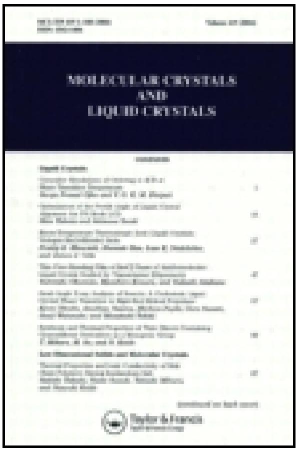

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NEW REACTIONS OF ELECTRONICALLY EXCITED RADICALS GRAFTED TO SiO_2 SURFACE AND IN SOLIDS

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Abstract Some new reactions of electronically excited radicals (vinyl, cyclohexadienyl, peroxy and thiylperoxy) were investigated both by the traditional method (in solid freezing matrices of different nature) and through the use of matrix isolation method on chemically activated silica surface (RSi).

INTRODUCTION

Reactions of excited radicals play important role in processes accompanging with simultaneous or consecutive formation of radicals and light action. In this connection it's very important to know the mechanism of their reactions including those which for the reason of high reactivity are not trapped in reactive matrices at temperatures about 77 K. It's important to note that the study of mechanisms of radical photochemical reactions in solids is complicated by the occurence of rapid intra- and quasicage processes, participation of environment molecules in the reactions. The investigation and the application of new methods, developing the matrix isolation method, and allowing in some cases both to discover the true mechanism of process and to reveal the environment influence for its individual stages, acquires special importance. In the present work we examined new reactions of electronically excited radicals and new data about the mechanism of familiar reactions.

PEROXY RADICALS

The mechanism of the peroxy radical transformations under UV irradiation for a long time is attracted the attention of investigators, because these species play an important role in various photooxidation processes. Among the pathways of phototransformations in peroxy radicals are presumed the following reactions[1]: photosubstitution, photodissociation of the C-O and O-O bonds in radicals. The traditional in this cases paths of the elucidation of elementary chemical act mechanisms (temperature depression for 4 K[2] or the use of the matrix isolation method[3]) revealed no single mechanism of the peroxy radicals phototransformation. These difficultes can be obtained by studying photolysis of radicals in the gas phase. So far, however, only a single experimental study is available[4] which concerns the photolysis of $\dot{H}O_2$ radicals in the gas phase and shows evidence for O-O rupture.

The possibility of using an activated silica surface for stabilization of radical centers was proposed earlier[5]. The surface paramagnetic defects involved in reactions with various gas-phase molecules allow one to obtain paramagnetic centers of the desired structure. This is essentially a kind of "matrix" isolation of highly reactive species, with the silica surface serving as an inert matrix. This method eliminates or at least considerably decreases the probability of intermolecular processes, thus allowing one to observe the low-molecular radicals and atoms formed in the course of the reaction studied. The acceptors for these radical products are silylenes =Si: present in high concentrations on the surface. The method for preparing the RSi samples are obtaining the surface centers of desired structure is similar to that described[6]. Table 1 presents the data on the composition of photolysis products of the same peroxy radicals.

The experimental data obtained for peroxy radicals of various nature show that O-O dissociation is a primary phototransformation step.

$$R\dot{O}_2 \Rightarrow R\dot{O} + O \qquad (1)$$

TABLE 1 Phototransformations of some peroxy radicals stabilized on the RSi surface at 77 K.

Radical	Paramagnetic products detected*	Proposed reactions
$\equiv SiO\dot{O}$	$\equiv Si\dot{O}$ (0,8±0,1)	$\equiv SiO\dot{O} \Rightarrow \equiv Si\dot{O} + O$
$\equiv SiCH{=}CHO\dot{O}$	$\equiv Si\dot{C}HCHO$ (0,7±0,1)	$\equiv SiCHCHO\dot{O} \Rightarrow \equiv SiCHCH\dot{O}$ $\equiv SiCHCH\dot{O} \Rightarrow \equiv Si\dot{C}HCHO$
$\equiv SiCH_2CH_2O\dot{O}$	$\equiv SiOCH_2\dot{C}H_2$ (0,8±0,1)	$\equiv SiCH_2CH_{2.}O\dot{O} \Rightarrow$ $\equiv SiCH_2CH_{.2}O \Rightarrow$ $\equiv SiOCH_2CH_2$

Note: * The values in the parenthesis indicate fractions of the paramagnetic products formed upon photolysis of the appropriate peroxy radicals.

Clearly the earlier experimentally observed[1,2] C-O dissociation is a result of the reverse "cage" reaction of the alkoxy radicals and oxygen atoms formed in reaction (1) (the reaction heat is about 250 kJ/mol, the C-O bond energy for methylperoxy radical is about 130 kJ/mol)

$$[R\dot{O} + O] \Rightarrow R\dot{O}_2^{*} \Rightarrow \dot{R} + O_2$$

CYCLOHEXADIENYL RADICALS

Unfortunately, the little available information on the effect of the photon energy on the quantum efficiency of radical reactions is restricted by data[1]. Up to the present time the reactivity of the radicals changes upon their excitation to higher doublet states was unclear. This is definitely of interest, since for the reactions of some arylmethyl radicals in the solid phase it has been thought that, chemical reactions can occur either from the lower or from the higher doublet states[7] depending on the nature of the radical. We chose to investigate the photochemical reactions of cyclohexadienyl radicals obtained upon radiolysis of polystyrene and solutions of benzene (0,5 M) in methanol at 77 K. In the case of this radicals[8], there is the possibility of excitation of the radicals to different vibritional sublevels of the lower excited doublet state (0-0 transition, 559 nm; ν_6, 510 nm), and also to the higher excited doublet state (316 nm). THe quantum yields presented in Table 2, showed that the significant increase in the quantum efficiency of reactions cyclohexadienyl radicals upon their excitation to the short-wavelength absorption band can be connected with occurence in the dissociation reaction from the upper excited doublet state. From the lower excited doublet state, the substitution reaction can occur with efficiency mainly determined by processes of dissipation the excess energy of the absorbed photon in the matrix.

TABLE 2 Effect of the photon energy on the quantum yield of reaction of cyclohexadienyl radicals at 77 K

Matrix	Methanol	Polystyrene
Φ_{559}	0.030±0.006	0.070±0.015
Φ_{510}	0.070±0.015	0.14 ± 0.03
Φ_{310}	0.3	0.21

A similar behavior was observed for photoexcitation within the D_0-D_2 transition band of this radicals "grafted" to the RSi surface. However, in this case the rupture of C-Si bond is a more efficient reaction. Stability of this radicals on RSi with respect to the D_0-D_1 excitation is an indirect evidence in favor on the suggestion, according to which of the reactions involve interaction of the excited radicals with matrix molecules, i.e., via a channel ruled out for the radicals "grafted" on silica.

VINYL RADICALS

In the literature there are no experimental data on the photochemistry of vinyl radical. The authors[9] suggested the dissociation reaction of excited vinyl radicals. High chemical activity and low thermal stability of vinyl radical is the main reason for the severity of the investigation of their photochemistry with the help of classic variant of matrix isolation method.

In this connection we studied the photochemistry of vinyl type radicals grafted to RSi surface. The extent of the reaction of vinyl types radical formation

$$\equiv\dot{\mathrm{S}}\mathrm{i} + \mathrm{C_2H_2} \Rightarrow \equiv\mathrm{SiCH{=}\dot{C}H}$$

and conversion was monitored by ESR spectroscopy.

It was shown that under light action with $\lambda \leq 420$ nm vinyl type radicals are dissociated with hydrogen atoms formation, accepted by silylenes and detected in this form:

$$\equiv\mathrm{SiCH{=}\dot{C}H} \Rightarrow \equiv\mathrm{SiC{\equiv}CH} + \mathrm{H}$$

$$=\mathrm{Si}: + \mathrm{H} \Rightarrow =\mathrm{SiH}$$

THIYLPEROXY RADICALS

In studying the oxidation reactions of thiyl radicals of cysteine by oxygen in 5 M LiCl glasses at temperature above 135 K (the vitrification temperature for 5 M LiCl ranges from 142 to 152 K), the ESR spectrum of thiylperoxy radicals with principal values of $g=2{,}037$, $2{,}009$ and $2{,}003$ was recorded.

Accumulation and consumption of thiylperoxy radicals is accompanied with the appearence and disappearence of weak absorption with a peak at about 19000 $\mathrm{cm^{-1}}$ in the optical spectra ($\varepsilon \simeq 400$ $\mathrm{M^{-1}cm^{-1}}$). In the marked optical spectrum, photolysis (λ=546 nm) result an increase of absortion at wavelengths shorter than 400 nm, and the appearance of a new signal in the ESR spectrum (an asymmetric single line with g=2,006 , possesed to sulfonyl radicals $R\dot{S}O_2$). The illumination of samples with λ>850 nm yielded the same results. The absence of any significant changes in red and near-infrared regions of absorption spectra (up to 1400 nm) allowed us to state that for thiylperoxy radicals $\varepsilon \leq 100$ $M^{-1}cm^{-1}$ in this region.

Both in thiyl and alkyl peroxy radicals a considerable positive shift in one of the g values is caused by the spin-orbital mixing of the ground and lower excited states of $H\dot{O}_2$ radicals with an energy difference of about 7000 cm^{-1}. Then it does not seem surprising that $RSO\dot{O}$ radicals may feature an electronic transition in the IR region. However, this is the first example known to us of radical transformation under IR excitation.

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