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FREE-RADICAL REACTIONS DURING THE INTERACTION OF OXYGEN WITH IRRADIATED POTASSIUM PALMITATE

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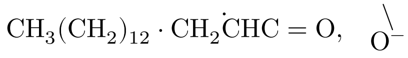
As was established earlier in a study of the EPR spectra of diphenylpicrylhydrazyl in benzene solution (^{1}), in the presence of oxygen the radicals partially disappear, but reappear when it is removed; moreover, the regeneration is the more complete the shorter the contact time. In these experiments no formation of peroxide radicals was observed. An analogous reversible oxygen effect was found for potassium palmitate (PP) and was subjected to more detailed study, the results of which are reported in the present paper. Data characterizing the radiation yield of radicals, their structure, transformations, and decay are given in papers (^{2},^{3}). The EPR spectrum of potassium palmitate irradiated in vacuum at 77° K corresponds to the simultaneous formation of several radicals, which gradually disappear or are converted into other radicals as the temperature is raised. The spectrum stable at room temperature is characterized by a doublet of triplets and corresponds to the radical



$$CH_3(CH_2)_{12}\cdot CH_2\dot{C}HC=O,\quad O^-$$

with which the present investigation was carried out. In the work, finely dispersed polycrystalline chemically pure PP was used without additional purification, m.p. 138° C. For irradiation a γ-source of Co^{60} was used; for recording EPR spectra, an RE-1301 radiospectrometer.

(Figure: Fig. 1. Repeated sorption of oxygen on irradiated PP as a function of the equilibrium pressure during primary sorption: a–1—$4\cdot10^{-2}$ mm Hg; 2—$1\cdot10^{-1}$; 3—3.1; b—5; v—10; g—21; d—100 mm Hg.)

Fig. 1. Repeated sorption of oxygen on irradiated PP as a function of the equilibrium pressure during primary sorption: a–1—$4\cdot10^{-2}$ mm Hg; 2—$1\cdot10^{-1}$; 3—3.1; b–5; v–10; g–21; d–100 mm Hg.

PP was irradiated in vacuum at 77° K and a dose rate of $5\cdot10^{16}$ eV/g • sec up to an absorbed dose of $5.4\cdot10^{20}$ eV/g in a device consisting of an all-glass system with one ampoule containing 3 g of PP as adsorbent and 15-20 thin test tubes made of special glass that gave no signals upon irradiation (^{4}), with 20-30 mg portions for recording EPR spectra. The irradiated system was kept in vacuum at 298° K until the structure and concentration of the radicals became constant, and was then sealed to the adsorption apparatus. This made it possible to admit oxygen simultaneously to all samples and to seal off, at each stage of the adsorption measurements, specimens for investigation of the EPR spectra. All measurements were carried out at 298° K in the range of P_{O2} from 10^{-6} to 400 mm Hg. To determine the degree of reversibility of sorption, isotherms of sorption were recorded again on PP pumped down to 10^{-6} mm Hg after equilibrium had been reached at various pressures. The data presented in Fig. 1 show that interaction with O_2 is completely reversible at pressures up to several mm Hg.

Investigation of the EPR spectra showed that the changes in the signals upon admitting O_2 are reduced mainly to a decrease in the intensity of the resonance absorption, without broadening and without the appearance of new lines (Fig. 2, spectra 1, 2). If, in the pressure region corresponding to reversible sorption, O_2 is removed 2-3 min after its admission, an increase in the signal intensity is observed without a change in its character, which obviously corresponds to an increase in the radical concentration (cf. spectra 2 and 3 in Fig. 2). At these same pressures, a 30-60-min contact with O_2 leads to the irreversible disappearance of the radicals, as does a 2-3-min contact at $P_{\mathrm{O2}} > 1$-2 mm.

(Figure: Fig. 2)

Fig. 2. EPR spectra of irradiated KP at 390° K: 1 —vacuum sample, 2 —2 min after admission of oxygen, 3 —after pumping for 10 min at 10^{-3} mm Hg.

Figure 3 presents, as a function of the O_2 pressure, the equilibrium concentration of radicals (curve I) and the equilibrium sorption of O_2 (curve II). As can be seen, in the region $P_{\mathrm{O2}} < 10^{-2}$ mm Hg, the sorption, which is disappearingly small, while the radical concentration remains constant; then there is an increase in sorption and, simultaneously, a fall in the radical concentration, which disappear completely upon attainment of the limiting sorption at $P_{\mathrm{O2}} \sim 2 \cdot 10^2$ mm Hg. The same figure shows individual points illustrating the reversibility of the disappearance of radicals.

(Figure: Fig. 3)

Fig. 3. Concentration of radicals (I) and sorption of oxygen (II) as a function of O_2 pressure: *a* —radical concentration during brief contact with O_2, *b* —the same after removal of oxygen.

As can be seen, after pumping out the oxygen the concentration of $\dot{\mathrm{R}}$ returns almost to its initial value, but in the presence of O_2 the points lie above curve I, because at the pressures considered here sorption equilibrium is not yet reached in 2-3 min.

Comparison of curves I and II in Fig. 3 shows that there is a quantitative correspondence between oxygen absorption and the loss of radicals at all O_2 pressures. To the limiting value $9.8 \cdot 10^{18}$ molecules O_2/g

corresponds to the complete disappearance of radicals, whose initial concentration in the sample is $6.9 \cdot 10^{18}$ $\dot{R}$/g. Within the accuracy of measuring the

Fig. 4. Dependence of radical concentration on time. A $-P_{O_2} = 180$ mm Hg; B $-P_{O_2} = 0.045$. 1 $-\sum$ rad.; 2 $-[\mathrm{RO}_2^\bullet]$, 3 $-\sum$ rad. $-[\mathrm{RO}_2^\bullet] = [R]$

Figure 1: Fig. 4. Dependence of radical concentration on time. A $-P_{O_2} = 180$ mm Hg; B $-P_{O_2} = 0.045$. 1 $-\sum$ rad.; 2 $-[\mathrm{RO}_2^\bullet]$, 3 $-\sum$ rad. $-[\mathrm{RO}_2^\bullet] = [R]$

absolute concentration of unpaired electrons by the EPR method, these two values may be regarded as practically coincident, which leads to the conclusion that the sorption of O_2 by irradiated PK is determined by the interaction of O_2 with free radicals. Indeed, special experiments showed that on unirradiated PK the adsorption of oxygen at 300°K is vanishingly small. Determination of the specific surface area by the BET method from krypton adsorption at 77°K (^{5}) gave values of 0.5 m^2/g for unirradiated and 0.7 m^2/g for irradiated PK. The increase in surface area is so insignificant that by itself it cannot be the cause of the oxygen sorption by irradiated PK observed at room temperature. The quantitative interaction of O_2 with radicals

$$\dot{R}\mathrm{CHC}\overset{\mathrm{O}}{\underset{\mathrm{O}^-}{\|}}$$

arising uniformly throughout the volume during irradiation shows that the layered structure of PK provides sufficiently high mobility of O_2 molecules in the crystals.

Fig. 4. Dependence of radical concentration on time.
$A -P_{O_2} = 180$ mm Hg; $B -P_{O_2} = 0.045$.
1 $-\sum$ rad.; 2 $-[\mathrm{RO}_2^\bullet]$, 3 $-\sum$ rad. $-[\mathrm{RO}_2^\bullet] = [R]$.

As in benzene solutions of DPPH, in all the experiments described the peroxide radicals were not detected in the EPR spectra. Consequently, either they are not formed, or at 300°K they are converted into final stable products too rapidly for detection. To clarify this question, the kinetics of transformation at 193°K was investigated for the radicals

$$\dot{R}\mathrm{CHC}\overset{\mathrm{O}}{\underset{\mathrm{O}^-}{\|}}$$

in samples of irradiated PK after admission of oxygen at various pressures in the range from 0.045 to 180 mm Hg. It turned out that in all cases peroxide radicals appear, but the kinetics of their formation and the balance between the disappearing radicals $\dot{R}$ and the appearing $\dot{R}O_2$ depend sharply on the oxygen pressure. Figure 4 presents the dependence of radical concentration on time for two limiting values of P_{O_2}. As can be seen, at $P_{O_2} = 180$ mm Hg all initial $\dot{R}$ are converted into $\mathrm{RO}_2^\bullet$ in a time $\tau \sim 30$ min. This permits the conclusion that the absence of $\mathrm{RO}_2^\bullet$ lines in the EPR spectra at $\tau \sim 300$°K and high O_2

pressures is determined only by the kinetics of their subsequent transformations. Simultaneously with the formation of $RO_2^\bullet$ upon admission of O_2, an increase in the total concentration of radicals is observed.

Similar effects have been noted previously for other objects (7). One possible cause of this increase is the transfer of electrons from radicals, for which they had served as traps, to O_2 molecules.

In contrast to the admission of O_2 at high pressure, the formation of $R\dot{O}_2$ at $P_{O_2} = 0.045$ mm Hg proceeds extremely slowly, while the total radical content drops sharply in the first 30 min. On prolonged holding, however, it returns to the initial value and even somewhat exceeds it; at the same time, a substantial increase in the concentration of $R\dot{O}_2$ is observed. The results obtained can be interpreted on the basis of the following reaction scheme:

$$R^- + O_2 \to \dot{R} + O_2^-, \tag{1}$$

$$\dot{R} + O_2 \to R\dot{O}_2, \tag{2}$$

$$2R + O_2 \to (2R, O_2), \tag{3}$$

$$(2R, O_2) \to \dot{R} + R\dot{O}_2. \tag{4}$$

In the early stages of the interaction, the consumption of O_2 is determined by reactions (1), (2), and (3), and the decrease of radicals by reaction (3), which masks their increase through reaction (1). In the final state, after completion of reaction (4), the consumption of O_2 is determined by reactions (1) and (2), and the total radical concentration by the initial value and the increase through (1).

Table 1

Time τ after admission of O_2	Σ	$R\dot{O}_2$	$\dot{R}$	Consumption of $\dot{R}$ by reactions (2)	Consumption of $\dot{R}$ by reactions (3)	Consumption of O_2 by reactions (1)	Consumption of O_2 by reactions (2)	Consumption of O_2 by reactions (3)	Consumption of O_2, total
						$n \cdot 10^{-16}$			
0	6.6	0	6.6	–	–	–	–	–	–
1.5 min	6.2	0	6.2	–	0.4	–	–	0.2	–

Time τ after admission of O_2	Σ	$R\dot{O}_2$	$\dot{R}$	Consumption of $\dot{R}$ by reactions (2)	Consumption of $\dot{R}$ by reactions (3)	Consumption of O_2 by reactions (1)	Consumption of O_2 by reactions (2)	Consumption of O_2 by reactions (3)	Consumption of O_2, total
6.5 min	3.7	0	3.7	–	2.8	–	–	1.5	–
36.5 min	2.0	0.3	1.7	0.3	4.6	–	0.3	2.3	2.6
94 h	6.9	2.8	4.1	2.8	–	0.3	2.8	–	3.1

The data given in Table 1, characterizing the quantity and composition of radicals in the sample (Fig. 4B), make it possible to estimate the oxygen and radical balance. Experimental conditions: P_{O_2} 0.045 mm, $t = 193°K$, sample weight 0.011 g, n—admission of O_2—$3.3 \cdot 10^{16}$ molecules, Σ rad. in the sample before admission of O_2—$6.6 \cdot 10^{16}$.

As can be seen, in the final state of the system ($\tau = 94$ h), oxygen is used almost completely for the formation of $R\dot{O}_2$ and the increase of $\dot{R}$ by reactions (1) and (2). In the intermediate state, the decrease of $\dot{R}$ radicals must correspond to the consumption of oxygen by reaction (3). Calculation shows that for $\tau = 36.5$ min, reactions (2) and (3) require $\sim 85\%$ of all the available oxygen. The experimental data obtained, according to which the initial radicals disappear without the formation of peroxide radicals at low oxygen pressures, confirm the earlier assumptions concerning the formation of labile nonradical products of the interaction of free radicals with oxygen at early stages of oxidative processes (1, 6). On prolonged holding, these labile products of composition $(2\dot{R} + O_2)$ undergo further transformations, the kinetics and direction of which depend on the conditions.

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Note: Figure translations are in progress. See original paper for figures.