STUDY OF THE INTERACTION OF MOLECULAR OXYGEN WITH A STABLE FREE RADICAL IN SOLUTION BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

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Abstract

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STUDY OF THE INTERACTION OF MOLECULAR OXYGEN WITH A STABLE FREE RADICAL IN SOLUTION BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

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Despite the wide dissemination of the modern radical-chain theory of the oxidation of organic compounds (1), there are still few direct experimental data characterizing the nature of the primary products of the addition of molecular oxygen. Recently, comparatively stable peroxide radicals formed in the solid phase upon the interaction of oxygen with radicals arising under the action of ionizing radiation in Teflon (2) and in polyethylene (3), and also upon interaction with the stable radical triparanitrophenylmethyl (4), have been detected and studied by the e.p.r. method. In contrast to solid polymers, in most frozen low-molecular compounds the stability of the radicals formed upon irradiation is low at temperatures above 77°K, and their interaction with oxygen has been little studied.

Of great interest in this respect are processes occurring in the liquid phase during radiolysis; however, because of the very short lifetime of the radicals arising in this case, direct study of their transformations is associated with great difficulties. It therefore seemed to us expedient first to investigate, by the e.p.r. method, the interaction of oxygen with a stable radical dissolved in an organic liquid. As the object we chose α, α'-diphenyl-β-picrylhydrazyl (DPPH), whose e.p.r. spectrum has been studied rather well. It is known that at concentrations below 10^{-3} mole/liter, solutions of DPPH exhibit a five-line spectrum corresponding to the interaction of the unpaired electron with two nuclei of the central nitrogen atoms (5). Recently, splitting of the lines of the five-line spectrum of DPPH, caused by the protons of the phenyl rings in the ortho and para positions (6), was detected experimentally, as had been predicted by theory (7).

This superhyperfine structure appears, however, only with extremely thorough removal of traces of oxygen and with high resolving power of the apparatus. In our investigation we used an EPR-2 IKhF spectrometer (8). In benzene solutions of DPPH* we obtained five-line spectra without additional superhyperfine structure. The number of paramagnetic centers in the sample was determined from the area under the integral curve of resonance absorption, calibrated with the aid of a carefully evacuated benzene solution of DPPH of known concentration. For each experiment, a portion of 0.08 cm^3 of solution was taken. The interaction with oxygen was studied from changes in the e.p.r. spectra.

* The preparation, recrystallized from benzene and prepared by the method of Arbuzov and Valitova ([9]), was kindly provided to us by the authors of the synthesis.

Figure 1 presents spectra obtained at the same instrument sensitivity in the initial evacuated $8 \cdot 10^{-4}$ M solution (a), in the same sample after admission, at atmospheric pressure, of air (b) and oxygen (c), and, finally, after repeated evacuation following admission of O_2 (d). As can be seen, the asymmetric spectrum characteristic of peroxy radicals does not appear. Contact with oxygen causes broadening of the lines up to disappearance of the hyperfine structure and a decrease in intensity; however, when oxygen is removed immediately after its admission, the initial, completely resolved spectrum is restored. Oxygen thus causes not only line broadening, but also a reversible decrease in the total number of paramagnetic centers, as is evident from the data given below, calculated on the basis of the spectra shown in Fig. 1.

	Atmosphere	Vacuum	O_2, 150 mm Hg	O_2, 760 mm Hg	Vacuum
Number of p.m.c.		$4 \cdot 10^{16}$	$3.4 \cdot 10^{16}$	$3.0 \cdot 10^{16}$	$3.8 \cdot 10^{16}$
Spectrum width		50 Oe	60 Oe	72 Oe	50 Oe

The sensitivity of the determination at this spectrum width was $3–4 \cdot 10^{14}$ p.m.c. in the sample.

To elucidate the effect of the duration of interaction with O_2, the following experiments were carried out: after preliminary evacuation and sealing-off, 1-2 control samples were prepared; into 10-15 identical portions of a DFPG solution of 0.08 cm^3, containing $4 \cdot 10^{16}$ p.m.c. each, O_2 was simultaneously admitted at atmospheric pressure. The ampoules were then sealed off with a ratio of the volumes of the gas and liquid phases ~ 8 and stored at ordinary temperature.

Fig. 1. EPR spectra of benzene solutions of DFPG ($8 \cdot 10^{-4}$ M). Signal of the vacuum sample (a), after admission of air (b), oxygen (c) at atmospheric pressure, and after repeated evacuation of oxygen (d).

At certain time intervals EPR spectra were recorded, first in the presence of oxygen, and then immediately after its removal by evacuation. Figure 2 shows the content of free radicals in oxygen and vacuum samples as a function of

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the time of contact of DFPG with oxygen. Both the amount of radicals in the presence of oxygen and the amount regenerated upon evacuation gradually decrease; at the same time the intensity of the coloration characteristic of DFPG decreases. After 90 days the radicals are no longer detected in the presence of O_2, although they still reappear upon its removal. In solutions that from the very beginning contained no O_2, the number of radicals over the same time changes practically not at all.

The rate of disappearance of DFPG depends on the total amount of O_2 in the closed system, as illustrated by Fig. 3, in which the curves correspond to different ratios of O_2 in the gas and liquid phases, from $V_{\text{gas}}/V_{\text{liq}} \sim 8$ to $V_{\text{gas}}/V_{\text{liq}} \sim 100$.

The described changes in the resonance spectrum of DFPG in the presence of O_2 can be interpreted as the superposition of two different effects: 1) che-

is a physical interaction due to the paramagnetic properties of the O_2 molecule, which leads to line broadening but does not affect the number of unpaired electrons in the system; and 2) an interaction that may be regarded as chemical, leading to the disappearance of DPPH radicals as a result of the formation of a nonradical peroxide-type compound, which decomposes reversibly when oxygen is removed and, in its presence, is converted into the final oxidation products of DPPH. As this peroxide, which is in equilibrium with dissolved O_2 and with DPPH radicals, disappears, the latter must be consumed, which is indeed observed experimentally.

Comparison of the curves in Fig. 3 shows that the rate of consumption of the radicals, which at first does not depend on the amount of O_2 in the system, remains constant until the radicals have completely disappeared only when there is a large excess of O_2. The smaller its content in the system, the sooner a sharp slowing of the process sets in. This permits the conclusion that the formation of the primary nonradical peroxide compound is a rapid reaction limited by the supply of O_2 from the gas phase; its subsequent transformations are complex in character and require more detailed study. It is noteworthy that the observed consumption of O_2 is substantially greater than the consumption of DPPH. This may be explained by the involvement of the solvent in oxidative processes, as indicated by the appearance among the reaction products of phenol, in an amount exceeding the number of phenyl groups of DPPH, as well as by the influence of the nature of the solvent on the rate of oxidation. Under the same

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Fig. 3. Change in the rate of disappearance of DPPH as a function of the total O_2 content in the sample. Ratio of the gas phase to the liquid phase ~ 8 (1), ~ 100 (2), ~ 50 (3). Solid curve for vacuum samples, dashed curve for oxygen-containing samples.

Figure 3: Fig. 3. Change in the rate of disappearance of DPPH as a function of the total O_2 content in the sample. Ratio of the gas phase to the liquid phase ~ 8 (1), ~ 100 (2), ~ 50 (3). Solid curve for vacuum samples, dashed curve for oxygen-containing samples.

conditions in *n*-heptane, DPPH radicals disappear in the presence of O_2 within several hours.

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The reversible broadening of the signal and the decrease in intensity in the presence of O_2 observed in the case of crystalline DPPH (10) can be explained by an analogous type of interaction with oxygen, in contrast to the interpretation of the authors, who assume that no actual decrease in the number of free radicals takes place.

The formation of a reversible molecular peroxide through the interaction of free radicals with oxygen in solution, as far as we know, has not previously been described in the literature; it represents a very early stage of oxidation reactions, which it has been possible to detect thanks to the use of the EPR method. It may be assumed that the existence of such a stage is fairly widespread in oxidative processes. The question of the mechanism of formation of this peroxide requires further consideration,

as well as the question of the analogy and differences between the formation of reversible peroxides in the liquid phase and on the surface of solids (11).

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