Long-wave light absorption and photochemical decomposition of peroxide radicals

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Photochemical decomposition of alkylperoxide radicals in glassy matrices at 77 K was experimentally studied. Irradiation with light up to 405 nm leads to the photodecomposition of peroxide radicals. The quantum yield of the reaction was estimated to be $\sim 10^{-2}$. A light-induced angular dependence of the ESR spectra of peroxide radicals resulting from photoselection was detected. The photoselection found proves that the photodecomposition is induced by the absorption of light in the inherent absorption band of $RO_2^{\cdot}$.

Key words: peroxide radical, photoreaction, photoselection, optical absorption spectrum.

Organic peroxide radicals play an important role in oxidative and photooxidative destruction of polymers, in atmospheric chemistry, and in biological systems.[1] The mechanism of photodecomposition of peroxyl radicals during absorption of short-wave light has been discussed in the literature.[1—3] It was shown that *para*-methoxybenzoylperoxyl decomposes in liquid hexane when irradiated with light having a wavelength of 308 nm.[3] There are data that peroxide radicals in polymeric matrices decompose under the action of light with wavelengths up to 400—450 nm,[4,5] and that peroxide macro radicals in polystyrene are quantitatively converted into alkyl radicals under the action of light with a wavelength of 365 nm.[6] However, it is known that the absorption band of organic peroxide radicals is located at substantially shorter wavelengths (λ_{max} = 230—290 nm, the extinction coefficient is 500—4000 L (mol cm)$^{-1}$).[1,7] The purpose of the present work is to verify the possibility of photochemical transformations of peroxide radicals under the action of long-wave light, including visible light, and to find out whether the transformations of peroxide radicals in polymers are due to the absorption of $RO_2^{\cdot}$ itself or are secondary processes in photochemical reactions of other species.

We studied the photochemical decomposition of alkylperoxide radicals in low-molecular glassy matrices. The photochemical generation of radicals in these systems makes it possible to obtain peroxide radicals with no substantial admixtures of ions and other products that are produced by γ-radiolysis and hamper the interpretation of the results.

Experimental

Methylcyclohexane (MCH), 3-methylpentane (3MP), and isopropanol (IP) frozen at 77 K were used as glassy matrices. Peroxide radicals were obtained in these matrices by increasing the temperature to oxidize matrix radicals with oxygen dissolved in the starting solvent.

The matrix radicals were generated by various photochemical methods: by photolysis of frozen solutions of Cl_2 with 365 nm light (the starting optical density at the maximum of the absorption band of chlorine is ~1) carried out until chlorine is exhausted (MCH and 3MP); by photolysis of frozen solutions of CH_3I with light at 254 nm (MCH and 3MP); by photolysis of frozen solutions of *tert*-butyl hydroperoxide (MCH, 3MP, and IP) or hydrogen peroxide (IP) with light at 254 nm.

Photolysis was carried out using an electrodeless low-pressure mercury lamp (254 nm) or a high-pressure mercury lamp (500 W), a quartz optical system for making a parallel beam, and a set of standard glass filters to separate light with the necessary wavelength. Polarized irradiation was carried out using a Glan prism. The intensity of the light was determined by ferrioxalate actinometry.

The ESR spectra were recorded on a Varian E-3 spectrometer; the optical absorption spectra were obtained on a Specord M-40 spectrophotometer at 77 K.

Results and Discussion

When a glass-like sample containing matrix radicals was heated to a temperature 10—20° lower than the glass transition temperature, the oxidation of matrix radicals to peroxide radicals, $RO_2^{\cdot}$, was detected by ESR in all of the cases studied (Fig. 1). Simultaneously, a new absorption band with λ_{max} = 270—290 nm and a half-width of ~40 nm appeared in the optical absorption spectra (Fig. 2). In conformity with the literature data, this band corresponds to the inherent absorption of the $RO_2^{\cdot}$ radicals.[1,7]

By double integration of the ESR spectrum and by comparing the resulting value with that of the double integral obtained for a preliminarily weighed single crystal of $CuCl_2 \cdot 2H_2O$, we determined the quantity of

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peroxyl radicals and calculated the extinction coefficient. Its magnitude (3300±900 L (mol cm)$^{-1}$) is in agreement with the reported values.

Irradiation of the specimens with light at 254, 313, 365, and 405 nm results in the consumption of peroxide radicals and formation of alkyl radicals (Fig. 1, spectrum *3*). The variation of the optical density during this process is not parallel to the variations in the ESR spectrum. This is probably due to the fact that the oxygen-containing products of the decomposition of peroxide radicals exhibit optical absorption in the same wavelength region. The optical absorption in this region of the spectrum is partially retained when the sample is defrosted/frozen after photolysis.

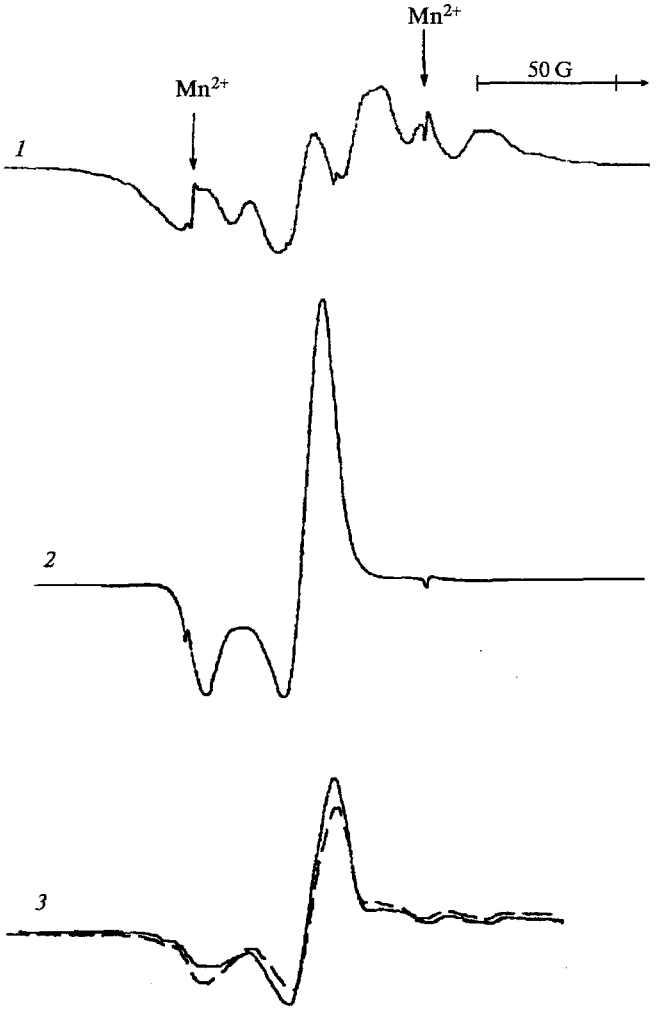

Fig. 1. ESR spectra of methylcyclohexyl radicals generated during the photolysis of chlorine at 77 K (*1*), after heating the sample to 98 K (*2*), for the sample heated to 98 K and then photolyzed at 77 K by polarized light at 365 nm (*3*); the solid and dashed lines are the spectra recorded at parallel and perpendicular mutual orientations of the direction of the magnetic field and electric vector of the light, respectively.

When irradiation is carried out with light at 405 nm, the rate of decomposition of $RO_2^{\cdot}$ is the lowest. In the case of isopropylperoxyl (in an isopropanol matrix),[8] the photochemical decomposition occurs rather slowly even when the specimen is irradiated with light of 365 nm wavelength. Irradiation with a parallel beam of nonpolarized light results in the ESR spectrum of the unchanged peroxyl radicals that reveal a light-induced angular dependence of the intensities of the components of the spectrum with $g_{||}$ and $g_{\perp}$ (see Fig. 1). The induced angular dependence increases when the irradiation is carried out with a parallel beam of polarized light. This effect is accounted for by photoselection, *i.e.*, by the fact that, during the photochemical reaction, those radicals are selected whose transition dipole moments are parallel to the electric component of the light wave. The fact that photoselection is manifested during

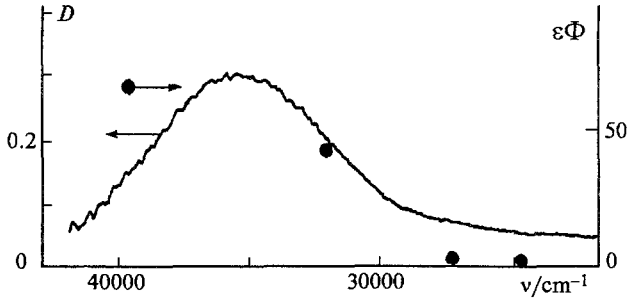

Fig. 2. Absorption spectrum of $RO_2^{\cdot}$ radical in a methylcyclohexane matrix (curve) and εΦ values for photolysis by light of various wavelengths (points).

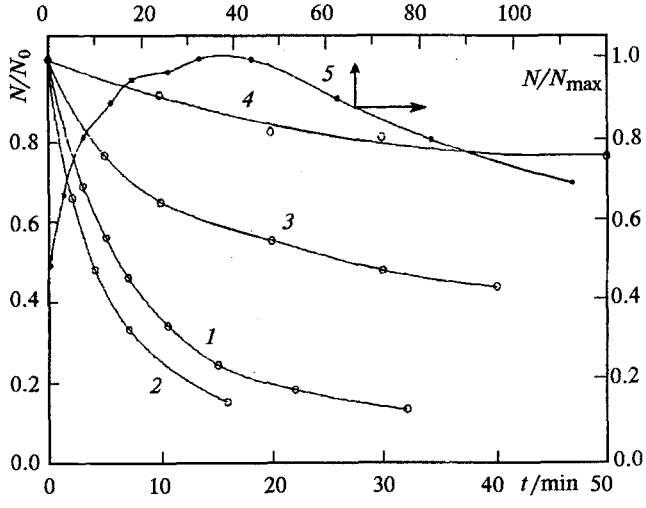

Fig. 3. Kinetic curves of the variation of the quantity of peroxide radicals in MCH when photolysis is carried out with nonpolarized light: λ = 254 nm (*1*), 313 nm (*2*), 365 nm (*3*), and 405 nm (*4*); *1*—*4*, generation by photolysis of chlorine, *5*, generation by photolysis of CH_3I.

decomposition of peroxide radicals proves that this photochemical reaction is stimulated by the light absorbed by the radicals themselves. Special experiments showed that irradiation of peroxide macro radicals in a polystyrene matrix with polarized light also results in a light-induced angular dependence of the ESR spectrum.

The initial sections of the kinetic curves of the photochemical decomposition are described by the equation:

$$\frac{1}{N_0}\cdot\frac{dN}{dt} = -2.3I_0\frac{l}{N_A V}\varepsilon\Phi,$$

where N_0 and N are the initial and current numbers of peroxide radicals in the sample, N_A is Avogadro's number, V is the volume of the sample, l is the length of the optical path, I_0 is the intensity of the incident light, ε is the extinction coefficient, and Φ is the quantum yield of the reaction.

The values of the products of the extinction coefficients and the quantum yields ($\varepsilon\Phi$) determined using this equation are the following:

λ_{max} /nm	254	313	365	405
$\varepsilon\Phi$ /L (mol cm)$^{-1}$	68	43	1.3	0.43

These values indicate that the radicals directly absorb light according to their absorption spectra (see Fig. 2). The quantum yields Φ of the photodecomposition of peroxide radicals determined from these values are 0.04 and 0.02 at 254 and 313 nm, respectively.

Thus, we showed that alkylperoxide radicals possessed a rather extended long-wave tail of the optical absorption band with $\lambda_{max} \sim 280$ nm (up to 400 nm). The absorption of light in this region results in photochemical decomposition of peroxide radicals.

Generation with CH_3I makes it possible to obtain substantial concentrations of matrix radicals. However, the quantity of the peroxide radicals formed during heating is 10—100 times lower than the quantity of the starting matrix radicals. When the specimen is irradiated with light, the number of peroxide radicals initially increases (by a factor of 3—5 in 3MP) and then they are consumed to give the radicals of the matrix (see Fig. 3). This behavior can be explained by assuming that the $RO_2^{\cdot}$ radicals produced during heating form complexes with iodine atoms or iodine-containing products of the primary photolysis. Due to the great spin-orbital interaction, these complexes cannot be detected by ESR. However, they can decompose under the action of light, and, owing to the photolysis, the quantity of the peroxide radicals initially increases.

Generation with chlorine and tert-butyl hydroperoxide affords radicals of the matrix and then peroxide radicals in pairs. Therefore, the ESR spectra of peroxide radicals are somewhat broadened.

Heating in isopropanol results in incomplete oxidation of the matrix radicals to give $RO_2^{\cdot}$. Quantitative measurements in this system are hampered, since the signals of the matrix radicals and the signals of peroxide radicals overlap.

In 3-methylpentane, oxidation of the matrix radicals to yield peroxide radicals occurs slowly (over a period of 24 h) even at the temperature of liquid nitrogen. The specimens saturated with oxygen at 1 atm already contain a mixture of alkyl and peroxide radicals during the generation of the radicals. Complete oxidation is observed when the material is kept for 5 min at liquid air temperature. No complete photochemical transformation of peroxide radicals into alkyl radicals occurs in these specimens.

In methylcyclohexane, the alkyl radicals obtained are a mixture of secondary and tertiary methylcyclohexyl radicals (6 and 7 ESR lines, respectively). When the generation is carried out with chlorine, the proportion of secondary radicals of the matrix is greater than in the case of generation by *tert*-butyl hydroperoxide. The forms of the lines corresponding to the peroxide radicals obtained in these two cases are also somewhat different.

Excitation with low-energy light quanta in the long-wave region of absorption bands results in efficient photochemical decomposition. The quantum yield of photodecomposition is $\sim 10^{-2}$. Photodecomposition of peroxide radicals is a more sensitive indicator of the absorption of light than spectrophotometry. A light-induced angular dependence of the ESR spectra of peroxide radicals that arises according to a photoselection mechanism during irradiation with both polarized and nonpolarized light was detected.

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