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On the Possibility of Applying the Method of Electron Paramagnetic Resonance for Recording Active Centers in Liquid-Phase Oxidation Reactions of Hydrocarbons

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In the present work the possibility is considered of applying the method of electron paramagnetic resonance (e.p.r.) to detect free radicals and to measure their stationary concentration in hydrocarbon oxidation reactions. We are interested in the possibility of detecting radicals under ordinary conditions in the course of the chemical process itself. Such a task is of considerable interest for chemical kinetics, since from measurements of the stationary concentration of free radicals one can directly obtain the rate constants of the elementary reactions entering into the overall process.

It should be noted that recording radicals under stationary conditions encounters considerable difficulties, connected mainly with the low concentration of radicals. For this reason, in particular, it has so far not been possible to detect active radicals in the course of liquid-phase oxidation of hydrocarbons.

In the chain reaction of hydrocarbon oxidation, active centers of two types participate: hydrocarbon radicals $\dot{R}$ and peroxy radicals $R\dot{O}_2$. At a sufficiently high oxygen pressure (for most hydrocarbons this pressure is above 100–200 mm Hg), the concentration of peroxy radicals is much greater than the concentration of hydrocarbon radicals ([1–3]), and the oxidation process proceeds according to the scheme: chain initiation—the formation of $R\dot{O}_2$, rate w_i; chain propagation

$$RH + R\dot{O}_2 \xrightarrow[k_2]{O_2} ROOH + R\dot{O}_2;$$

chain termination

$$R\dot{O}_2 + R\dot{O}_2 \xrightarrow{k_6} \text{inactive products},$$

where RH is the hydrocarbon and $ROOH$ is the hydroperoxide. The concentration of peroxy radicals is determined by the rates of chain initiation and

termination:

$$\frac{d(R\dot{O}_2)}{dt} = w_i - k_6(R\dot{O}_2)^2.$$

In the stationary regime

$$\frac{d(R\dot{O}_2)}{dt} = 0 \quad \text{and} \quad (R\dot{O}_2) = \sqrt{\frac{w_i}{k_6}}. \tag{1}$$

Thus, at a given initiation rate, the stationary concentration of peroxy radicals is the higher, the smaller the value of the rate constant of the recombination reaction of peroxy radicals.

For a number of substances this constant is known. Its values are given in Table 1, which also gives the values of the stationary concentration of peroxy radicals at a certain average value of the initiation rate, which was used in our experiments. The values of the activation energy E_6 of the recombination reaction of peroxy radicals are also given there.

Table 1

Substance oxidized	Temp., °C	$k_6 \cdot 10^6$, l/mol · sec	Number of peroxy radicals per 1 cm^3 at $w_i = 10^{-4}$ $\frac{\text{mol}}{\text{l·sec}}$	E_6, kcal/mol	Literature
Cyclohexene	15	0.95	$6.2 \cdot 10^{15}$	<2	(4)
Methylcyclohexene	15	0.5	$8.5 \cdot 10^{15}$	<2	(4)
1-Octene	25	0.3	$1.1 \cdot 10^{16}$	<2	(5)
Dihydromyrcene	15	0.65	$7.5 \cdot 10^{15}$	1	(4)
Ethyl linoleate	15	0.5	$8.5 \cdot 10^{15}$	<2	(4)
Dipropenyl	25	0.3	$1.1 \cdot 10^{16}$		(5)
Tetralin	15	20	$1.35 \cdot 10^{15}$	~1	(4)
Ethylbenzene	70–90	22	$1.3 \cdot 10^{15}$	<1	(7)
Cumene	50	0.028	$3.6 \cdot 10^{16}$	<1	(1)
n-Decanal	15	7.5	$2.2 \cdot 10^{15}$	<1	(4)
Benzaldehyde	15	200	$4.3 \cdot 10^{14}$	~1	(6)

In view of the small magnitude of E_6, the steady-state concentration of peroxy radicals at a given initiation rate changes only slightly with temperature.

It is seen from Table 1 that, for all the olefinic hydrocarbons investigated, the recombination constants are approximately the same. A threefold difference in the constants leads to a difference in the steady-state concentrations of only 1.7 times. For aromatic hydrocarbons—tetralin and ethylbenzene, in which the peroxy group is located at a secondary carbon atom—the recombination constant is 1–2 orders of magnitude higher. Of the substances investigated, the cumyl peroxy radicals recombine with the lowest rate constant.

The ordinarily attainable sensitivity of modern EPR spectrometers is approximately 10^{13} particles of diphenylpicrylhydrazyl, while the width of the absorption line of diphenylpicrylhydrazyl is 1.5–2 oersteds. The effective width of the absorption line of peroxy radicals in the solid phase is 15–30 oersteds. ([8]) If it is assumed that the effective width of the absorption line of peroxy radicals in solution has approximately the same value (15–30 oersteds), then, in order to detect peroxy radicals, their concentration must be no less than $1 \cdot 10^{15}$—$5 \cdot 10^{15}$ radicals/cm^3. Thus, one may expect that peroxy radicals can be detected in the oxidation reactions of various olefins and cumene. In the present work, cumene was chosen as the object of study, since in its oxidation the highest radical concentration may be expected.

The experiments were carried out on an EPR spectrometer IKH-2 with high-frequency modulation of the magnetic field ([9]). The instrument recorded the first derivative of the EPR line of the peroxy radical simultaneously with the signal from a standard sample (charcoal). An ampoule containing the hydrocarbon being oxidized was heated to the required temperature by a stream of hot air directly in the resonator. The temperature was measured with a thermocouple immersed in the ampoule containing the hydrocarbon. The temperature reading was taken during the recording of the spectrum. During the experiment, oxygen was continuously bubbled through the hydrocarbon.

The oxidation was carried out with various initiators: azobisisobutyronitrile, dicyclohexyl percarbonate, cobalt stearate, and cobalt acetate. As is seen from Fig. 1, identical spectra were obtained in experiments with different initiators. The observed EPR spectrum is a broad, nearly symmetrical singlet ($\Delta H \simeq 18 \pm 2$ oersteds) with a g-factor equal to 2.015 ± 0.001. In the magnitude of the shift of the g-factor and in the effective line width, the observed spectrum is close to the EPR spectrum of peroxy radicals in the solid phase ([8]). Naturally, the shapes of the signals in the solid and liquid phases are different, since in the liquid phase the anisotropy of the g-factor is averaged as a result of the thermal motion of the particles. In control experiments, in which isopropylbenzene was replaced by ethylbenzene, EPR spectra were not observed with any of the

of the initiators used. In addition, after the oxygen was turned off and the ampoule was briefly purged with nitrogen, the EPR absorption disappeared. When oxygen was turned on again, the EPR spectrum reappeared in less than 10–15 sec.

The greatest number of experiments was carried out with azobisisobutyroni-

Fig. 1. EPR spectra of cumyl peroxide radicals

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Fig. 2. Comparison of calculated and measured concentrations of peroxide radicals

Figure 2: Fig. 2. Comparison of calculated and measured concentrations of peroxide radicals

trile, since the rate of initiation produced by its decomposition is well known [10]. From the known values of w_i and k_6, the values of the steady-state concentrations of cumyl peroxide radicals were calculated at different

Fig. 1. EPR spectra of cumyl peroxide radicals:
a—in the reaction catalyzed by cobalt stearate ($6.4 \cdot 10^{-8}$ mol/liter), $t = 105°$; *b* —the same spectrum, recorded together with the ethanol spectrum (angle). At equal signal amplitudes, the number of peroxide radicals in the sample is $1.8 \cdot 10^{16}$; *c*—in the reaction initiated by azobisisobutyronitrile (0.22 mol/liter), $t = 88°$; *d*—in the reaction initiated by dicyclohexyl percarbonate (0.126 mol/liter), $t = 77°$.

rates of initiation. Experiments to measure the steady-state concentrations of cumyl peroxide radicals were carried out in the temperature range 70–90° and at azobisisobutyronitrile concentrations of 0.05–0.55 mol/liter.

At the specified high rates of initiation, the rate of oxygen absorption is high. Therefore, to obtain EPR spectra of peroxide radicals it is necessary to ensure a sufficiently high rate of oxygen feed into the hydrocarbon. In this case the EPR absorption increases up to a certain limit as the rate of oxygen dissolution increases.

Fig. 2. Comparison of calculated and measured concentrations of peroxide radicals

The largest values of the peroxide-radical concentration $(\dot{R}O_2)_{meas}$ observed in the experiments are compared in Fig. 2 with the calculated values $(\dot{R}O_2)_{calc}$ at different magnitudes of the initiation rate. The absolute values of the concentrations $(\dot{R}O_2)_{meas}$ lie within the range $2 \cdot 10^{15}$–$4 \cdot 10^{16}$ radicals/cm^3. In Fig. 2 the dashed line marks the ratio $(\dot{R}O_2)_{calc}/(\dot{R}O_2)_{meas} = 1$. As can be seen from the figure, the points lie close to the dashed straight line. This means that the measured steady-state concentration of RO_2-radicals is close to the calculated value. Direct measurements of the radical concentration give a value of k_6 that practically coincides with that previously obtained by the intermittent-illumination method [1].

In experiments in which oxidation was initiated by dicyclohexyl percarbonate, radical concentrations from $4 \cdot 10^{15}$ to $2 \cdot 10^{16}$ radicals/cm^3 were observed. The rate constant for the decomposition of dicyclohexyl percarbonate into radicals is

unknown. If it is assumed that the rate of decomposition is equal to the rate of decomposition into radicals [11], and the rate of initiation is thereby calculated, then it turns out—

It turns out that the measured concentrations of RO_2 radicals are 2–4 times smaller than the calculated ones.

In experiments in which oxidation catalyzed by cobalt acetate and stearate was carried out, the rate of initiation is unknown. Therefore the measured and calculated radical concentrations cannot be compared.

In conclusion, we would like to emphasize that measurement of the stationary concentration of radicals during the reaction opens up new prospects in studies of oxidation processes. It may be expected that further development of work in this direction will also make it possible to advance investigations of the kinetics of chemical processes of other types.

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REFERENCES

1. H. W. Melville, S. Richards, J. Chem. Soc., 1954, 944.
2. J. L. Bolland, Quart. Rev. London, Chem. Soc., 3, 1 (1949).
3. L. Bateman, Quart. Rev. London, Chem. Soc., 8, 147 (1954).
4. H. R. Cooper, H. W. Melville, J. Chem. Soc., 1951, 1993.
5. L. Bateman, G. Gee, Trans. Farad. Soc., 47, 155 (1951).
6. T. A. Ingles, H. W. Melville, Proc. Roy. Soc., A218, 163 (1953).
7. V. F. Tsepalov, V. Ya. Shlyapintokh, DAN, 124, 883 (1959).
8. Yu. N. Molin, Yu. D. Tsvetkov, V. V. Voevodskii, Vysokomolekul. soed., 1, 1805 (1959).
9. A. G. Semenov, N. N. Bubnov, PTE, 1, 92 (1959).
10. F. M. Lewis, M. S. Matheson, J. Am. Chem. Soc., 71, 747 (1949).
11. G. A. Razuvaev, L. M. Terman, ZhOKh, 30, 2387 (1960).

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