANSFER IN POLAR MEDIUM.

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The effect of applied external magnetic field (B) on the yield of the recombination products of geminate radical-ion pairs (RIP) was discovered in 1976 [1,2]. This was verified by a series of theoretical calculations [3] reporting that the application of B should lead to both a double increase of the yield of the recombination products of singlet (S) RIP and a 30% decrease of the yield of the recombination products of the triplet (T) ones. However, despite a great number of papers, until recently the theoretical magnitudes of magnetic field effects (MFE) were not observed experimentally.

In this work the exciplex system pyrene (Py)+N,N,dimethylaniline is used in different polar solvents to demonstrate how one can experimentally obtain the theoretical magnitudes of MFE in the recombination products of T-pairs. Besides, the paper gives the reasons for which these magnitudes have not so far been obtained. These reasons are the following: 1) The absence of time-resolution; 2) the existence of homogeneous (not geminate) pairs in the system [4,5].

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KINETICS AND MECHANISM OF DISSOCIATIVE ELECTRON TRANSFER IN HOMOGENEOUS AND HETEROGENEOUS REACTIONS.

SOLVENT EFFECTS.

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This work has been aimed at studying the kinetic features of electron-transfer reactions accompanied by a chemical bond rup-ture. Solvent effect on activation parameters of electron transfer were also within the scope of our work.

The kinetic parameters of chlorocuprate (II) complex reduction in acetonitrile at a conventional glassy carbon electrode and at a Pt microelectrode were determined taking into account the double-layer effect. Rate constant was found to be very low, and free activation energy (26 kJ/mol), pre-exponential factor (30 cm/s) and transfer coefficient (0.31) were also determined. Their comparison with corresponding data on similar homogeneous reactions obtained by us previously suggests that ~~the~~ fast escape of chloride ions from the inner coordination sphere, which follows the electron transfer step, retards the EC reaction rate. If the two steps of the reaction are practically inseparable, the barrier top broadens resulting in a decrease in frequency factor.

Structure of the metal electrode-polar solvent interface were theoretically studied in the scope of a density-functional theory, and effect of the electrode potential on transfer coeffi-cient was determined. Dynamical solvent properties were determined by NMR relaxation measurements in the acetonitrile-benzene and acetonitrile-carbon tetrachloride binary mixtures. It was found that correlation times do not change more than 50% in the whole range of mole fraction. That is why some stochastic models have been considered to account for a marked solvent effect on pre-exponential factor and activation energy.

PPK-45

CONVERSION OF SOLID INORGANIC COMPOUNDS UNDER THE EFFECT OF GAS PHASE CHAIN REACTIONS

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The chemical reactions of gaseous molecular reagents with solid inorganic compounds require as a rule high activation energy. Therefore, they proceed at high temperatures.

This report represents a new approach to the realization of heterogeneous conversion in a gas-solid phase system. The essence is that atoms and free radicals interact with different compounds rather faster than molecules, because they need lower activation energy. As a source of free radicals the gas phase chain reaction can be used.

If active species, generated from gas phase reaction, interacting with solid substance lead to the formation of new active centres, which are able to propagate the reaction chains, then an effective conversion of solid phase would take place. In spite of low concentration of free radicals, formed during chain reaction, the rates of radical-chain conversion in gas-solid phase system may be higher under certain conditions. It becomes possible to realize the conversion at significantly lower temperatures.

Experimental data confirm the correctness of this approach and show new possibilities for realization of heterogeneous chemical processes.

The reactions of reduction of metal oxides and sulphides, transformation of metal oxides into chlorides, extraction of iron and other metals out of metallurgical slags and natural mineral raw materials, etc. have been studied. It has been shown that the effective reduction of iron and copper oxides under the effect of chain reactions of hydrogen and hydrocarbons oxidation takes place at T=600-800 and 400 °C respectively. The copper powder, obtained in this way is more resistant against further oxidation than that obtained using conventional methods. For molybdenum sulphide and chalcopyrite the kinetics of the process was studied. Free radicals were detected in these processes and found to be changed during the course of the reaction, what indicates the formation of new radicals in heterogeneous process.

Iron is extracted out of metallurgical slags, natural quartzites and pearlites as a water-less chloride at T=600-700 °C and removed from reaction zone by gas flow. Under the same conditions chalcopyrite is transformed into copper and iron chlorides and elemental sulphur. Titanium oxides are transformed into titaniun tetra-chloride without any additional reductant.

So, a new field for gas phase chain reactions application hasbeen revealed, which is the scientific base for working out the new high-effective chemical and metallurgical processes.

PPK-46

NEW POTENTIALS FOR THE STUDY OF CONVERSION MECHANISMS AND REACTIVITY OF ACTIVE INTERMEDIATES

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The study of conversion mechanisms and reactivity of different active intermediates of radical or biradical nature in organic solids have been hampered by the influence of surrounding molecules on the direction and efficiency of these processes. The fast secondary reactions which can occur in these conditions also make the identification of primary products of these conversions difficult. The use of the matrix isolation method in few cases gives no way of obtaining the information on the mechanisms and efficiency of bimolecular reactions or unimolecular ones when their products can react to one another.

The matrix isolatiom method on silica surface activated by different techniques is found to be extraordinarily useful for the purpose in hand. This method have been used in our work to study:

1. The mechanism and efficiency of reactions of sulfur dioxide with carbon-centered free radicals $R\dot{S}O_2$ and $RO\dot{S}O$ adducts are reversibly formed in these reactions. The $RO\dot{S}O$ adducts appear to be more thermochemically stable, however, the formation of the sulfonyl ones is more kinetically favorable. The equilibrium thermodinamic parameters are presented.

2. The primary products of photochemical reactions of different types of radicals (peroxy, allyl, vinyl ones). The new unimolecular photoconversion of allyl type radicals have been observed. For example, the externally conflicting data on the photochemistry of peroxy radicals reactions in organic solids were explained on the basis of these results.

3. The mechanism of alyciclyc and certain sulfurcontainig compounds reactions with paramagnetic centers on activated silica surface and the nature of intermediates which were produced under these reactions.

4. The mechanism and efficiency of reactions of silylene centres (SC) on activated silica surface in ground state with different organic compounds. For example, SC were found to insert into H-S and C-S bonds. The reaction of SC with ethylene oxide proceeds via ring-opening with a further cyclization to give presumably a 5-membered surface siladioxolane heterocycle.

This work was financially supported by a Russian Fundamental Research Foundation (project 95-03-08119) and International Science Foundation (project MFV300).

PPK-47

INTRAMOLECULAR CHARGE TRANSFER IN PHOTOCHROMIC SPIROCYCLIC STRUCTURES

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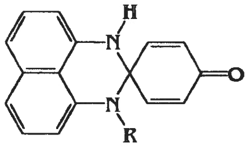
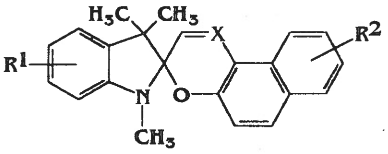
By experimental (absorption spectra, photochemical kinetics and X-ray analysis) methods and quantum chemical calculations (AM-1, CNDO/S), with use of the model structures,the photochromic spirans of the perimidine series (I) and spiropyrans, spirooxazins (**IIa**, **IIb** respectively) have been studied.



I

R= H, CH$_3$



IIa: X=CH; IIb: X=N

R^1, R^2 =H, OCH$_3$, N(CH$_3$)$_2$, NO$_2$

According to the experimental and quantum-chemical data the absorption spectra of **I** are formed by both localized and Photoinduced Charge Transfer (PICT) electronic transitions.

In **IIa**, **IIb** the lowest PICT transition is found to be localized on the chromene moiety with the electron donor and withdrawing substituents. The dependence of the photochromic properties and irreversible reactions on the PICT transition nature in **I** and **II** is discussed.

The work is supported by International Science Foundation and Russian Goverment **(projects RN-6000 and RNG-300)**

PPK-48

SPIN-CATALYSIS

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The term "spin-catalysis" denotes a large range of phenomena for which the overcoming of spin-forbidness in chemical reaction and an increase of rate constants can be introduced by interaction with catalysator. The majority of stable chemical products are diamagnetic; they have a singlet ground state with the excited triplet state well separated in energy. However, in the vicinity of activated complexes, where chemical bonds grow weak, the singlet-triplet (S-T) energy gap is not large and can even become negative. The possibility of S-T transitions must be taken into account for a large number of chemical reaction rates and paths. The important example is O_2 reactivity. The ground triplet state oxygen molecule, $^3O_2$, cannot react directly with diamagnetic products of oxydation because of spin-forbidness. This is reason for that a large variety of such processes proceed through radical chain reactions. Certain substrates react spontaneously with $^3O_2$ in the dark; they often only need to be heated. These spontaneous reactions of $^3O_2$ with compounds which are diamagnetic and have redox potentials forbidding an outer electron transfer must find a way to circumvent the spin barrier. What is presently needed is a consistent theoretical treatment explaining why some O_2-substrate pairs undergo such a thermaly induced intersystem crossing and others do not. The understanding of these mechanisms could result in the possibility to create catalyzators which can provide effective oxidizing synthesys, like combustion processes. What must be considered in the general is a paramagnetic spin-catalysis when a catalysator with unpaired electrons assist in S-T transition in reacting system through intermolecular exchange interaction. The spin-forbidness is then lifted by supplying unpaired electrons without magnetic perturbations.

Two types of spin-catalysts exist: 1) Those of magnetic nature, that is spin-orbit coupling providing catalysts and catalysts which work in the presence of external magnetic field, and, 2) Those of paramagnetic-exchange type. The second type of catalysts are paramagnetic substances which supply their unpaired electrons during the catalytic contact with a diamagnetic molecule in order to assist the S-T transitions in its chemical rearrangement. The first type involves will be studied the external heavy atom effect photochemical application and investigations the SOC effect in such processes: 1) The external heavy atom effect (EHA) on radiative S-T transitions; 2) The EHA affect in intersystem crossing in Norrish type II reactions; 3) The SOC effects in Norrish type II and ethylene combustions reactions. The second type catalysis will be studied for the reactions cis-trans-isomerizations in ethylene, butadiene and hexatriene, induced by collision with O_2 and NO

Reactions of fluorine atoms with molecules, isolated in solid argon at 10 - 30 K.

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H atom abstraction and addition to C=C double bond of alkenes are the most common reaction mechanisms of hydrocarbons with halogens. In this paper we wish to present preliminary experimental findings of studying these mechanisms for reactions of photogenerated F atoms with CH_4 and C_2H_4, isolated in Ar matrix. One of the most significant aspects of this research is that the free radical intermediates are detected directly in the experiments with EPR technique. This permits a detailed analysis of the overall photochemical mechanisms involving both photogenerated "translationally hot" and trapped thermalized atoms.

The thin films of $Ar/CH_4/F_2$ and $Ar/C_2H_4/F_2$ were deposited through separate gas inlets (Ar/CH_4 and Ar/F_2 or Ar/C_2H_4 and Ar/F_2) onto the surface of a sapphire rod cooled to 13 K. F atoms were generated by UV photolysis with the 337 nm output of a pulsed nitrogen laser. F_2 photodissociation gives translationally hot F atoms with excess energy ~0.5 eV.

There are two important channels of radical formation.

I) Hot F atoms abstract an H atom from CH_4 molecule forming HF + CH_3 during the laser photolysis period. In $Ar/C_2H_4/F_2$ mixtures hot F atoms add to C_2H_4 giving CH_2F-CH_2.

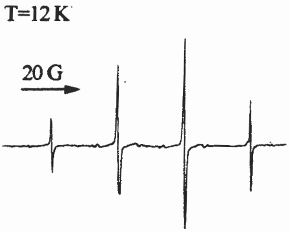
EPR spectra of the radicals are shown in figure. The changes of FWHM of CH_3 lines are caused by the slow rotation of radical incompletely averaging anisotropies of g and hyperfine interaction tensors. The shape of the EPR lines of C_2H_4F is due to anisotropic hyperfine splittings on F, two inequivalent α, two β protons and, possibly, torsional oscillations of the α-CH_2 group. The line broadening observed on heating the samples to 25-30 K is caused by incomplete averaging of the inequivalent protons as result of slow rotation about the C-C bond.

Quantum yield of radicals is linear with the mole fraction of hydrocarbon molecules and below 20 K is 1.1×10^{-3} at $CH_4/Ar=10^{-3}$ and 5×10^{-3} at $C_2H_4/Ar=10^{-3}$.

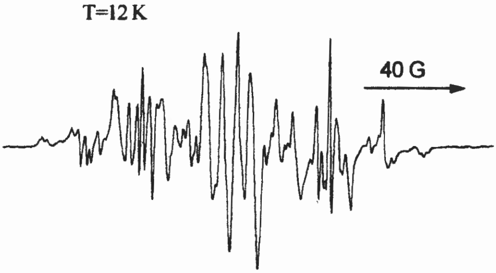
II) Above 20 K we observed thermally activated reactions of diffusing F atoms giving the same products. The duration of the dark reaction was ~10^3 s at 20 K. In $Ar/CH_4/F_2$ mixtures additional formation of CH_2F radicals was detected. The radicals form in reaction of the atoms with CH_3F formed under photolysis of CH_4/F_2 pairs: $[F_2+CH_4]\rightarrow[CH_3F+HF]$.

We estimated the rate constants and activation energies of atom recombination (k_1 and E_1) of reactions of F atoms with CH_4 (k_m and E_m) and with C_2H_4 (k_{et} and E_{et}) from growth curves after photolysis at 20 K and during warming the sample photolyzed at 15 K. $E_1 \approx 1.1-1.3$ kcal/mol and $k_1 \sim 10^{-22}$ cm^3s^{-1} at 20 K. The rate constant k_m at 20 K is 4 orders of magnitude smaller than that of diffusion limit and it activation energy $E_m \approx 1.5-1.8$ kcal/mol exceeds that in the gas phase (1.25 kcal/mol) The rate constant k_{et} is approximately 10 times smaller than k_1 but more than 2 orders of magnitude higher than k_m. This difference is probably due to the lower activation energy for addition to the double C=C bond as compared to that of the hydrogen abstraction. We suppose that the k_{et} is limited by steric hindrance as it was shown in the gas phase.

This work was supported by the Russian Fund of Fundamental Investigations (Grant No. 95-03-08509), the International Science Foundation and Russian Government (Grant No. REM300).



EPR spectrum of CH_3 radicals formed under photolysis of $Ar/CH_3/F_2 = 500:1:1$ samples.



EPR spectrum of CH_2FCH_2 radical formed under photolysis of $Ar/F_2/C_2H_4 = 1000/1/1$ sample.

PPK-50

CORRELATION OF KINETIC NON-EQUIVALENCY OF SOLID STATE PHOTOCHEMICAL REACTIONS WITH ELEMENTARY REACTION ACT DIRECT MONITORING

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The most fundamental question of chemistry is how does the individual molecule really undergo chemical conversion. Investigation of the elementary act of the chemical reaction in the solid phase is of special interest due to opportunities to understand the ways of influence of media on the chemical reactivity.

Frequently observed kinetic non-equivalence of the solid-state reactions is the macroscopic exhibition of the influence of the local surrounding on the reactivity of molecules. It will be very interest to understand the mechanism of this influence on the scale of molecular sizes.

The method of determination of the molecular fragment rotation in the instant of the elementary act of the chemical reaction was developed for this purpose [1]. This method is based on the photoselection. It allows to monitor the angle of the rotation of the chromophore fragment of reacting molecule (in the instant of chemical conversion) in the every point of the kinetics.

Experimentally developed method was applied to the photoisomerization of (3'-pyrenyl)-5,5-dimethylpyrazolidone-3-azomethine imine in glassy polystyrene. Previously it was found that this compound had a non-equivalent kinetics in the solid glasses [2] and demonstrated the successful photoselection in glassy polystyrene even at room temperature [3]. The data of UV-VIS spectroscopy were used.

The experiments reveal the correlation of the appearing of the kinetic non-equivalence of the reaction at the temperature of 77K with the magnitude of rotational movements of pyrenyl fragment of the molecule in the instant of the chemical conversion (the angle of pyrenyl group's rotation is decreased from 25° at 293K down to 0-8° at 77K).

Such a correlation is discussed.

Acknowledgement. This work was made possible in part by Grant NBU300 from International Science Foundation and Russian Government, and by Grant 95-03-08505 from Russian Foundation for Fundamental Research.

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PPK-51

CO Hydrogenation under Mechanochemical Treatment

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A new method of CO hydrogenation to CH_4 at atmospheric pressure and ~ 30°C during mechanochemical activation process was elaborated following [1]. A flow mechanochemical reactor constructed in our laboratory was applicated as a catalytic one. Ni-Zr containing systems, well-known catalysts for CO and CO_2 hydrogenation, were used to realize a mechanochemical reaction: (1) - equimolar mixture of Ni and Zr metallic powders; (2) - the sample (1) transformed to the $Ni_{0.5}Zr_{0.5}$ amorphous alloy by a mechanochemical treatment on Ar atmosphere; (3) - the sample (2) transformed to the Ni-Zr-H_{2-x} system by a mechanochemical treatment on H_2 atmosphere.

It was found that two ways of CO conversion take place at the mechanochemical activation of Ni-Zr containing systems in CO/H_2 (1:1) flow: 1 - CH_4 formation and 2 - dissotiative adsorption followed by carbon and ZrO_x formation. A correlation between them depends on the nature of the catalyst. CH_4 is a unique gaseous product of the reaction. Neither H_2O nor CO_2 were detected.

It was shown that on Ni-Zr-H_{2-x} catalyst CH_4 can be obtain from CO in the abcence of H_2 in the gas flow by utilizing an active hydrogen dissolved in the catalyst volume. In this case the CH_4 formation rate is much higher and dissotiative adsorption decreases. It was ascertained that two separate prosesses of CO hydrogenation take place. Under the reaction conditions all the catalysts transformed to the Me/ZrO_x/C systems with different morphology.

We suppose that a mechanism of CO hydrogenation under mechanochemical conditions is completely different compared the traditional ones. The experiments with a metallic nickel confirm it: CO_2 and nickel carbonyls were found as the products of reaction during mechanochemical treatment on CO/H_2 mixture, CH_4 was absent.

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APPLICATION OF CIDNP TECHNIQUE TO STUDY PHOTOINDUCED CHARGE TRANSFER REACTIONS IN THE GAS PHASE

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Earlier [1] we have reported on the observation of the effects of chemical nuclear polarization (CIDNP) in the radical-ion reaction of the gas-phase photooxidation of triethylamine by naphthalene. The observation of CIDNP effects on the samples with a polar buffer gas (acetonitrile) has been related to the formation of clusters in the gas phase involving reagents and a buffer substance.

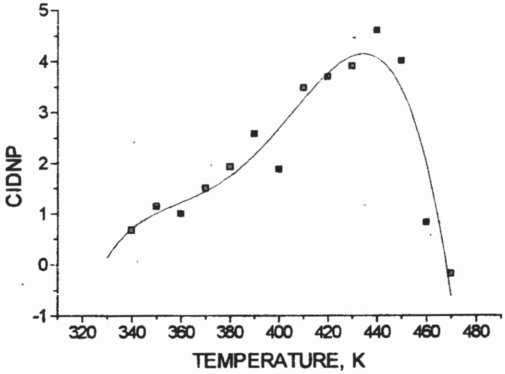
To record NMR spectra, we used F-90 Q ("JEOL", Japan) and AM-250 ("Bruker", Germany) spectrometers. NMR spectra in photochemical reactions in the gas phase were experimentally observed directly in NMR spectrometer probe heads. Irradiaton of specimens was performed with the optical system including quartz lenses, mirror, light guide and automatic curtain. The specimen was irradiated with full light of DRSh-1000 mercury lamp with temperature ranging from 330 to 450K. The temperature was set with the accuracy of ±1K.

Experimental studies of the processes of cluster formation were performed by nozzle molecular beam method. The following reagents: naphtalene, triethylamine, acetonitrile and cyclohexane were used as test specimens. All of them were subjected to extra purification by routine procedures. Deuterated reagents ("Isotope", Russia) did not undergo further purification.

Molecular beam method shows directly that molecular clusters may be formed in the system studied.

The collision of an excited naphthalene molecule with electron molecule-donor (triethylamine) can cause electron transfer to naphthalene and give rise to a radical-ion pair (RIP). The ions in the gas phase can become the centers of condensation. In this case, the polar molecules, displaying a considerable dipole moment, will condense easier. When the molecules in the buffer gas fill several coordination spheres, the ions can be separated by some distance with the compensation of the energy losses of direct interaction by the energy of "medium" polarization. With reverse electron transfer, the stabilizing action of the Coulomb RIP interaction ceases, and the molecules, forming the cluster, scatter. Usually, the radical-ion pair forms in a certain spin state (singlet or triplet). The rate of reverse electron transfer also depends on the multiplicity of the state of unpaired RIP electrons. The magnetic interactions (Zeeman, h.f.i.) in a solvate separated RIP cause the changes in its spin state and, hence, affect the efficiency of reverse electron transfer. This effect is known to result in the formation of nonequilibrium populaton of nuclear spins (CIDNP) in the products of radical recombination [2].

The magnitude of polarization is determined by the mechanism of the relative motion of a radical-ion pair and substantially depends on the cluster size that, in turn, is defined by the pressure of buffer gas and its temperature. Studying the dependence of the effects of spin nuclear polarization on pressure and temperature, one can get information about the processes of cluster formation, particularly, about the mean sizes of the cluster.



The Figure depicts the temperature dependence of CIDNP effects for the protons of triethylamine methylene groups. A characteristic dependence of the change of CIDNP intensity on sample temperature confirms the given cluster model. At the initial stage of heating in the gas phase, on the one hand, the number of clusters increases together with cluster size, and on the other hand, the number of active radical pairs also increases because the reagent concentration increases with temperature and the saturation of the quantum yield of radical-ion pairs has not occurred yet. In this case, with increasing temperature there are two competing processes, i.e. the formation and destruction of clusters. Starting with some temperature, the second process becomes dominating. This leads to the decrease of cluster size (the increase of exchange interaction in radical-ion pair) which is sure to cause the decrease of CIDNP effects to zero and even the change of the CIDNP sign.

Mechanisms of the CIDNP effect have been analyzed and the mathematical model of the process under study has been developed.

This work has received the financial support of the Russian Foundation of Fundamental Investigation (Project Code 93-03-5035).

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A NEW PROMISING WAY TO SYNTHESIZE SUPERHARD DIAMOND-LIKE MATERIALS

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The work is devoted to a new promising way for synthesis of the superhard materials such as diamond, cubic boron nitride or covalent carbon nitride. The way was developed on the base of thermodynamic computations of the phase diagram of carbon and explosion processes of rich-in-carbon explosive compositions. Most of the superhard substances are metastable under normal pressure and can be synthesized in volume only under very high pressures. Another problem is that to form a new phase it is needed rather high temperture.

The idea of the proposed way consists in creating the thermo-dynamic conditions suitable for superhard material synthesis and keeping them favourable for further growth of crystals while products are cooling down to temperatures at which the synthesized crystals become metastable, i.e. frozen.

In comparison with the known method of diamond synthesis from graphite where the high pressure is produced by a heavy press machine and high temperature is attained due to an electric discharge the new method requires only comparatively simple device for keeping explosion products from expanding more then it is admissible. As to the detonation synthesis of ultra-dispersed diamond then the submitted way allows to expect the higher output and larger crystals of the desirable product.

PPK-54

Flame Structure and Kinetics of Chemical Reaction In $H_2/O_2/Ar$ Flame at High Pressure.

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The result of flame structure studies, i.e. spatial distribution of species, concentration and temperature in flames are the main source of our knowledge on the kinetics and mechanism of chemical reactions in flames. The approach based on simultaneous experimental study and modeling of flame structure is the most effective one for investigation of kinetics and mechanism of chemical reactions in flames. At present there are a lot of works on flame structure, kinetics and reaction mechanisms in flames at pressures ≤ 1 atm. but there are practically no similar works in field of high pressures (>1 atm.), which is practical importance. Molecular beam mass spectrometry (MBMS) is the most effective, universal and reliable method of flame structure study. Nevertheless this method has not been used so far for the study of high pressure (>1 atm.) flame structure. The first results on structure of $H_2/O_2/Ar$ flame at pressure 10 atm. have been obtained in this work by MBMS and modeling. Hydrogen-oxygen flame was chosen as a subject of the investigations, being most simple and most thoroughly studied. A 10% H_2+5%O_2+85% Ar mixture results in a final temperature of ca. 1400K, temperature of burner surface being ca. 363K. Probing allowed to obtain distribution of H_2, O_2 and H_2O concentration as well as of temperature, measured independently using thin thermocouple. Sampling was shown to be correct enough, spatial resolution comprising ca. 0.1 mm. The flame zone width was ca. 0.7 mm, variation of the velocity gas mixture the near burner surface from 4.4 cm/sec up to 13.4 cm/sec resulting in change in this magnitude less than on 0.1 mm. The similarity of profiles of water vapor concentration and of temperature is obtained. Calculation, carried out with CHEMKIN code using J.Miller's mechanism (that is a set of reactions with rate constants), the most reliable one among those available in literature, evidenced data obtained: the calculated flame reaction zone turned to be 1.5 times wide. Simultaneously the calculated rate of flame propagation at 10 atm. (~9 cm/sec) is considerably less than the lower evaluation of experimentally measured rate of flame propagation (13.4 cm/sec), which is impossible in general. At the same time experimental data at 1 atm and calculations according to the above mechanism coincide. These facts suggest a direct extrapolation kinetics data from the low pressure field toward the high one to be unfounded and the reaction mechanism with rate constants to require inspection for the high pressure. It should become a subject of further investigations.

The research described in this publication was made possible in part by grants No.RC1000 and No.RC1300 from International Science Foundation.

PPK-55

COORDINATION SATURATION AND DONOR-ACCEPTOR INTERACTION OF NEUTRAL METAL HELATES

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Reactions of formation of electronic donor-acceptor complexes (EDA-complex) from neutral metal helates with bases play an important role in chemical technology and homogeneous catalysis. Formation energy is described by in terms of acid and base as it is taken in Lewis theory. Feature of complex formation from helate of metals consists in that the interaction energy is determined both by charge transfer between frontier complex and bases orbitals and corresponding electron density redistribution, and by change of energy of core orbitals of the central complex atom. Formally, this phenomena is described as deviation of Koopmansm theorem.

The quantum-chemical analysis of interaction between metal helates and bases is the purpose of this work. These calculations have been done in LCAO MO SCF INDO approximation using s,p,d-orbitals of central helate atom in the basis set. The method is used appropriate for electron structure study in molecules with nonzero spin because it takes into account the difference in repulsion of electrons with the parallel and antiparallel spins. The latter is important in the case of compounds with d-elements. Geometrical parameters of both initial molecules and compound formed were taken from published data of X-ray structure analysis.

Formation heats have been calculated for mix-ligand bis(acetylacetonate)nickel complexes with ethanol, pyridine and 4-methylpyridine $[Ni(acac)_2(C2H_5OH)_2$, $Ni(acac)_2(Py)_2$, $Ni(acac)_2(4\text{-}MePy)_2]$. Those correlate with electron-donor ability of basis and difference the LUMO-HOMO energies: the decrease of this energy accompanies by enlargment of reaction heat in the series of compounds mentioned.

This work is supported by Russian Found for Fundamental Studies (RFFI 93-03-4575) and Soros International Scientific Foundation (ISF MA-9000).

PPK-56

PHOTOCHEMISTRY OF UNUSUAL NICKEL COMPLEXES

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In present study the photochemical reactions of the dithiocarbamate and hydroxylamineoximate nickel complexes are considered. The dithiocarbamate complexes contain an unusual valent state of the nickel ion - Ni (IV). The hydroxylamineoximate complexes of the Ni(II) ion contain free radicals in coordination sphere as ligands.

The dithiocarbamate $Ni(IV)(dtc)_3^+$ complexes exhibit fairly high photochemical activity in red region of spectrum (λ_{exc} = 632 nm, $\varphi \approx 0.68$) [1]. After irradiation, the system returnes to its initial state with the same isosbestic points [2]. The result of photoreaction is the formation of the $(dtc)Ni(tds)^+$ complex with the coordinated thiuramdisulphide (tds).

$$Ni(dtc)_3^+ \xrightarrow{h\nu} [Ni^{4+}(dtc^-)_3]^*$$

$$[Ni^{4+}(dtc^-)_3]^* \longrightarrow [(dtc^-)_2Ni^{3+}\text{-}SC(^{\bullet}S)NR_2]$$

$$[(dtc^-)_2Ni^{3+}\text{-}SC(^{\bullet}S)NR_2] \longrightarrow [(dtc^-)Ni^{2+}\text{-}\{SC(^{\bullet}S)NR_2\}_2]$$

$$[(dtc^-)Ni^{2+}\text{-}\{SC(^{\bullet}S)NR_2\}_2] \longrightarrow [(dtc^-)Ni^{2+}{=}tds]$$

The reverse dark reactions are shown to be due to both the reactions of the disproportionation of the Ni^{2+} ion complex (photolysis product) and it reaction with the initial $Ni(dtc)_3^+$ complex.

$$[(dtc^-)Ni^{2+}{=}tds] + [Ni^{4+}(dtc^-)_3] \longrightarrow 2\,Ni(dtc)_3^+$$

$$[(dtc^-)Ni^{2+}{=}tds] + [(dtc^-)Ni^{2+}{=}tds] \longrightarrow 2\,Ni(dtc)_3^+$$

It is established that about 10^4 cycles of photochromic transformations for each molecule cause no decrease in the initial concentration of the complex.

We have recently synthesized a new group of compounds - Ni(II) complexes with the radicals whose lifetime in noncoordinated state is short (with the derivatives of sterically inhibited 1,2-hydroxylamine oximes by oxidative dehydration of Ni(II) with initial 1,2-hydroxylamine oximes via N-H of hydroxylamine fragments). In solvents such as benzene hydroxylamineoximate Ni(II) complex ($Ni(RNO)_2$) is photochemically stable. However, some CCl_4 added to benzene leads in irradiation to rapid disappearance of the initial optical spectrum of the complex [3]. During the photolysis 4 isosbestic points are preserved. In the end of the photolysis a new broad absorption band is formed with a maximum at 25000 cm^{-1}. The quantum yield increases with concentration of CCl_4 and it shows that the primary photoprocess is the electron transfer from the excited state to CCl_4 molecule.

$$Ni(RNO)_2 \xrightarrow{h\nu} (Ni(RNO)_2)^*$$

$(Ni(RNO)_2)^{*} + CCl_4 \longrightarrow Ni(RNO)_2^{+} + CCl_4^{-}$

In the course of the photolysis of $Ni(RNO)_2$ in the mixture methanol and CCl_4 at 77 K the spectrum preserves also four isosbestic points. Under irradiation two new absorption bands appear at 27400 cm^{-1} and a broader one - in vicinity of 20000 cm^{-1}. The first is the band of the radical anion CCl_4^{-}.

After a laser pulse for CCl_4 solution of $Ni(RNO)_2$ a broad absorption band appears also with a maximum near 20000 cm^{-1}. The kinetic changes involve two steps: a fast process taking 5 μs and a longer process taking about 200 μs. The effective rate constant of fast process is linear with the initial concentration of $Ni(RNO)_2$ with zero intercept on the ordinata. Thus, this fast process is a reaction of the intermediate with $Ni(RNO)_2$. The bimolecular rate constant at room temperature is equal $1.3{\bullet}10^{9}$ $M^{-1}s^{-1}$. The radical anion CCl_4^{-} in methanol glasses is stable at 77 K. However, at higher temperatures, especially in liquid solutions, this species undergoes fast dissociation to the radical CCl_3 and ion Cl^{-}. It is naturally to associate the fast kinetic process with a rection involving the radical CCl_3.

$CCl_3 + Ni(RNO)_2 \longrightarrow CCl_3^{-} + Ni(RNO)_2^{+}$

It is known that the broad absorption band at 20000 cm^{-1} in pulse radiation-chemical experiments corresponds to the solvated pair $(CCl_3^{+}\backslash Cl^{-})$. This species appear owing to the charge exchange of a positive "hole" with the radical CCl_3. In our case, such a "hole" can be only $Ni^{3+}(RNO)_2$ complex, i.e. CCl_3^{+} formation can be accounted for by electron transfer back from the radical CCl_3 to the complex Ni^{3+} in primary geminate pair.

$(RNO)_2Ni^{2+}...CCl_4 \longrightarrow [(RNO)_2Ni^{3+}...Cl^{-}...CCl_3]$

$[(RNO)_2Ni^{3+}...Cl^{-}...CCl_3] \longrightarrow [(RNO)_2Ni^{3+}] + Cl^{-} + CCl_3$

$[(RNO)_2Ni^{3+}...Cl^{-}...CCl_3] \longrightarrow [(RNO)_2Ni^{2+}..Cl^{-}\backslash CCl_3^{+}]$

About 50% of CCl_3 escaped into the bulk solvent. For the slow process k_{eff} increases linearly with ΔD at zero intercept on the ordinata and it is a direct evidence of a kinetic process of the second order. Coordination of the ion Cl^{-} of the pair leads to the stabilization of $(CCl_3^{+}\backslash Cl^{-})$ pair and to the decay only in second-order reaction ($k = 1.36{\bullet}10^{9}$ $M^{-1}s^{-1}$).

$2[(RNO)_2Ni^{2+}...Cl^{-}\backslash CCl_3^{+}] \longrightarrow 2Ni(RNO)_2 + 2CCl_4$

The financial support of Russian Foundation for Fundamental Researches is greatefully acknowledged (Research Grants N 94-03-08933).

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PPK-57

Photooxidation of N-acyl-1,4-dihydropyridine by various quinones

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Recently it has been shown the efficiency of the CIDNP method to investigate the photooxidation of NAD(P)H and its synthetic analogs - 1,4-dihydropyridines (DHP) [1,2] by electron acceptors. According to these studies there are the strong dependence of the reactivity of various substituted DHP on the structure of substitution groups. In the present study we have investigated photoinitiated interaction of N-acyl-substituted DHP with quinones in the media of different polarity.

The first stage of the process was identified as the excited CT complex formation. The further behaviour of the CT complex doesn't show any dependences on irradiation wavelength or oxygen saturation. The conclusion on the formation of radical-ion pairs (in polar solvent) and neutral radical pairs (RP) in nonpolar solvent was drown from the analysis of the CIDNP effects and its concentration dependences. In all cases the main product of the reaction is pyridine, which is formed by fragmentation of DHP cation radicals as well as neutral DHP radicals, with abstraction of acyl group.

The number of polarized acyl-containing products leads us to conclude the formation of the neutral acyl radical from both cation- and neutral DHP radicals. From the chemical shifts and CIDNP concentration dependences the products QH-CO-CH_3 were identified as the cage recombination products, and Cl-CO-CH_3 and CH_3-CO-CO-CH_3 as the escape products for Cl-substituted quinones used as electron acceptors.

In the present study it has been shown that the structure of the paramagnetic intermediates in the photooxidation reaction of N-acyl-1,4-DHP depends on the nature of acceptor.

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Photochemistry of acetylenic ketones in micellar and homogeneous solution as studied by time-resolved PYESR and CIDNP techniques

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The reaction mechanism for the photolysis of acetylenic ketones: Ph-C≡C-CO-R (R = -Ph (I); -C≡C-Ph (II); Ph-CH_3 (III)) as well as the dynamic of radical pair (RP) and magnetic field effect (MFE) on the spin-adduct yield were studied by time resolved CIDNP and pulse-mode PYESR techniques [1]. The photolysis of I-III was investigated in homogeneous solutions as well as SDS micelle. In hydrocarbon solutions the main process is the photoreduction of excited ketones. Beside that, the Norrish-1 process was observed under laser pulse irradiation of II. We suppose the possibility of a double quantum processes in this case. The reaction scheme for the photoreduction process was determined by using steady state and time-resolved CIDNP as following [2]:

$$K + h\nu \rightarrow {}^1K^* \rightarrow {}^3K^* \qquad (1)$$

$${}^3K^* + RH \rightarrow {}^3(KH\cdot\ \cdot R) \qquad [k_H] \qquad (2)$$

$${}^3(KH\cdot\ \cdot R) \Leftrightarrow {}^1(KH\cdot\ \cdot R) \rightarrow \text{cage products} \qquad [k_r] \qquad (3)$$

$${}^3(KH\cdot\ \cdot R) \rightarrow KH\cdot\ \cdot R \qquad [k_{esc}] \qquad (4)$$

$$KH\cdot \rightarrow \text{escape products} \qquad [k_p] \qquad (5)$$

where K is ketone and RH is hydrogen donor. k_p for pinacone formation was calculated from the time-resolved CIDNP study. The same scheme of the reaction was determined from analysis of CIDNP effects for the photolysis of ketones I-III in SDS micellar solution. In this case the micelle molecule works as a hydrogen donor. The absence of the chemical polarization on the initial ketone leads us to conclude that the reactions of back proton transfer or proton exchange are not effective in this case. The latter is due to the fact that only one molecule of ketone is situated in one micelle. On the other hand, in this situation one can expect a significant magnetic effects [1].To measure the MFE on the RP dynamics in SDS solution the water solulible spin trap (ST) for SDS radical was added in the reaction system: $R\cdot + ST \rightarrow$ Spin adduct $[k_{ST}]$ (6)

Strong magnetic field and microwave effects on the spin adduct yield were observed in the photolysis of ketones I-II in SDS micellar solution. Spin adduct yield increases gradually without saturation with increasing the MF up to 600 mT. The MFE reaches to ca. 350% for all cases. As it has been concluded in previous studies for benzophenone system, the "relaxation mechanism" is the main mechanism of MFE for the acetylenic ketones from the similarity in the shape of MF dependences. Magnetic field dependence of the spin adduct yield shows ESR spectrum of transient RP, when we irradiate the X-band MW simultaneously with the laser pulse. The shape of the experimental spectra are in good agreement with the calculated ESR spectra of RPs composed with SDS and ketyl radicals. From these results and INDO calculations it was concluded that the unpaired electron of the latter is delocalized in both the phenyl and acetylenic groups. High spin density on the acetylenic group may suggest the possibility for the recombination reaction at both acetylenic and carbonyl groups.

Pulse-mode PYESR method includes the observation and theoretical simulation of the spin adduct yield as function of the delay period between laser and MW pulses in a few pulse sequences. The result shows the time profiles of the growth and decay of the RP concentration. The kinetic and relaxation parameters (τ_C - rotational correlation time and H_L - anisotropic hfi) for ketones I-II were obtained from the simulation of these results and MFE.

Ketone	k_H/ s^{-1}	k_T/ s^{-1}	k_{esc}/ s^{-1}	k_{ST}/M $^{-1}$s^{-1}	τ_C / ns	H_L/ mT
I	10^6	$6.5 \cdot 10^6$	$2.0 \cdot 10^5$	$2.0 \cdot 10^8$	0.44	1.2
II	10^7	10^7	$2.0 \cdot 10^5$	$2.0 \cdot 10^8$	0.44	1.2
BP	$3.7 \cdot 10^6$	$7 \cdot 10^6$	$2.0 \cdot 10^5$	$2.0 \cdot 10^8$	0.25	1.5

To discuss the difference in reactivity on hydrogen abstraction for I and II (10 times) the MO calculations with geometrical optimization were made for triplet excited states of these ketones. According to these calculations, the p-electron density of the singly occupied orbital with lower energy on the carbonyl oxigen nucleus are 0.44, 0.54 and 0.49 for I, II and benzophenone (BP) as a reference system. A considerable decrease of k_H for I can be explained by the fact that the unpaired electron density in the excited triplet of I is more delocalized compared with II and BP. The equal values of the escape rates ($2 \cdot 10^5$ s^{-1}) for all ketones leads us to conclude that the main way for escape process is diffusion out of the SDS radical from the micelle. In conclusion we can say, that the reactivity of acetylenic ketones is mainly determined by delocalization of unpaired electrons and MFE is formed by relaxation mechanism. The latter fact can explain the absence of MFE in homogeneous solution.

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photochemical transformation is dechlorination as a result of hydrolysis of electronically excited molecules of photochemical transformation of 2,4,5-TCP and PCP we have detected higly toxic compouds - polychlorinated dibenzodioxins (DDCD) and dibenzofurans (DDCF).

In real conditions, in complicated and multicomponent systems such as natural waters and waste waters direct photolysis is accmpanied by photosensitization and photoinduced processes of radical oxidation of pollutants. We studied the kinetics of 2,4,5-tcp and pcp transformation in humificated natural waters and in the presence of model photosensitizing agents: Bengal Rose (BR), Methylene Blue (MB) and Eosine (E).

It has been found that mainly the anion form of 2,4,5-TCP is involved in the photosensitization reactions. Among the products of sensitized transformation of 2,4,5-TCP, the proportion of formed DDCD and DDHP is higher than during direct photolysis.

The transformation of 2,4,5-TCP in the presence of photosen-sitizing agents occurred under the action of O_2 which is indicated by inhibition of the process by O_2 traps - azide-ion and DABCO. As this takes place, along with transfer of an electron and accompanying formation of fre radicals and products of their recombination, 2,4,5-TCP is dechlorinated to form 2,5-dichlorohydroquinone. It is presumed that as well as during direct photolysis, formation of 2,5-dichlorohydroquinone is the result of triplet excited molecules of 2,4,5-TCP, whereas during the hydrolysis of singlrt excited molecules cyclopentadienes are formed.

PPK-58

Mechanisms of Photochemical Transformations of Organochlorine Compounds (examplified by polychlorinated phenols).

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The work is done as part of INTAS-93-1226 project aiming at development of high-efficiency photocatalytic systems for mineralization of organic pollutants, in particular organochlorine compounds, using UV and visible radiation regions.

As model compounds we used pentachlorophenol (PCP) and trichlorophenols (2,4,5-TCP and 2,4,6-TCP) and their derivatives, in particular 2,4,5-trichloroacetic acid (2,4,5-T). The analysis of transformation products of chlorophenols was performed using HPLC and mass-spectrometry.

The photchemicol transformation rate of chlorophenols is strongly dependent on pH of the medium. The acid-basic dissociation rate (pKa) for 2,4,5-TCP determined from spectral and kinetics data was found to be 6,7±0,2. The quantum yield of 2,4,5,-TCP direct photolysis reaction is $(6,0\pm0,7)10^{-2}$ and does not depend on incident light wavelength and pH of the medium.

The studies of 2,4,5-TCP photochemical transformation kinetics in aerobic and anaerobic conditions has shown that neither the transformation rate, nor the composition of the direct photolysis products depend on the presence of oxygen in the medium. This suggests that electronically excccited states of 2,4,5-TCP do not interact directly with molecular oxygen. This is also indicated by the facthtat hydrogen peroxide was not detected in aerobic conditions. On the contrary, the substances effectively interacting with H_2O_2 in the peroxidase reaction have been found to accumulate.

The analysis of 2,4,5-TCP photolysis products show that chloride ions and 2,5,-dichlorohydroquione and dichlorocyclopentadienes accumulate in the system. The formation of these products suggests that the primary step of 22,4,5-TCP

METHODS TO GENERATE SUBSTITUTED CYCLOPROPYL RADICALS GRAFTED TO SILICA SURFACE, THEIR STRUCTURE AND PROPERTIES

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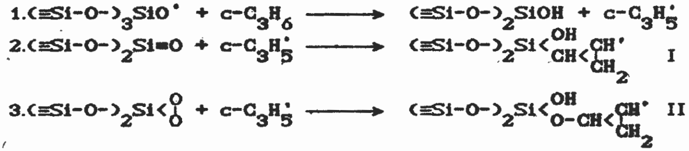
This report is devoted to the structure and reactivity of cyclopropyl radicals grafted to the SiO_2 surface. The general procedure proposed earlier [1,2] has been used for generation of reactive intermediates on the silica surface.

1. Cyclopropyl free radical $c\text{-}C_3H_5^{\bullet}$ captured by diamagnetic centers at the SiO_2 surface.

The cyclopropyl type radicals have been produced by $c\text{-}C_3H_5^{\bullet}$ radicals capture by silanon $(\equiv Si\text{-}O\text{-})_2Si{=}O$ and siladioxirane $(\equiv Si\text{-}O\text{-})_2Si{<}\genfrac{}{}{0pt}{}{O}{O}$ centers at 200 K (Scheme 1, reactions 2 and 3, structures I and II). Their structure has been identified by ESR technique.

Scheme 1.



$$1.\ (\equiv Si\text{-}O\text{-})_3SiO^{\bullet} + c\text{-}C_3H_6 \longrightarrow (\equiv Si\text{-}O\text{-})_2SiOH + c\text{-}C_3H_5^{\bullet}$$

$$2.\ (\equiv Si\text{-}O\text{-})_2Si{=}O + c\text{-}C_3H_5^{\bullet} \longrightarrow (\equiv Si\text{-}O\text{-})_2Si{<}\genfrac{}{}{0pt}{}{OH}{CH{<}\genfrac{}{}{0pt}{}{CH^{\bullet}}{CH_2}} \qquad I$$

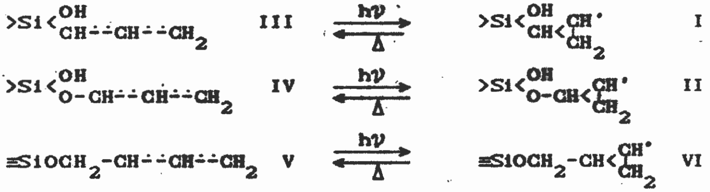
$$3.\ (\equiv Si\text{-}O\text{-})_2Si{<}\genfrac{}{}{0pt}{}{O}{O} + c\text{-}C_3H_5^{\bullet} \longrightarrow (\equiv Si\text{-}O\text{-})_2Si{<}\genfrac{}{}{0pt}{}{OH}{O\text{-}CH{<}\genfrac{}{}{0pt}{}{CH^{\bullet}}{CH_2}} \qquad II$$

Reaction 1 has been used for the generation of cyclopropyl free radicals $c\text{-}C_3H_5^{\bullet}$.

2. Photocyclization of allyl type radicals to cyclopropyl radicals.

The photocyclization of allyl radical has been reported in [3] as a new way leading to cyclopropyl radical. This technique has been used in our study for the conversion of radicals III, IV and V into radicals I, II and VI respectively (see Scheme 2). The estimated activation energies for the reverse thermal isomerization of the cyclopropyl radicals into the allyl radicals are 19, 16 and 20.5 kcal/mol for I, II and VI respectively with $A = 10^{13} s^{-1}$.

Scheme 2.

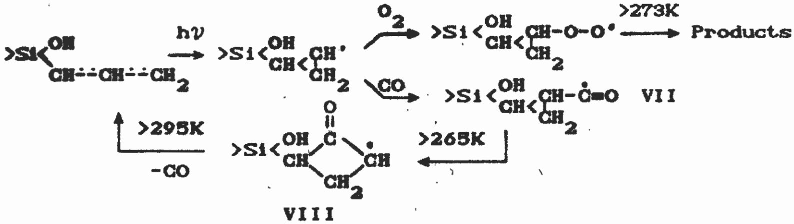


Quantum chemical calculations have been used for analysis of photocyclization mechanisms of c-$C_3H_5^{\bullet}$ and for thermal isomerization of $C_3H_4X^{\bullet}$, where X = H, F, OH, CH_3, SiH_3. The HFS constants have been also assigned. The results obtained are in agreement with experimental data.

3. Cyclopropyl radicals reactions with O_2 and CO.

Cyclopropyl radicals I, II and VI react with O_2 and CO even at 77 K. The structure of the products VII and VIII for the radical I as the starting reactant is given on the Scheme 3.

Scheme 3.



Acyl radical VII transforms quantitatively under heating to the initial allyl radical III through the cyclic radical VIII.

This project is supported by Russian Fundamental Research Foundation (grant No 94-03-09137) and International Science Foundation (grant MK9-000).

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PPK-60

Reaction kinetics in microemulsions

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The kinetics of the chemical processes in the microemulsions and micellar solutions is very complex even for the simplest bimolecular reaction. In analyzing reaction kinetics in these systems one has to take into account two effects. One is that the diffusions space of reactants is restricted and the other effect is that the reactants are nonuniformly distributed among the micelles. Reactants migrate between micelles and its number in each micelles fluctuates [1]. One of the feasible example is the preparation of the semiconductor colloidal nanoparticles using the ion exchange reactions in water-in-oil microemulsions [2]. But only one case is known when the microemulsions kinetic problem is solved exactly. This is the case when one of the reactants is present in large excess. One of the best suited process for investigation and modeling of this kinetics problem is the fluorescence quenching in micellar and microemulsion assemblies [3]. On the other hand the fluorescence quenching in micelles is a valuable tool to measure micellar size as will as the dynamic properties of the aggregates and of the solubilized species.

This report submits the results of mathematical modeling of the exchange dynamic of solubilized molecules in microemulsions, considers the fluorescence self-quenching kinetics in micellar solutions. The effect of distribution statistic of solubilized molecules on reaction kinetics is discussed. The problem of calculation the microemulsion particle distribution function for solubilized molecules with consideration of limited solubilization and interaction of solubilized molecules is examined based on methods of statistical physics. The condition for significant distortion of the distribution function and the occurrence of critical phenomenon in the molecular solubilization was found. Some new results concerning with formation nanometer-sized AgI clusters within reverse micelles are submitted. Agglomeration occurs discontinuously, suggesting a "magic number" of molecules to be included within the developing cluster.

This work was supported by the Russian Foundation for Scientific Research (Project Code N 93-03-09-89a).

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PPK-61

FEATURES OF LOW TEMPERATURE SiO_2 THIN FILM DEPOSITION IN BRANCHED CHAIN PROCESSES OF SILANE AND DICHLOROSILANE OXIDATION AT LOW PRESSURES

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This paper describes a number of investigations in an original field of SHS -self-propagating low temperature synthesis(SLS).SLS processes are the gaseous branching chain combustion processes leading to solid products being of practical value, in particular,to thin films,being widely used in integrated circuits (IC) processing.The lowering of thin film deposition temperature is of importance in IC on the basis of matherials with high mobility of charge carriers (A^3B^5,A^2B^6) and high temperature superconductors. Moreover, these materials change composition under heating with marked decrease in mobility of charge carriers.

A number of low temperature deposition methods in different regimes of silanes oxidation conditioned by the branching chain nature of these processes namely by the existence of ultimate phenomena in self-ignition and flame propagation has been worked out in present paper.This paper describes the deposition methods: a)in self-ignition area at the low limit (400K) ; b) in the flame propagation area at the low limit of non-thermal flame propagation (373K) ; c) beyond the flame propagation area with decaying flames being used(300K).The experiments have been carried out over the temperature range 300-400 K and the pressure range 0.5-2.3 torr.The gas mixtures contained 10-50% of fuel (silane or dichlorosilane) with O_2.The new designs of hot wall and cold wall deposition reactors have been developed. The techniques scope for one- and multisubstrate SiO_2 deposition.The film properties and composition have been determined by means of X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and IR spectroscopy. XP and AE spectra have been recorded using LAS-2000-RIBER apparatus with the base pressure 2.10^{-10} torr. The XP spectra have been exited using an unmonochromated MgK_α X-ray source. Argon ions accelerated up to 3.5 KeV have been used in profile analysis. The IR spectra have been measured on the two beam IR grating spectrophotometer SHIMADZU-IR-435, purified silicon wafers being used for compensation.

It has been shown by means of XPS and AES that the composition of SiO_2 films obtained in all aforementioned conditions is near stoichiometry; the deposition proceeds uniformly and homogeniously over the substrate surface and the film thickness. The chlorine content in films is negligible. It means that the chlorine atoms take part only in gaseous elementary reactions.

It has been also shown by means of AES and IR spectrophotometry that the films deposited in the process of dichlorosilane oxidation contain low concentrations of hydrogen atoms and hydroxyl groups being compared with commercial SiO_2 films deposited by LPCVD at 700 K. Moreover, the concentrations of hydrogen (Si-H) and hydroxyl groups (Si-OH) being undesirable in IC processing are markedly lower than those measured in films obtained in our conditions by all methods developed in the present work for silane oxidation. It means that the dichlorosilane oxidation is quite promising in low temperature thin film deposition. The results obtained are in accordance with our previous data [1,2].

Therefore, the original SLS methods have been developed in present work. The use of dichlorosilane as a fuel offers the marked increase in Si-H and Si-OH groups concentrations. The films obtained at low temperatures are homogeneous and uniform.

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PPK-62

PECULIARITIES OF REACTIONS IN LOW TEMPERATURE ORGANIC FILMS

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Codeposition of organic and inorganic substances on different surfaces in the temperature region of 10-80 K is widely used in matrix isolation and preparative cryochemistry. The thickness of the films obtained by codeposition is usually limited by values suitable for spectroscopic investigations. But it was shown that the thickness of the low temperature films influences on the processes occurring in these films resulting in the critical phenomena in cocondensates.

The films thus obtained are thermodynamically non equilibrium, mechanically stressed, and possess some redundant energy. Interaction of chemical particles in low temperature films responsible for critical phenomena is influenced by their kinetical, energetical, and thermodynamical inequivalence.

Critical phenomena in low temperature organized films are discussed on the following examples: halogenation and hydrohalogenation of olefins, interaction of magnesium with halogenalkanes and reaction of acetylchloride with diethylamine.

Interaction of halogens and hydrohalogens at low temperature in the films is taking place through formation of weak donor-acceptor complexes. As it was shown by IR spectroscopy data, this complex formation depends on the codeposition rate; and could be as high as 100% by yield or completely absent. The chemical reaction takes place only in the first case.

Upon codeposition the films destruction is exhibited for the systems Mg - phenylhalides and Mg - 1,2-dichloroethane. The reaction is effected by film thickness upon equal experimental conditions. Some explosion reaction were observed in the acetylchloride - diethylamine cocondensates.

The mechanical stresses arising in the growing film were detected for all systems mentioned above. A connection was found between mechanical stresses and critical thickness of the film. The new model describing the evolution of growing films and arising the specific effects was proposed. It was suggested that the formation of the films proceeds in three stages. At first stage the structure typical for volume samples is forming in growing film. When passing through the second stage the plastic deformation of the film takes place. Under this condition the molecular mobility increases in the growing film. This can stimulate fast reaction and in some cases -explosive processes. At third stage the fragile destruction of the sample by mechanical stresses could take place resulting in the explosive process either.

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Acknowledgements.

The work was partially supported by ISF (grant MLS 000).

SIZE EFFECTS IN REACTION OF SOLID ORGANIC COMPOUNDS WITH METAL CLUSTERS.

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Although physical properties of metallic particles of size more than 100A have been studied including influence of cluster size on the melting temperature, optical, electric, magnetic properties, the nanometer-scale particles are not examined properly. The use of low temperature techniques allows one to solve the problem. High reactivity of these particles preventing studies of their chemical reactions. Investigations were been carried out on the systems obtained by codeposition of metal vapours and organic substances on the surfaces cooled to 77 K. Cocondensates were prepared in special reactors as films of different thickness ready for spectroscopic investigations. The temperature of surface was varied from 77 to 110K. The codeposition rates were 10^{14}-10^{16}mol/s·cm^2. The ratio metal to organic ligand was varied from 1:1 to 1:1000.

The samples thus obtained are not thermodynamically stable possess some redundant energy and show high reactivity. The energy accumulated in the systems depends on the cluster size and film thickness. As a rule, the reactivity of metal particles increases, with decrease of particle size. Therefore, the particle size may be considered as an analogue of temperature influence in thermodynamic aspects. The models are analysed which relate chemical interaction of organic substance with nanoclusters in solid films of different thickness to re-action heat or structure non-equilibrity observed in mechanical stresses.

Examples of chemical transformations in the following systems have been considered: magnesium- alkylhalides (1,2-$C_2H_4Cl_2$, C_6H_5Br, C_6H_5I), co-condensates of samarium with alkanes and cyclo-alkanes in the hydrogenation reactions of olefins, reactions of atoms and clusters of Na, Mg, Sm, Yb with acetone. Reactivity and product yield of clusters and bulk metals have been compared.

The explosion interaction of magnesium with 1,2-dichloroethane has been analysed in detail. It has been shown that this process depends on the temperature of support, film thickness, film formation condition, external effects. We demonstrate, that increase of the temperature of surface results in decrease of the reaction probability, while increase the codeposition rate results in the spontaneous reaction. Spontaneous explosion reactions in the growing solid films of co-condensates may be considered as process of brittle destruction of the formed film.

Acknowledgements.

The work was partially supported by RFFI (grant 94-03-09987).

PPK-64

MECHANISMS OF PHOTOCHEMICAL REACTIONS OF RADICAL CATIONS IN ORGANIC SOLIDS

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Radical cations are known to be the essential intermediates and in many cases the main ones defining the proceeding of various chemical processes in solids.

The new quantitative data of electronic spectra and the main mechanisms of photochemical reactions of radical cations of different types formed under action of ionizing radiation on freezing solutions of corresponding organic compounds (esters, amides, tetramethylurea, aldehydes, ketones, carbon acids) in freones ($CF_2ClCFCl_2$, CF_2BrCF_2Br, $CFCl_3$) and freones mixture at 77 K were obtained in this work. The photochemistry of intermediates, produced in irradiated pure freones and their mixture were studied. The nature of intermediates and quantum yields of their photoconversions were determined.

Radical cations of organic compounds have been found to involve in different types of chemical reactions under action of light (the electronic spectra of the majority of radical cations being studied lie in visible or nearest UV-region):

1. Photostimulated intramolecular hydrogen atoms transfer (it is observed for radical cations of tetramethylurea)

$$(Me_2N)_2CO^{+\cdot} \Rightarrow Me_2N\overset{+}{C}(OH)N(Me)\dot{C}H_2$$

2. Photostimulated neutralization (it is observed for radi-

cal cations of esters, amides, aldehydes, ketones being insulated in matrix of $CFCl_3$).

$$RH^{+\cdot} \Rightarrow (RH^{+\cdot})^{*} \quad \Rightarrow \quad RH + CFCl_3^{+\cdot}$$

$$CFCl_3^{+\cdot} + CFCl_3^{-\cdot}(Cl^{-}) \Rightarrow CFCl_3 + CFCl_3\ (Cl^{\cdot})$$

3. Photodissociation of radical cations (it is exhibited for radical cations of linear, cyclic and substituted acetales)

$$(MeO)_2CH_2^{+\cdot} \Rightarrow CH_3OCH_3 + CH_2O^{+\cdot}$$

4. Photostimulated ion-molecular reactions (they are seen for dimeric radical cations of ketones, carbon acids)

$$[\,Me_2CO...Me_2CO\,]^{+\cdot} \Rightarrow \dot{C}H_2COCH_3 + Me_2COH^{+}$$

The data on quantum yields of radical cations photoconversions in various types of reactions at 77 K were obtained in the freones mixture: $CFCl_3/CF_2BrCF_2Br$. The possible reasons for different directions of processes with participation of electronically excited radical cations were discussed.

This work was financially supported by a Russian Foundation for Basic Research (projects 95-03-08110).

PPK-65

DIMERIZATION OF SOME LIQUID CRYSTALLINE 4,4'-ALKYLCYANOPHENYL DERIVATIVES IN SOLID PHASE AND INERT MATRICES

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Molecular association of liquid crystalline 4,4'-pentyl-cyanobiphenyl (5CB), 1-p-cyanophenyl-4-pentylcyclohexane (5CH), 2-p-cyanophenyl-5-pentyl-pyridine (5Py) has been studied in bulk, solutions and inert matrices at 77-330 K by low temperature reflection IR-spectroscopy and isothermal Calve calorimetric method.

IR-study of thermal behaviour of monomeric liquid crystalline films obtained by condensation of molecular beam on cooled copper surface showed that at 270-290 K the effective process of inner dimers formation took place in solid phase. This transformation was accompanied by CN-stretch band shift to lower frequencies [1]. The effect was confirmed by computer modelling of theoretical IR spectra of dimer and monomer forms of 5CB and it's derivatives. The spectroscopic data for bulk monomeric liquid crystals are the same as for high diluted solutions of liquid crystals in nonane and pentane. More precise data were obtained by matrix isolation technique for IR spectroscopy of liquid crystals monomers and dimers in argon matrix (LC:Ar=1:2500 and 1:10) at 5-10 K. The computer treatment of experimental spectra for bulk liquid crystals at different temperatures allowed us to obtain the values of dimerisation enthalpy DH=19±5 (5CB), 3±1 (5CH), 12±5 (5Py) kJ/mol.

Kinetics of the dimerization process in liquid crystalline mesophase has been studied by Calve calorimetric method. Using temperature jump method allowed us to obtain the dimers concentration higher than equilibrium value at experimental temperature. The analysis of experimental data in assumption of simple kinetic scheme of the dimerization process: $2M \leftrightarrow D$ allowed us to obtain the kinetic parameters. In the case of 5CB at 298K $k_1=3*10^{-4}\ s^{-1}$, $k_2=2.3*10^{-3}(s*M)^{-1}$; at 293.5K $k_1=2.4*10^{-4}\ s^{-1}$, $k_2=1.9*10^{-3}(s*M)^{-1}$; at 276K $k_1=1.3*10^{-4}s^{-1}$, $k_2=1.7*10^{-3}(s*M)^{-1}$. So the characteristic time of dimerization process is about 300s and is significantly (100-1000 times) more than specific time of diffusion processes in studied liquid crystals.

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Acknowledgements.

The work was partially supported by ISF grant N MLS 000

Rearrangement and ion-molecular reactions of $C_5H_8^{+\cdot}$ related radical cations as studied by ESR in frozen freonic matrices and spin trapping technique in liquid hydrocarbon.

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In the present study we have examined the thermal reaction of the related $C_5H_8^{+\cdot}$ radical cations (vinylcyclopropane, 1,3- and 1,4-pentadiene, cyclopentene), which of structures possess the most stability in gaseous phase. R.C. generated in X-rays irradiated at 77 K of substrate solution in freons $CFCl_3$ and $CF_2ClCFCl_2$(F-113) were investigated by ESR in the range of 77-160 K. Neutral radicals were trapped in liquid hydrocarbons at 295 K by 2,4,6-tertbutylnitrosobenzene (BNB) as a spin trap.

1. VINYLCYCLOPROPANE radical cations ($VCP^{+\cdot}$). Gauche and anti-$VCP^{+\cdot}$ were found to be the primary R.C.and these were rearranged at 105-110 K (the range for the phase transition in F-113 matrix) with ring-opening to different distonic R.C. possessed the different electronic and geometric structures: dist(90,0)-$C_5H_8^{+\cdot}$ and dist(0,90)-$C_5H_8^{+\cdot}$, respectively. The "solid, liquid and gas phase" conditions were modelled by variation of freon matrix, temperature and substrate concentrations. Allylic radicals were formed after heating to 115-130 K. In liquid VCP X-irradiated at 293 K using BNB as a spin trap 5 different radical adducts with primary alkyl (CH_2CH_2R), sec-alkyl, tert-alkyl and allylic radical as the products of rearrangement and ion-molecules reactions were recorded.

2. 1,3-PENTADIENE R.C. is instable in $CFCl_3$ at 77 K and rearrange into the R.C. of cyclopentene ($a(4H)$ = 50,2 G, $a(4H)$ = 8,6 G). Essentiely the same spectra were recorded for X-irradiated 0,5-2% mol. cyclopentene solution in $CFCl_3$. This rearrangement is due to a loose and symmetric cavities in frozen poly crystal freons. In glassy F-113 matrix the rearrangement does not happen. The σ-dimerization of 1,3- and 1,4-pentadiene R.C. and H-atom transfer from neutral molecules to R.C. proceed concurrently in glassy F-113 matrix upon the phase transition (110 K). The isolated R.C. of 1,3-pentadiene (septet $\alpha(6H)$ = 16 G) transform at 110 K into multiplet 4x2x3x3 α(3H=15,8 G $\alpha(1H)$ = 21 G, $\alpha(2H)$ = 11,0 G, $\alpha(2H)$ = 3,5 G from allylic radical (pentadienyl radical is recorded as a small dopant). In

concentrated 1,3-diene solution in F-113 it were also recorded the lines from cyclic allylic radical as a final product of 1,3-pentadiene R.C. isomerization into cyclopentene R.C. In X-irradiated 1,4-pentadiene (0,1-16%) in $CFCl_3$ the quintet of 1,4- pentadiene R.C is recorded in the range of 100-160 K ($\alpha(4H)$ = 11 G), which must correspond in planar structure. In F-113 glassy matrix 1,4-pentadien R.C. transform at 115 K into pentadienyl radical ($\alpha(5H)$ = 9,0 G) but at 125 K pentyl-2-en-4 radicals $CH_3\text{-}\dot{C}H\text{-}CH_2\text{-}CH{=}CH_2$ were recorded as products of ion-molecular reaction ($a(2H_\beta)$ = 5,9 G, $\alpha(1H_\beta)$ = 39 G, $\alpha(1H_\alpha)$ = 19,5 G, $\alpha(2H_\beta)$ = 29 G). In X-irradiated liquid solution of BNB in 1,3- and 1,4-pentadiene only two radical adduct were recorded: multiplet 3x2x3 (a^N = 13,6 G, $a_\beta^H(1H)$ = 21,2 G, $a_m^H(2H)$ = 0,9 G (1) from trapped sec-alkyl radical -CH- type, and multiplet 3x3x3 (a^N = 13,7 G, $a_\beta(2H)$ = 17,0 G, $a_m(2H)$ = 0,9 G) (2) from trapped allylic radical. Yield ratio of adducts (1):(2) varies from 10:1 in the case of 1,3-pentadiene R.C. to 1:1 in the case of 1,4-pentadiene. This sharp distinction is the result of two concurrent processes: σ-dimerization of diene R.C. and ion-molecular reaction of H-atom transfer. σ-dimerization in the case of 1,4-pentadiene R.C. is unlikely, since product of dimerization $CH_2{=}CH\text{-}CH_2\text{-}\dot{C}H\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{C}H\text{-}CH_2\text{-}CH{=}CH_2$ have instabilized cationic and radical centers, whereas in the case of 1,3-pentadiene R.C. cationic and radical centers were stabilized by allylic system: $CH_3\text{-}CH{=}CH\text{-}\dot{C}H\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{C}H\text{-}CH{=}CH\text{-}CH_3$. Therefore in the case of 1,4-pentadiene R.C. $CH_2{=}CH\text{-}\dot{C}H\text{-}CH{=}CH_2$ pentadienyl radical will most likely formed as a result of H-atom transfer from diene to R.C. Spin density is about the same in the center and at the ends of pentadienyl radical.

3. R.C. of cyclopentene (**C.P.**) in F-113 matrix at 110 K transform into cyclic allylic radical $a(4H_{4,5})$ = 29,2 G, $a(2H_{1,3})$ = 14,2 G, $a(1H_2)$=3,1 G as a result of deprotonation from highest spin density sites (a^{4H}= 50 G) in R.C. In concentrated **C.P.** solution in $CFCl_3$cyclopentadienyl radical is formed. In dilute solution C.P. in F-113 (0,02 % mol) distonic R.C. dist(0,90)-$C_5H_8^{+\cdot}$ with ring opening is recorded. Adduct BNB with $\dot{C}H_2CH_2R$ radical were recorded in X-irradiated liquid cyclopentene as a result of ring opening and formation of distonic $\dot{C}H_2CH_2R$ radicals.

.Support: International Science Foundation, Grant № NBB000

FEATURES OF COPPER PHTHALOCYANINE SYNTHESIS OCCURRING IN THE PRESENCE OF ULTRAFINE POWDERS

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The search for ways of copper phthalocyanine (Cu Pc) synthesis occurring under milder conditions is an actual problem. For this purpose we used ultrafine copper powders (UFP) obtained by the electric explosion of a conductor in argon, 1-amino-3-imino-isoin dolenin (AII) and solvents.

In the presence of UFP the synthesis of Cu Pc was found to proceed even at the room temperature. And if the specific surface of the powder (Ssp) was in the range of 16-18 m^2/g the reaction ran 8-10 days and if Ssp was about 70 m^2/g it ran only 3-5 hours. The reaction was accompanied by the change of suspension colour from yellow-brown to blue-green and blue.

In some time after component mixing an additional EPR signal appears and grows at a wide sigment signal (spectrometer EPR-20, T=77K). It has a superfine structure (SFS). The presence of ten components in SFS is connected with the location of unpaired electron at a nitrogen atom. A probable intermediate represents an ion-radical of a linear structure, one end of which contains Cu^+, while the other - an unpaired electron at a nitrogen atom. AII and Cu^+ ion are known to form a brown intermediate of a linear structure, which contains 6-8 monomer chains. Further oxidation of Cu^+ to Cu^{2+}, causes the change of electron configuration from $4S^23d^{10}$ to $4S^23d^9$ with a corresponding coordination change of isoindoline fragments.This is a templant mechanism of the synthesis.

The formation of a linear intermediate of brown colour is to our mind a limiting stage in the process. The decrease in activation energy of its formation is achieved due to UFP activity. The formation of Cu Pc in the presence of UFP (Ssp is about 70 m^2/g) gives a pigment of a special crystal structure.

The synthesis of Cu Pc proved the ultrafine powders obtained by the electric explosion to be promising agents in organic synthesis especially for the products obtained under strict conditions.

PPK-68

MECHANISM OF OXIDATIVE POLIMERIZATION HEAVY PETROLEUM SYSTEMS INHIBITED

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Various heteroatomic structures present in petroleums and petroleum products provide the inhibition of radical reaction by diverse mechanisms. Numeruos studies prove the presense of inhibitors - antioxidans by testing on the model reaction of cumene oxidation.Since the oxygen present in the monomer in the form of solution is actively involved in the inhibition process the determination of inhibitors interrupting the chain reactions by interaction with alkyl radical becomes difficult.

The reactive microcalorimetry permitted to study heavy petroleum systems as concerns the presence of inhibitors -antioxidants and the presense of inhibitor-alkyl radical acceptors using unique experimental procedure . The studies have demonstratied that the quantity of inhibitors interacting with the alkyl radicals in petroleum systems is insignificant.

On the base of the theory of polymerization of vinyl monomers in presence of antioxidants and oxygen we have developed the calorimetric prosedure of complex petroleum mixtures testing for inhibiting activity. The reaction of styrene polymerization in presense of oxygen and in vacuum was the model reaction. It has been demonstrated that the petroleum systems are the active inhibitors only in the presence of oxygen, in appears that the petroleum structures having phenol and amino groups in their composition are responsible for the inhibition. Therefore,the proposed method allows to testify ingibiting activity of the complex mixtures and calculate the constants of elementary inhibition acts speed.

FREE RADICAL MECHANISM OF PHOTONUCLEATION OF TRIETYLAMINE AND HALOIDBENZENE VAPOURS.

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Physical aspects of nucleation has been described in details since pioneering Wilson investigation. Kinetics and chemical mechanisms of UV light induced aerosol formation are still poorly studied experimentally and ill interpreted theoretically. These processes may be important in the atmosphere and during photosmog.

The main goal of this investigation is to find the photochemical aerosol formation under near- UV irradiation of some organic molecules and to study the chemical kinetics of products formation and chemical stages of this process.

The experimental set-up for investigation of photochemically induced aerosol formation includes automated aerosol spectrometer [1] ,flow system of reagents vapours in the gas carrier and Hg light source. It permits to investigate kinetics of growth of particles the range from 100 to 10000000 1/cc and size distribution of particles range from 2.5 to 200 nm.

The gas phase photolysis of haloidbenzenes (PhHal; Hal= Cl,Br ,I) has been studied and the formation of nanometer-sized particles has been detected [2,3]. The rate of particle formation decreases in the order PhI>PhBr>PhCl. In the air the rate of aerosol formation increases 500-100 times than in helium.Aerosol and gas phase products have been analyzed [4]. The participation of halogen and oxygen substituted aromatic compounds in nucleation was proved. Benzene, phenols and halogen were found among gaseous products. Ozone participation in PhHal photonucleation was detected. The mechanism of chemical stages of photochemical aerosol formation in the inert gas and in the air has been suggested.

The sub-microne aerosol particles are produced at triethylamine (TEA) photolysis in the inert gas or in the air. The kinetics of the aerosol particles growth have been investigated and the mechanism of their formation has been proposed [5].The concentration of particles is large in the air and small in argon.

Kinetics of PhHal and TEA photonucleation share the common properties. The aerosol particles formation and growth takes place only UV irradiation. The addition of oxygen into reagent mixture greatly increases aerosol concentrations. The notion of the irradiation doze as to photonucleation is yet unequivocal for applying.

On the base of all the data obtained for PHhal and TEA the conclusion is that free-radical mechanism aerosol formation prevails under PhHal and TEA vapors photolysis.

This paper is supported by RFFI grant No.94-03-08076a

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MARY-SPECTROSCOPY OF SHORT-LIVED ION RADICAL PAIRS.

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The study of magnetic field effects on reaction yield (MARY-spectroscopy) of chemical reactions provides valuable information on short-lived spin-correlated radical pairs. The coherent nature of radical ion pairs reveals itself in characteristic features at zero field [1] and at triple (*hfi*) constant [2], opening possibilities for identification of short-lived paramagnetic species and studying the reactions they are involved in. The breaking down of spin coherence in the course of resonance charge transfer reaction should lead to broadening of narrow MARY-spectra lines thus allowing one to extract quantitive information on the rate of this process. In present work this technique was employed to demonstrate that in liquid solution cation radicals of *cis*- and *trans*-decalin take part in the reaction of resonance charge transfer to neutral molecule. In diluted solutions the rate of this process is proportional to acceptors concentration and is quite close to diffusion controlled one. So it is demonstrated that reactions involving short-lived radical ions could be studied basing on the effects of quantum coherence of radical pair spin system.

Cation radicals of *trans*-decalin are unstable in liquid alkane solutions and their signals were observed only at liquid helium temperatures. Fig. 1 presents MARY-spectra of the short-lived *trans*-decalin cation radical in cyclohexane taken at room temperature.

Since alkanes are widely used as solvents in radiation-chemical experiments, the ability of alkane radical cations to take part in positive charge hopping is widely debated. But, unfortunately, there are still no direct proofs for ion-molecular resonance charge transfer in saturated hydrocarbons. Very fast hole hopping was proposed to explain the conductivity measurements in cyclic hydrocarbons [3], but this explanation was questioned in subsequent publications [4]. It is generally believed that the rate of hole hopping is actually not large. Therefore, this work presents first direct spectroscopic verification of *cis* and *trans*-decalin radical cations participation in resonant charge transfer reaction in liquid solution. In diluted solutions the rate of this process is proportional to decalin concentration and is quite close to diffusion controlled one. In MARY-spectra of concentrated solutions of *trans*-decalin narrow line of *p*-terphenyl cation radicals

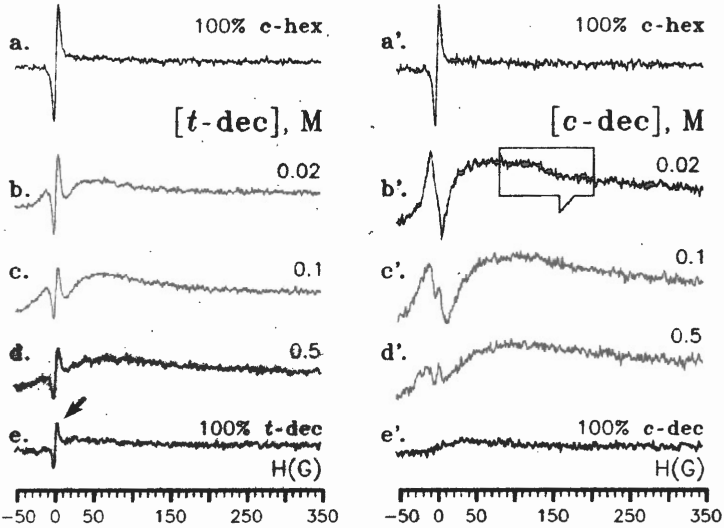

Figure 1: Experimentally taken MARY-spectra of *cis*- and *trans*-decalin solutions in cyclohexane for different decalin concentrations (room temperature). *P*-terphenyl-d_{14} (10^{-3} M) was added as luminophore. For convenience the satellite line at $H^* = 3a$ is put into box. Arrow indicate narrow line of *p*-terphenyl cation radicals.

is observed. The appearance of this line could be explained by fast hole transport among solute molecules.

Acknowledgement. The work performed under the auspices of International Science Foundation, Grants #RCE000 and #RCE300, INTAS Grant #93–1626 and Russian Fund of Fundamental Research, Grant #93–03–5035.

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PPK-71

PECULIARITIES OF MECHANISM OF Ag^+ IONS REDUCTION BY Zn^+ AND Cd^+ IONS

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The mechanism of the reduction of Ag^+ with zinc and cadmium ions in unusual oxidation states (Zn^+ and Cd^+) was studied using pulse radiolysis with a fast optical detection of short-lived products.

The experimental conditions ensured the preferential formation of the Zn^+ and Cd^+ ions in reactions with hydrated electrons at the initial stages of the radiation-chemical transformations of aqueous solutions containing silver and zinc or cadmium perchlorates as well as isopropanol or sodium formiate as the acceptor of hydroxyl radicals. Previously, it was shown that the reduction of Ag^+ ions to Ag^0 atoms further leds to the formation of $Ag_2{}^+$, $Ag_4{}^{2+}$, and Ag_8^{2+} clusters and ends with the formation of metal sols. The Zn^+ ions reduce Ag^+ ions to Ag^0 in a reaction with an electron transfer. The rate constant for this reaction is $2*10^9$ l/(mol*s). Ag^0 react with Ag^+ ions to form Ag_2^+ dimers. Unlike Zn^+ ions, Cd^+ ions react with Ag^+ to form a short-lived mixed cluster $(CdAg)^{2+}$ (the rate constant for the formation of this clusters is $3*10^9$ l/(mol*s)). This cluster has an absorption band with λ_{max} = 270 nm and the extinction coefficient = $1.5*10^4$ l/(mol*cm). The subsequent interaction of the clusters with

Ag^+ ions leads to the formation of the dimeric Ag_2^+ ion. The subsequent stages of the reduction of silver ions in solutions with zinc or cadmium additives and without them do not differ significantly. The computer-aided modeling of the process (with due regard to the combination of reactions, including the participation of the resulting organic radicals) allowed the calculation of the kinetic parameters of the reactions of the interaction of silver, zinc, and cadmium ions.

The peculiarities of the mechanism of the interaction of these metal ions in unusual oxidation states with Ag^+ and the possibility of the formation of intermediate mixed clusters are discussed in terms of the relationship of their redox potentials.

PPK-72

^{1}H CIDNP EVIDENCES FOR COMPLEXING IN THE REACTIONS OF DIMETHYLSILYLENE AND DIMETHYLGERMYLENE WITH CARBON TETRACHLORIDE

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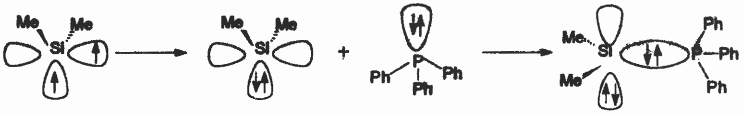
A distinguishing feature of heavy carbene analogs, silylenes and germylenes, is their capability to form complexes with the species possessing lone electron pairs [1]. The current concept is that the complexes are formed due to interaction of the lone pair of substrate with one of the vacant orbitals of the metal atom of heavy carbene in $^1A_1$ state [2].



By this is meant that silylenes and germylenes enter the reaction of complex formation in a singlet state. It is also known that complexing changes their reactivity. For example, reaction rate constant of dimethylgermylene Me_2Ge with CCl_4, $K = 1.2 \times 10^7$ $M^{-1}s^{-1}$, in the presence of triphenylphosphine Ph_3P is reduced to $K = 3.4 \times 10^6$ $M^{-1}s^{-1}$ [3]. Whether or not a complexing changes the elementary mechanism of the reactions of silylenes and germylenes with various substrates remains unknown. On the other hand, radical stages in the reactions of dimethylsilylene Me_2Si and dimethylgermylene Me_2Ge were successfully studied by means of CIDNP technique [4].

The present report is devoted to ^{1}H CIDNP studies of Me_2Si and Me_2Ge reactions with CCl_4 in the presence and in the absence of complexing reagent, triphenylphosphine Ph_3P.

It has been found that in all cases the reaction proceeds via the formation of radical pair (RP) of chlorodimethylgermyl (or -silyl) and $^{\cdot}CCl_3$ free radicals. Main reaction products are $Me_2E(Cl)CCl_3$, Me_2ECl_2, and $Me_2E(Cl)E(Cl)Me_2$ (E = Si, Ge).

Dimethylgermylene both in a free state and in the complex with Ph_3P forms singlet RP, whereas reaction of Me_2Si with CCl_4 gives rise to a triplet radical pair, similar to the case of the reaction with thiacycloheptyne [5]. Here, the multiplicity depends on the concentration of the reagents. It follows herefrom that complexing is capable to accelerate the process of T → S conversion of heavy carbene analogs under study.

The financial support of Russian Foundation for Basic Research (grants No. 93-03-5026, 93-03-5452, 94-03-08975) is gratefully acknowledged.

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SHELL–GROWTH POLYMERIZATION OF WHITE PHOSPHORUS IN WATER EMULSIONS

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For systems in emulsifier–free emulsions polymerization with particle diameters greater than 0,15 mkm to 0,2 mkm, a shell–growth mechanism for particle growth was proposed [1]. According to this mechanizm, the polymeric radicals propagate only within the shell region having a thickness about equal to the most probable end–to–end distance of the terminated polymer. This mechanizm was considered to result from anchoring of the hydrophilic end of growing radicals at the particle surface and from high average number of radicals per particle.

We have investigated the radiation–induced polymerization of white phosphorus in water emulsions stabilised with various surfactants. The formation of microcapsules turned out to take place, the thickness of the shell depending on the absorbed dose and the nature of the surfactant. At high absorbed doses the solid product was formed, containing 70–80% mass. of phosphorus, 5–9% of C, 4–6% of H, up to 20% of O. IR, NMR (P31) and roentgenoelectron spectroscopy data confirmed the product being the polymeric form of phosphorus (red phosphorus).

The rates of red phosphorus formation have been estimated. It was shown that the polymerization of white phosphorus proceeds via two reaction passways: the bulk polymerization in the inner part of the emulsion droplet and the surface polymarization, the effective rate constrant of the latter depending strongly on the nature of the organic radical formed under the irradiation. The correlation was obtain between the electron density on the free radical and the rate constant of the radical addition to the white phosphorus molecule.

The role of OH–radicals in the formation of the shell is discussed, the compounds containing phosphorus in the lower oxidation states inhibiliting the oxidation of white phosphorus by OH–radicals.

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The authors wish to thank the ISF for financial aid through the grant MOU 000.

PPK-74

MECHANISM OF AUTOCATALYTIC THERMAL DEGRADATION OF POLY(VINYL CHLORIDE)* STUDIED BY ESR SPECTROSCOPY

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In recent years,the mechanism Of the thermal degradation of PVC has been intensively studied. It has been shown that HCl, the main volatile product of PVC degradation, accelerates the dehydrochlorination of the polymer. The mechanism of the autocatalytic degradation of PVC is not yet clarified. In the papers [1,2] the new hypothese has been proposed that the autocatalytic PVC degradation is a branched chain reaction with degenerated branching of chain. It has been offered that the products of the thermal PVC degradation, such as polyenes and HCl,interact with each other and produce new active species which cause additional initiation of the thermal dehydrochlorination of normal units of PVC by a chain mechanism.

In this study the mechanism of the autocatalytic degradation of PVC has been investigated by ESR spectroscopy. It is well known that in the thermal degradation of PVC, residue polyene sequences have paramagnetic centers which are stable at elevated temperatures. An ESR singlet signal placed at about free electron g-value is observed. The signal is very stable in vacuum and also in air. The paramagnetic character of the degraded PVC is attributed to stable polyenyl radicals or to unpaired electrons of polyenes which are in thermally excited triplet state.

In this study the influence of HCl on the concentration of paramagnetic centers forming in the thermal degradation of PVC has been investigated for the first time.

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* The research described in this publication was made possible in part by Grant №. NOX000 from the International Science Foundation and by Grant №. NOX300 from the International Science Foundation and Russian Government.

The dehydrochlorination of PVC under vacuum with continuous removal of HCl and in the presence of HCl has been studied at 200°C.

It has been ascertained that the time of PVC degradation at which the ESR signal appears, the intensity of the signal and the variation of the signal intensity with the time of polymer degradation depend considerably on the concentration of HCl in PVC. In the PVC degradation in the presence of HCl the ESR signal is observed at an early stage (at about 15 min degradation), the curves of the dependence of spin concentration on time of degradation and on dehydrochlorination percentage have an autocatalytic character. In the nonautocatalytic PVC degradation with continuous and effective removal of HCl ESR signal appears after > 250 min degradation and its intensity rises insignificantly with increase of degradation time and conversion percentage. At the same percentage of dehydrochlorination the spin concentration is significantly more in the PVC degradation in the presence of HCl than that with continuous removal of HCl.

The conclusion has been made that in the thermal degradation of PVC the process of formation of paramagnetic centers in degraded PVC is intensifyed by the presence of HCl.

By special experiments it has been shown that during autocatalytic PVC degradation hydrogen does not practically form.

The obtained results has been discussed in the frames of the theory of the autocatalytic thermal degradation of PVC as the branched chain reaction with degenerated branching of chain.

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PPK-75

MECHANISM OF DEGENERATE CHAIN BRANCHING IN THERMAL DEGRADATION OF POLY(VINYL CHLORIDE)

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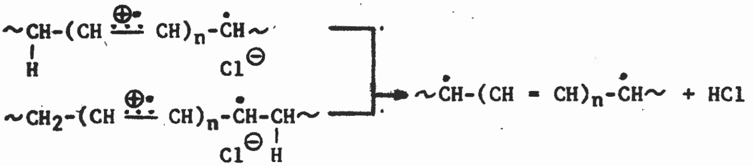
It is known that the termal degradation of PVC is complicated by the catalytic effect of evolving HCl.The mechanism of the autocatalytic and nonautocatalytic degradation of PVC is not yet clarified. Previously, we have suggested that the non-autocatalytic PVC degradation mostly proceeds by a molecular mechanism complicated by radical reactions.

In this study the most probable initiation reaction of the nonautocatalytic PVC degradation by a radical mechanism has been offered:

$$\sim CH_2-(CH=CH)_n-\underset{Cl^{\delta\ominus}}{\overset{\delta\oplus}{CH}}\sim \longrightarrow \sim CH_2-(CH\overset{\oplus\bullet}{\cdots}CH)_n-\underset{Cl^{\ominus}}{\dot{C}H}\sim \qquad (1)$$

where n=2-20.

Due to some factors, such as the great affinity of Cl atom for electron, low values of ionization potentials of polyenes, low singlet and triplet levels of polyenes, there is a probability of the thermal excitation of the polyene fragment with formation of the ion-biradical pair by the intramolecular transference of electron. Then subsequent transformation of the ion-biradical pair into the biradical may occur by means of interaction of proton with nucleophilic particle, Cl :



$$\left.\begin{array}{l}\sim \underset{H}{CH}-(CH\overset{\oplus\bullet}{\cdots}CH)_n-\underset{Cl^{\ominus}}{\dot{C}H}\sim \\ \sim CH_2-(CH\overset{\oplus\bullet}{\cdots}CH)_n-\underset{Cl^{\ominus}}{\dot{C}H}-\underset{H}{CH}\sim\end{array}\right] \longrightarrow \sim\dot{C}H-(CH=CH)_n-\dot{C}H\sim + HCl \qquad (2)$$

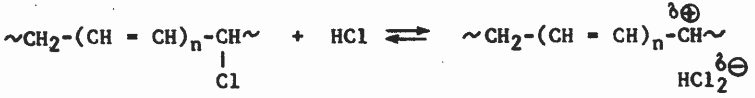
* The research described in this publication was made possible in part by Grant N NOX000 from the International Science Foundation and by Grant N NOX300 from the International Science Foundation and Russian Government.

In the triplet state the biradical may react with macromolecule units. This leads to initiation of a chain of radical transformations.

The elementary acts (1) and (2) are the stages of the reaction of degenerated branching of chain in the nonautocatalytic PVC degradation.

Recently, we have proposed the new hypothese that the autocatalytic degradation of PVC is a branched chain reaction with degenerated branching of chain.The numerous experimental data, obtained previously,concerning inhibition of the autocatalytic PVC degradation by some compounds,which do not react with HCl, such as active dienophiles, some metals (Hg,Ag), triethyl silane, as well as the results concerning retardation of PVC degradation in the presence of HCl by toluene and triphenylmethane are evidence for this hypothese.

In this study several mathematical models for the initial stage of the autocatalytic PVC degradation which are concerned the different mechanismsof this process have been considered. It has been shown that experimental curves at a definite constant concentration of HCl in the polymer may be described by the expression which is typical for kinetics of branched chain reactions. The mechanism of degenerated branching of chain in the autocatalytic PVC degradation has been proposed. HCl may form the following complex with the polyene fragment :



$$\sim CH_2-(CH = CH)_n-\underset{\underset{Cl}{|}}{CH}\sim \; + \; HCl \rightleftarrows \sim CH_2-(CH = CH)_n-\overset{\delta\oplus}{\underset{HCl_2^{\delta\ominus}}{CH}}\sim \qquad (3)$$

For this complex the probability of transformation into the ion-biradical pair is more than that for the polyene fragment [eq.(1)] because there is the additional energy gain equal to ~14 kcal/mol due to formation of $HCl_2^{\ominus}$ ion. Then the ion-biradical pair transfersinto biradical.

The conclusion has been made that in the autocatalytic PVC degradation HCl is the catalyst of the reaction of degenerated branching of chain which takes place in the nonautocatalytic polymer degradation.

PPK-76

Cross-relaxation mechanism of nuclear polarization formation: quantitative study by time-resolved CIDNP.

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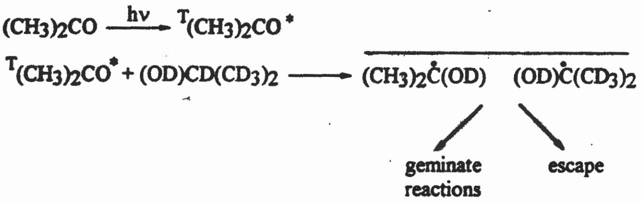
In the present work we have studied CIDNP, arising during the photolysis of acetone in isopropanol-d_8 (Scheme 1) by time-resolved CIDNP technique. Radical pair mechanism of net nuclear polarization formation requires the difference in g-factors of radicals forming a radical pair [1]. Since photoreaction of acetone in isopropanol produces only one type of ketyl radicals in solution, the observable net nuclear polarization on the reaction products can not be explained in the frames of radical pair mechanism of CIDNP formation. The account of scalar electron-nuclear cross-relaxation has been shown to be necessary for the interpretation of the results obtained [2]. The CIDEP effects observed in 2-hydroxy-2-propyl radicals also were explained taking into consideration cross-relaxation processes [3].

Scheme 1



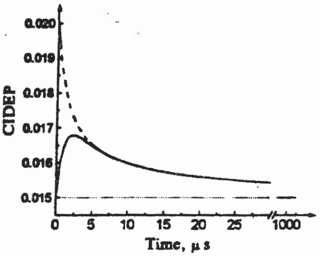


Fig. 1. Calculated time dependences of CIDEP per 2-hydroxy-2propyl radical at different initial electron polarizations P: solid line - P(0)=γ, dashed line - P(0)=4/3γ, where γ is Boltzman factor (0.015 in our magnetic field).

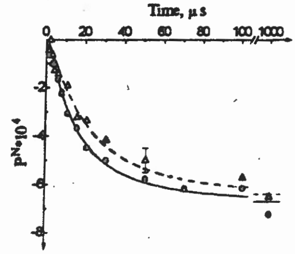


Fig.2. Kinetics of net polarization formation for CH_3-protons of isopropanol. ● - experimental points, solid line - calculation at the initial radical pair concentration $5.9x10^{-5}$ M; Δ, dashed line - the same at the initial radical pair concentration $2.2x10^{-5}$ M.

In the present work kinetics of CIDNP formation at different initial concentrations of 2-hydroxy-2-propyl radicals is quantitatively analyzed. It is demonstrated in model

calculation that spin-selective radical recombination leads to the appearance of net electron polarization (fig.1). Kinetics of net nuclear polarization formation in the products of 2-hydroxy-2-propyl radicals recombination (or disproportionation) is well described in the frames of such a model taking into account electron-nuclear cross-relaxation. Comparison of experimental and calculated data (fig.2) allowed to obtain characteristic cross relaxation time of these radicals, which was estimated as 46±8 μs.

Acknowledgement

This work was supported by Russian Foundation for Fundamental Researches (grant 93-03-18593) and by International Science Foundation and Russian Goverment (grant JJD100).

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PPK-77

ACTIVATION OF PEROXIDE O-O BOND RUPTURE BY ONIUM SALTS. QUANTUM CHEMISTRY ANALYSIS OF ASSOCIATIVE INTERACTION

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Association of benzoyl peroxide (BP), tert- butylperbenzoate (TBPB) with cations ($Q^+ = Et_4N^+$, Et_4P^+, Ph_4P^+, $Ph_3(PhCH_2)P^+$) and anions ($X^- = Cl^-$, Br^-, J^-) and O-O bond rupture in the models of [peroxide...Q^+] (1), [peroxide...X^-] (2), [Q^+...peroxide...X^-] (3) have been simulated with MO LCAO method in the AM1 approach for the purpose to study changes in electron and stereochemical structures of aromatic diacyl peroxides and peroxy esters, which were observed in their decay processes activated by onium salts. Obtained results showed, that considerable decrease of the energy barrier was observed for the peroxide decomposition in the model (3) only. Analysis of stereochemical and electron structures of peroxides in the basic isolated state and in the model (3) has demonstrated, that association with ions lead to significant polarization and conformation changes in the peroxo substratum, which destabilized peroxide labile O-O bond. It has been shown, that anion nature effected both on the energy barrier height of rupture of O-O linkage and on its length in the transition state. The transition state shifted to the right along reaction coordinate (r_{O-O}) and energy barrier increased in the model of [Hal^-...BP...$^+NEt_4$] in following row: J^-, Br^-, Cl^-. These facts are in agreement with kinetic data. Analysis of cation nature influence on peroxide decomposition has been considered in the model of Cl^-...BP...Q^+, where $Q^+ = Et_4N^+$, Et_4P^+. Results showed, that cation central atom nature effected on reaction energy barrier.

The research described in this paper was made possible in part by Grant N U1H200 from the International Science Foundation and it also was supported, in part, by International Science Education Program (ISSEP) through Grant N APU053101.

KINETICS AND MECHANISM OF $CF_3 + NO_2$ REACTION AT $T = 296$ K

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The kinetics of the title reaction was studied at $T = 296$ K within the range of total pressure 300–600 Torr. Mixtures containing CF_3NO, NO, NO_2, and helium were irradiated by a pulsed ruby laser ($\lambda = 694.3$ nm). The CF_3 radicals arising in the photodissociation of CF_3NO were involved into competitive pseudo-first-order reactions with NO and NO_2. The concentration of CF_3NO after the photolyzing pulse was monitored in real time by intracavity absorption of cw He–Ne laser radiation ($\lambda = 632.8$ nm).[1] Measuring the relative amplitudes of the kinetic curves of CF_3NO formation, obtained at different $[NO]_0/[NO_2]_0$ ratios allowed us to obtain the following rate constant for CF_3 removal by NO_2: $k_1 = (3.2\pm0.7)\times10^{-11}$ cm^3/s (the rate constant of the reaction $CF_3 + NO \longrightarrow CF_3NO$, measured earlier,[1] was used as reference). This value of k_1 is in reasonable agreement with the values reported by Sugawara et al.[2] (2.5×10^{-11} cm^3/s) and Francisco and Li[3] (2.5×10^{-11} cm^3/s) and differs significantly from that obtained by Rossi et al.[4] (2.7×10^{-12} cm^3/s).

Analysis of end products has shown that the main carbon-containing products of the $CF_3 + NO_2$ reaction are CF_3NO_2 (about 35% of the total product yield) and CF_2O (balance). The product yields differ substantially from those reported in other works.[2–4] The results obtained strongly support the mechanism involving association as a primary stage of the reaction:

$$CF_3 + NO_2\ (+M) \longrightarrow CF_3NO_2\ (+M) \qquad (1a)$$

$$CF_3 + NO_2 \longrightarrow CF_3ONO^* \longrightarrow CF_2O + FNO \qquad (1b)$$

Acknowledgment. This work was financially supported by Russian Foundation for Fundamental Research, grant No. 93-03-05018.

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PPK-78 a

THE RATE CONSTANTS OF THE SELF-COMBINATION REACTIONS OF CF_3, C_2F_5, AND n-C_3F_7 RADICALS AT $T = 296$ K.

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The kinetics of self-combination of CF_3, C_2F_5, and n-C_3F_7 radicals was studied at T = 296 K and at a total pressure of 600 Torr. Mixtures containing RNO (R = CF_3, C_2F_5, n-C_3F_7) and helium as a buffer gas were irradiated by a pulsed ruby laser (λ = 694.3 nm, pulse energy ≈1 J). The radicals R arising in the photodissociation of RNO were involved into the following main reactions:

$$R + NO\ (+He) \xrightarrow{k_1} RNO\ (+He) \qquad (1)$$

$$R + R\ (+He) \xrightarrow{k_2} R_2\ (+He) \qquad (2)$$

The concentration of RNO was monitored in real time by the intracavity absorption of cw He–Ne laser radiation (λ = 632.8 nm).[1,2] The rate constants of R + R reactions were derived from the relative amplitudes of the kinetic curves of RNO formation after the photolyzing pulse. The rate constants of the reactions R + NO, measured earlier,[1,2] were used as reference rate constants.

The rate constants obtained for the self-combination of the title radicals are as follows:

R	CF_3	C_2F_5	n-C_3F_7
k_2, cm^3/s	$(3.9 \pm 1.3) \times 10^{-12}$	$(3.4 \pm 1.2) \times 10^{-12}$	$(3.2 \pm 1.1) \times 10^{-12}$

The kinetic results are compared with the data available in the literature. The attempts are made to describe the experimental rate constants using statistical theories of unimolecular reactions.

Acknowledgment. This work was financially supported by Russian Foundation for Fundamental Research, grant No. 93-03-05018.

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REACTIONS WITH NONEQUILIBRIUM EXCITATION. MICRO- AND MACROKINETICS, ACTIVE MEDIA, LASERS.

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The very important events happened on the verge of the 1960-1970-th stimulated the progress in investigations of the elementary chemical reaction dynamics. That is the invention of the first chemical lasers, on the one hand, and the development of unique experimental methods of investigations of chemical processes at single collision conditions to determine the energy states of the products, on the other hand. In the report advances in both fields are followed up to date.

The inverse or strong nonequilibrium excitation of products in an elementary chemical act is needed to realize the chemical laser. However, a number of problems must be solved involving the choice of regime of carrying out the chemical reaction which would include in its mechanism a perspective elementary act, selection of the appropriate design, decrease of losses due to optical nonhomogeneity of active media and so on. The analysis of more than 300 available energy distributions in products of elementary chemical acts have shown that some tens of them are perspective for realization in lasers. For more than ten of the latter the amplification and generation regimes were demonstrated and only four of them were brought to corresponding laser developments.

In the report some examples of solutions of fundamental kinetic and involved constructive problems are presented for cases of hydrogen-fluorine pulsed and continuous wave lasers, carbon disulphide-oxygen and oxygen-iodine lasers what enables one to realize laser complexes on their basis. Though the noted problems are special for every listed type of lasers, some of them such as: peculiarities of transformation of initial nonequilibrium energy distribution in active media; the regime of heat self-acceleration in initiated chain processes (photothermal explosion); the role of chain branching -

inhibition of it in hydrogen-fluorine mixtures and more effective exhibition of it in carbon disulphide-oxygen mixtures, and some other are of common scientific interest. Last time the study of chemical processes with nonequilibrium excitation is aimed to even higher extent at the search of systems with electronic excitation. In this connection some examples of such systems are considered, where the formation of electronically excited species can be expected.

PHOTOSELECTION AND PHOTO-ORIENTATION AS THE METHODS OF THE INVESTIGATION OF MOLECULAR MOVEMENTS AND ELEMENTARY REACTIONS IN SOLIDS.

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Photoselection as the method of investigation of liquid phase reaction by the polarization of luminescence is well known. Photo-orientation is the process of light-induced molecular reorientation. In both cases, the irradiation of the initially disordered solid with both polarized and unpolarized light induces the long-lived alignment of absorbing molecules. This alignment may be viewed as light-induced macroscopic anisotropy of the irradiated samples. The most simple methods to measure anisotropy are the measurements of an optical dichroism and measurements of angular dependence of ESR spectrum.

These measurements may be used in the investigation of following points:

i. Molecular mobility in the solids can be measured as relaxation time of induced anisotropy. Temperature dependence of anisotropy relaxation allows to study the rotation mobility of molecules as well as the translation mobility of more mobile particles - electron, electron holes, protons, etc.

ii. Mobility measurements may be used as a sensitive method of the structure examination of solids. Comparison of reaction rate and molecular mobility is helpful for understanding the kinetic behaviour of investigated system.

iii. The measurements of alignments of initial and product molecules in course of chemical reaction give information about the mechanism of elementary act of reaction.

iv. ESR method permits to determine the orientation distribution function for investigated molecules. The mechanism of the molecular rotations, as well as details of the photochemical transformation can be investigated in this way.

Most important requirements and limitations for these observations are following:

1. The rotation time of studied molecules must be longer then characteristic time of the experiments;
2. Considered experiments can be carried out only with the enough anisotropic molecules (symmetric particles as an atoms or octahedral complexes can not be ordered by light);

3. Light absorption and reaction must take place with the same molecule; the energy transfer and migration of reaction center can violate the induced alignment.

Experimental examples of described approaches are presented and discussed.

Rotation times have been measured for photoselected nitroxide probe by means of the anisotropy relaxation. Obtained values are compared with the rotation times calculated from the shape of ESR signal. Differences of the rotation time values obtained by different method are discussed.

The observation of the induced alignment of initial and product molecules in the course of the photoreactions of N_2O_4 permitted to estimate the displacement of the molecular fragments in the elementary act of reaction. The different routs of photoreaction of N_2O_4 differ in required molecular mobility. The products of photoisomerization conserve orientation of dipole transition moment of the initial molecules. In contrast to isomerization, the reaction of dissociation is associated with the leaving the matrix cage by resulted particles. It leads to the random orientation of product of dissociation (NO_2- radicals). Optical measurements of anisotropy relaxation and simultaneous thermal reaction showed the close agreement of activation parameters of both processes in case isomerization of tert-butylantracene in polystyrene matrixes.

The angle of the rotation displacement of pyrene chromophore in the elementary act of isomerization of (3'-pyrenyl)-5,5-dimethylpyrazolidone-(3)-azomethine imine in polystyrene film was found to be 20 degree at the room temperature and depends on temperature.

The orientation distribution function obtained from angular dependence of ESR spectra for hole defects in halogenide-contained glasses as well as for carbenes in alcohol glass.

This work was made possible in part by Grants NBU000, NBU300 from International Science Foundation and Russian Government, and by Grant 95-03-08505 from Russian Foundation for Fundamental Research.

Pt(II) DIIMINE-DITHIOLATE COMPLEXES: PHOTOCHEMISTRY AND PHOTOPHYSICS

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In order to elucidate the role of central atom in photophysics and photochemistry of mixed-ligand metallo-compexes, $(R\text{-}C_6H_4\text{-}S)_2Pt(phen)$ (R = H (I), MeO - (II)) have been studied to be compared with Zn complexes of the same composition [1]. The problem of primary interest was the involvement of central atom in photoinduced charge separation taking place in the lowest ligand-to-ligand charge transfer excited states of the complexes.

The absence of long-wave absorption band (see table) in spectra of 'parent' $Pt(phen)Cl_2$ and $(NH_3)_2Pt(PhS)_2$ and its' negative solvatochromism allowed us to assign this band to LLCT-transition.

Compound in C_3H_7CN	$\nu^{max}{}_{abs}$ (ε) cm^{-1}	$\nu^{max}{}_{lum}$ cm^{-1}	$\Delta\nu$ cm^{-1}	φ_{lum} (77 K)	$\frac{\varphi(R=H)}{\varphi(R=MeO)}$
$(PhS)_2Pt(phen)$	21000 (1170)	16000	5000	0.035	
$(MeOPhS)_2Pt(phen)$	20600 (1830)	15930	4670	0.014	2.2
$(PhS)_2Zn(phen)$	27400 (779)	17600	9800	0.050	
$(MeOPhS)_2Zn(phen)$	27400 (751)	17000	10600	0.007	7.1
$(NH_3)_2Pt(PhS)_2$	37000	20200	16800		
$Pt(phen)Cl_2$	25640 (3630)	16390	11250		

As their Zn-analogs, (I) and (II) were found to be luminescent as polycrystalline solids and in low-temperature glasses. The lifetime of the excited state, responsible for the long-wave emission, for Pt(II) as well as for Zn complexes, is by order of microseconds; so, smaller Stocks-shift for Pt(II) than for

Zn-complexes was resulted from less structural reorganization in the excited state of the former. The absence of temperature dependence of long-wave emission intensity in the range 77-113K for Pt(II) - complexes (for $(PhS)_2Zn(phen)$ $E_{act}=14 \pm 2$ kJ/mol) indicates that this less structural reorganization is probably caused by larger E_{act} of reorganization process in square-planar Pt(II)-complexes than in tetrahedron Zn-ones. Closely spaced emission maxima of (I), (II) and $Pt(phen)Cl_2$ indicate, that, in contrast to Zn ones, in Pt(II) complexes MLCT and LLCT states are close in energy.

Both (I) and (II) undergo irreversible photooxidation and photoelectron transfer to viologens in deaerated solutions at 298K. System $(PhS)_2Pt(phen)$ - methylviologen is photochromic.

The excited state responsible for emission and electron-transfer reactions of (I) and (II) is supposed to be populated from primary excited LLCT-state with quantum yield in order by 10^{-3}. Less structural reorganization in the excited state, less influence of thiolate-ligand donor ability on emission maximum and quantum yield for Pt(II)-complexes than for Zn-ones may be caused by considerable participance of Pt d-orbitals in HOMO-orbital of (I) and (II).

Authors are grateful to Russian Fundamental Research Foundation for financial support (Grant N 93-03-05916).

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PPK-82

KINETICS AND MECHANISM OF DECOMPOSITION OF $C_3H_5C(CH_3)_3$ MOLECULES UNDER PULSE IR-LASER RADIATION

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The aim of study is to investigate the kinetics and mechanism of decomposition 4,4-dimethylpentene-1 induced pulse IR-laser in the gas phase.

There are no data available on decomposition of $C_3H_5C(CH_3)_3$ under IR multiphoton excitation (IR MPE).

The molecules are irradiated by TEA-CO_2 laser (τ = 180 ns) tuned at 985 cm^{-1}, 10R(36), resonant to CH_2 bending vibration (in C_3H_5 radical). The laser beam was focused at the cell using BaF_2 lenses of focal lengths 5, 15 and 30 cm. Analysis of products after irradiation was done by gas chromatography. The role played by radicals in the formation of reaction products was studied using mixtures $C_3H_5C(CH_3)_3$ with O_2 as radical scavenger. Reactions were investigated in both collisionless and thermal equilibrium conditions (1100±50 K). Detected products were C_3H_6, iso-C_4H_8, C_6H_{10}, C_3H_4, C_2H_6 and CH_4.

The major unimolecular channels under both collisionless and collisional conditions are six-centered C_3H_6 elimination (1) and C_3H_5-C bond rupture (2):

$$C_3H_5C(CH_3)_3 \longrightarrow C_3H_6 + CH_2{=}C(CH_3)_2 \qquad (1)$$

$$C_3H_5C(CH_3)_3 \longrightarrow C_3H_5 + C(CH_3)_3 \qquad (2)$$

The channel ratio (1)/(2), γ, is found to decrease with increase of fluence of IR laser pulse. The energy barrier for reaction (1) is estimated to be lower than that for reaction (2). The high-energy channel (2) can compete with channel (1) because of the much higher frequency factor.

The activation energy for C_3H_8 elimination is measured (E_1 = 51 ± 2 kcal/mol under the temperature of reaction zone 1100 ± 50 K).

The fragmentation of $C(CH_3)_3$ produced by the C_3H_8-C bond rupture occurs through splitting of H atom under both collisionless and thermal equilibrium conditions:

$$C(CH_3)_3 \longrightarrow H + CH_2{=}C(CH_3)_2 \qquad (3)$$

Collisioless fragmentation of $C(CH_3)_3$ is "spontaneus", i.e. $C(CH_3)_3$ radicals receive excitation energy from the dissociation of molecules $C_3H_8C(CH_3)_3$. The conditions of "spontaneous" fragmentation of $C(CH_3)$ are calculated by assuming statistical behaviour for the intramolecular dynamics using the equation of work [1]. These conditions are realised for $C(CH_3)_3$ under IR MPE of molecules $C_3H_8C(CH_3)_3$.

Thus the unimolecular C_3H_8 elimination and C_3H_8-C bond rupture are the major competing reactions in the gas phase under irradiation of $C_3H_8C(CH_3)_3$ by TEA-CO_2 laser. The channel ratio γ is controled by both fluence of laser pulse and pressure.

The collisionless reaction behavior of $C_3H_8C(CH_3)_3$ corresponds to statistical intramolecular dinamics.

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PPK-83

Absorption and Diffusion of Free Radicals in Porous Media as Studied by EPR Imaging.

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Mass transfer and intermediate states in porous media are of great theoretical and applications interest. Novel approaches to studies of such systems are opened due to the EPR imagine technique. The latter is based on EPR detection in the presence of strong magnetic field gradients which allows to restore the spatial distribution of spin centers at different periods of time and it's dependence on chemical origin and supermolecular structure of sample.

We have studied adsorption and transfer processes in model systems of two types: (a)- porous catalyst supports based on aluminium oxide and (b) -biomimetic membranes represented by nitrocellulose ultrafilters impregnated with fatty acid ethers. The mobile centers were spin probes 2,2,6,6-tetramethyl-4-hydroxy-piperidine-1-oxyl (I) and perchlorotetraphenylmethyl (II).

For polar molecules I a strong adsorption on the outer surface of Al_2O_3 support was observed with spatial distribution being practically unchanged at room temperature within hour time scale (Fig.1). Meanwhile the analogous picture for nonpolar probe II changes rather rapidly. The concentration profile shape was analysed by solving proper diffusion equations and effective values of the diffusion coefficient D_e were determined for different samples of catalyst support.

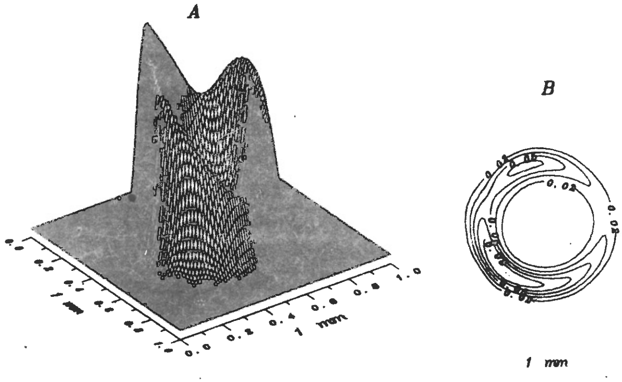

Fig.1 The spatial distribution of radical I in cylinder granule of catalyst support (type 1) as a result of mass transfer process from the solution of radical in CCl4 into the granule preliminary soaked in pure solvent. The starting conditions are in accord with nonequal distribution of solution around the granule. The spatial distribution presented as a relief surface with amplitude proportional to spin density in arbitrary units (A) and as a contour line map (B). (The amplitude value of a contour line are presented in arbitrary units with step 0.015 from the maximum value 0.095 (that corresponds to the

position of a point in a figure), magnetic field gradient $\nabla_y B = 560$ *G/cm, the spatial resolution is equal to 300* μm*).*

The Table 1 represents structural parameters of samples together with diffusion coefficients as measured here experimentally. The values of D_e change about 3 times. The interpretation may be done under the assumption that surface does not influence significantly on the probe diffusion and apply the capillary model which considers the sample as a set of parallel capillaries with radiir. The model predicts for diffusion coefficient:

$$D_e = D_r \, \varepsilon/\xi \qquad (1)$$

with D_r being the diffusion coefficient in the pore of radius r, ε- the dimensionless porosity of sample, ξ- the tortuosity factor determined as ratio of length of capillary to the grain thickness. The in-capillary diffusion coefficient D_r may be estimated as $D_r = [1/D_m + 1/D_k]^{-1}$, with D_m being the molecular diffusion coefficient (in the unrestricted space) and D_k - the Knudsen diffusion coefficient (jumps between the points of collisions with walls of pore). As the spin probe II is supposed to be non-interacting with surface, we may assume $D_k >> D_m$ and $D_r \approx D_m$. Then we may use eq.(1) and experimental values of D_e to determine values of factor ξ which is important for characterization of catalyst support properties. The corresponding values are given in Table 1.

Table 1. Physical properties of catalyst support, obtained values of D_e *of spin probe II and* ξ*.*

Type of sample	Pore volume V_ε, cm^3/g	Specific surface S_{sp}, m^2/g	Pore radius r_p, A°	$D_e \cdot 10^6$, cm^2/s	Tortuosity factor ξ
1	0,42	10	4000, 200	(2,9±0,4)	1,1
2	0,35	200	<100	(0,9±0,07)	2,8

For the second (biomimetic) type of sample we have studied diffusion of II from nitrocellulose filter impregnated with concentrated solution of II to the stack of filters impregnated with pure solvent. The diffusion coefficients D_e obtained in this way are shown in Table 2 for different solvents.

Table 2. Viscosity and diffusion parameters for different solvents.

Solvent	Viscosity η, cPz	$D_e \cdot 10^7$, cm^2/s
isobuthyllaurate	5.7	8.0 ± 0.2
methylmeristate	5.5	6.6 ± 0.4
methyloleate	15.1	2.5 ± 0.1
squalan	41.3	1.1 ± 0.1

The D_e values are correlated to the kinematic viscosity of solvent in accordance with the simple Stock's equation. Therefore we may again relate the main effect of media to that of tortuosity and ascribe it as the homogenous diffusion along the larger route as compared to the external geometry of system.

Proton Transfer in Inorganic Acids and Acid Salts.

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Proton transfer is of great importance for the number of chemical and physical processes such as catalysis, sorption, energy transformation and transport etc... Besides it can play the role of elementary step for the wide range of catalytic processes and over chemical reactions. One of the most interesting questions in this area is the search of correlation between the proton transfer frequency, activation energy, proton conductivity level and structural factors. The correct solution of this problem should open the possibility of the direct search and synthesis of new substances possessing such properties. This paper deals with the effort of the proton transfer frequency and activation energy estimation for different hydrogen bonded systems as a function of hydrogen bond lengths. The proton conductivity is also discussed as one of the most descriptive exhibition of the proton transfer.

In the most cases the proton transport is the chain of protoncontaining groups rotation and proton jumps between them along H-bond. Both their frequencies depends on the number of factors. The most important are the hydrogen bond length and protonaccepting ability of atoms taken part in the proton transfer. Conductivity is determined by charge carriers concentration and their mobility. Charge carriers concentration can be calculated by equation:

$$C = C_0 \cdot \exp(-\Delta H/2RT) \qquad (1)$$

where C_0 is the concentration of donor-acceptor couples (in the most cases they are the part of H-bonds available to the proton transfer processes) and ΔH is the enthalpy of carrier formation reaction. Carriers concentration is maximal for the donor and acceptor with equal protonaccepting ability. At 298 K this concentration decreases by one order of magnitude when ΔH increases by 11 kJ/mol. It means that the best results can be achieved for the proton transfer in the chain of atoms with close protonaccepting ability. We shall limit ourselves by the consideration of these processes including the atoms with protonaccepting ability close to H_2O oxygen one because of easy carrier formation and transfer.

As it was mentioned above, each transfer act consists of two steps: rotation of protoncontaining group and proton jump. If they take place with the frequencies ν_r and ν_j, we can get for the proton transfer frequency:

$$\nu_t = \nu_r \nu_t / (\nu_r + \nu_j) \qquad (2)$$

Both frequencies ν_r and ν_j are submitted to the Arrhenius law:

$$\nu = \nu_o \cdot \exp(-E_a/RT) \qquad (3)$$

where ν_o is the oscillation frequency and E_a is the activation energy. The last one is the function of hydrogen bond lengths. Meaning this condition we can estimate activation energy of protoncontaining group rotation by the method described in [1]. For the proton jumps the Zundel's data [2] are the most reliable.

For the most part of H-bonds n_o in equation (4) for the proton jumps is equal to 10^{14} s^{-1}. This value decreases about two times only for very short H-bonds, when the possibility of rotation is negligible. For rotation process n_o value is about 10^{12} - 10^{13} s^{-1}. Thus, the calculated dependence of the proton transfer frequency and its activation energy on the H-bonds lengths (l_1, l_2, l_2) for the aquaoxonium ion with superfluous protonaccepting groups is shown on fig.1a. The activation energy minimum is about 16 kJ/mol.

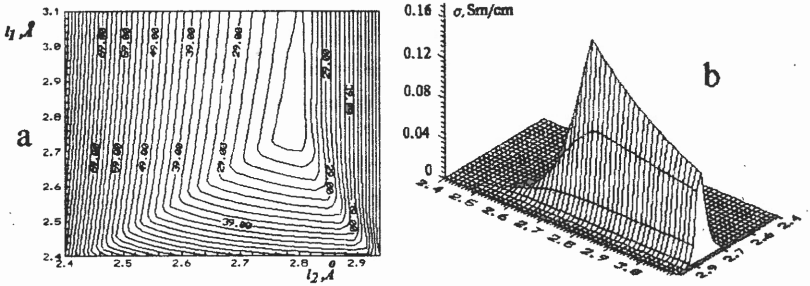

Fig.1. The dependence of activation energy (a) of proton transfer and H-conductivity (b) on the hydrogen bonds length (l_1, l_2 and l_2).

For the conductivity level estimation we can get the data which are showing on the fig.1b. At room temperature when l_1=l_2=2.77 A we have maximal s value about 0.16 Sm/cm. It's in the good agreement with experimental data for heteropolyacids. This maximum is very sharp, what is why it is rather difficult to find another substances with the similar structure and conductivity.

The research described in this publication was made possible in part by Grant N9Q000 from the International Science Foundation.

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Investigation of spin and molecular dynamics of biradicals by time-resolved magnetic spectroscopy

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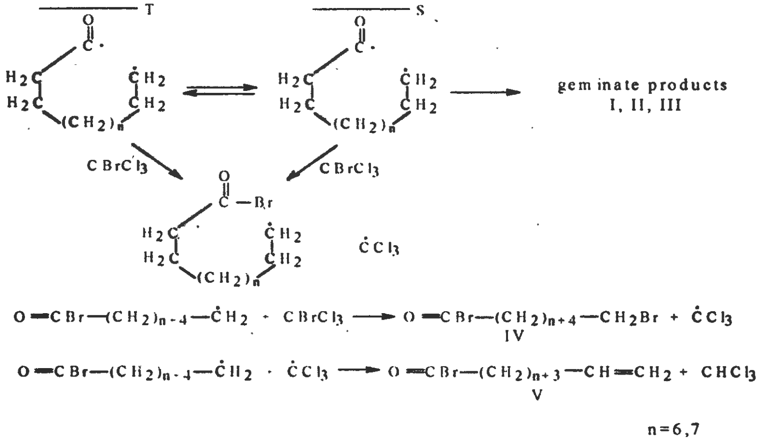
The influence of molecular and spin dynamics on geminate evolution of spin-correlated radical pairs (RP) is one of the principal problems in studying magnetic and spin effects in chemical reactions. This influence manifests itself most pronouncely in electronic and nuclear spin polarizations (CIDEP and CIDNP) whose values are strongly dependent on the mechanism of molecular dynamics [1]. Submicrosecond flash-CIDNP was used to study the dependences of the kinetics and amplitude of CIDNP, arising in biradicals on the photolysis of cyclic aliphatic ketones on the temperature and viscosity of medium.

It has been found out that for biradicals the geminate CIDNP increases with the diffusion coefficient of medium. The theoretical consideration of geminate recombination kinetics is based on the numerical solution of the stochastic Liouville equation for the Fourier transform of spin density matrix. The dependences of nuclear polarization on the lifetime of the triplet state of initial ketone, on electronic paramagnetic relaxation times, on scavenging rate, and on exchange interaction have been analyzed and compared with experimental data.

Biradical life-time was reduced by addition of the effective scavenger bromotrichloromethane. An important effect of the reaction with the scavenger on the formation of geminate CIDNP is the removal of biradicals, disregarding their nuclear and electron spin projections, from geminate recombination or disproportionation. The presence of $CBrCl_3$ molecules leads to the attachment of a Br atom to one of biradical ends followed by reactions according to the reaction scheme 1.

Investigation of the CIDNP field dependences of acyl-alkyl biradicals formed by Norrish type I reaction during the photolysis of cycloundecanone and cyclododecanone in the presence of the scavenger $CBrCl_3$ has been performed at low (up to 0.08 T) magnetic fields. In addition to the emissive polarization with the main maxima caused by the $S\text{-}T_-$

mechanism we observed an absorptive polarization with maxima at low fields (<0.01T) for α-CH_2 protons of initial ketones. A quantitative analysis of CIDNP amplitude dependences on scavenger concentration allows the estimation of the kinetics of biradical geminate recombination near the emissive maxima. It is demonstrated that biradical scavenging rate constant can be determined using the kinetic data for high magnetic fields.



$$O{=}CBr{-}(CH_2)_{n-4}{-}\dot{C}H_2 + CBrCl_3 \longrightarrow O{=}CBr{-}(CH_2)_{n+4}{-}CH_2Br + \dot{C}Cl_3$$

$$O{=}CBr{-}(CH_2)_{n-4}{-}\dot{C}H_2 + \dot{C}Cl_3 \longrightarrow O{=}CBr{-}(CH_2)_{n+3}{-}CH{=}CH_2 + CHCl_3$$

The scavenging rate constant of $CBrCl_3$ estimated by this method is $(2.3\pm0.4)\cdot10^{9}M^{-1}s^{-1}$ Two competitive channels of singlet-triplet conversion have been revealed and the qualitative picture of their contribution to the kinetics of the low-field CIDNP is presented

Acknowledgment. This work was supported by Russian Foundation for Fundamental Researches (grant 93-03-18593) and by International Science Foundation and Russian Goverment (grant JJD100).

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Editor: Professor Valentin N. Parmon

Подписано в печать 11.11.95 Формат 60x80/16
Печ.л. 11.25 Заказ № 267 Тираж 400

Отпечатано на Полиграфическом участке издательского отдела Института катализа СО РАН
630090, Новосибирск, пр. Академика Лаврентьева, 5