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Abstract

Full Text

Chemistry

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Mechanism of Formation of Dialkyl Peroxides during the Radiation Oxidation of Hydrocarbons

(Presented by Academician A. N. Frumkin, July 18, 1964)

The results obtained in the first studies on the low-temperature radiation oxidation of hydrocarbons ($^{1-3}$) led to the conclusion that characteristic of hydroperoxides ROOR, peroxides ROOR, and other oxygen-containing compounds is their simultaneous and independent formation by competing reactions involving peroxide radicals arising from the primary products of radiolysis. It was assumed, in particular, that dialkyl peroxides are formed through the interaction of $R\dot{O}_2$ radicals with one another or with $\dot{R}$ radicals. In ($^{1-3}$), hydroperoxides and dialkyl peroxides were distinguished by the kinetics of their interaction with iodine ions.

An attempt to refine this insufficiently reliable separation within the framework of iodometry did not give satisfactory results (^{4}). Recently we returned to these studies, combining the polarographic method with the iodometric one, and obtained, using isooctane and *n*-heptane as examples, data that make it possible to give a new interpretation of the mechanism of radiation formation of dialkyl peroxides.

Fig. 1. Formation of hydroperoxide during the radiation oxidation of isooctane:
1 –sum of peroxide compounds, $1.6 \cdot 10^{-2}\ M\ O_2$;
2 –ROOH, $1.6 \cdot 10^{-2}\ M\ O_2$;
3 –sum of peroxide compounds, $3.2 \cdot 10^{-3}\ M\ O_2$;
4 –ROOH, $3.2 \cdot 10^{-3}\ M\ O_2$;
5 –sum of peroxide compounds, $0.8 \cdot 10^{-3}\ M\ O_2$;

Fig. 2

Figure 2: Fig. 2

6 –ROOH, $0.8 \cdot 10^{-3}$ M O_2.

As was shown in a specially designed study (5), at a mercury dropping electrode in benzene-methanol and aqueous-alcohol solutions all hydroperoxides are reduced, but peroxides with polyatomic alkyl groups–expected in the radiation oxidation of alkanes with long chains–are not reduced. Such dialkyl peroxides can be determined in mixtures only by difference, using independently obtained data on the content of hydroperoxides and the sum of peroxide compounds. Carefully purified and dried isooctane (2,2,4-trimethylpentane) and *n*-heptane were subjected to x-ray (70 kV · max) and gamma (Co^{60}) irradiation at a dose rate of $2 \cdot 10^{16}$ eV/ml · sec, a temperature of 0°C, and continuous passage of mixtures of $O_2 + N_2$ of various composition. In the irradiated liquid, hydroperoxides were determined polarographically in a benzene-methanol solution against a background of 0.3 M LiCl, and the sum of peroxide compounds iodometrically, by heating the sample for 3 hr with KI in a mixture of glacial acetic and hydrochloric acids in an atmosphere of N_2 purified of O_2, followed by potentiometric titration with 0.01 N $\mathrm{Na_2S_2O_3}$ (6). Alcohols were determined spectrophotometrically as alkylnitrites (7), and carbonyl compounds colorimetrically as 2,4-dinitrophenylhydrazones (8).

Figure 1 presents the results of iodometric and polarographic analysis of isooctane irradiated at oxygen concentrations of $1.6 \cdot 10^{-2}$, $3.2 \cdot 10^{-3}$, and $0.8 \cdot 10^{-3}$ M. As can be seen, the results of both determinations

coincide in all three cases. It follows from this that, in the initial dose region under consideration, the peroxide compounds are represented only by hydroperoxides, as is confirmed by their quantitative extraction with an aqueous LiOH solution.

On the polarogram there is only one wave with $E_{1/2} = -1.06 \pm 0.02$ (N.C.E.) in benzene-methanol solution and $E_{1/2} = -0.18 \pm 0.02$ in 10% aqueous-alcoholic solution after extraction. Under the same conditions, for specially synthesized tertiary isooctyl hydroperoxide (2,2,4-trimethylpentyl-2), the corresponding values obtained were 1.05 ± 0.02 and -0.16 ± 0.02.

This agreement makes it possible to consider that, in the radiation oxidation of isooctane, it is specifically tertiary isooctyl hydroperoxide that is formed. Indeed, for all hydroperoxides with a smaller number of C atoms that could have been formed in the decomposition of C_8H_{18}, the corresponding $E_{1/2}$ values are by $\sim$ 0.1–0.15 V more negative (9). The yield $G(\mathrm{ROOH}) = 1.07 \pm 0.05$ does not depend on the concentration of O_2 within the range $0.8 \cdot 10^{-3}$–$1.6 \cdot 10^{-2}$ M.

Fig. 2. Formation of hydroperoxide, dialkyl peroxide, and alcohol during radiation oxidation of isooctane; $O_2 = 0.8 \cdot 10^{-3}$ M: **1** –sum of peroxide compounds;

2 —hydroperoxide; **3** —alcohol; **4** —dialkyl peroxide

With further irradiation the linear increase in [ROOH] is disrupted. At the same time, the polarographic values begin to lag behind the iodometric ones, and the formation of alcohol is accelerated. Fig. 2 presents data obtained with isooctane containing, during irradiation, $0.8 \cdot 10^{-3}$ mole/liter O_2. Formation of ROOR begins at a dose of 3–$4 \cdot 10^{19}$ eV/ml, at which [ROOH] reaches 0.6–$0.7 \cdot 10^{-3}$ M, i.e., becomes of the same order as $[O_2]$. In the case $[O_2] = 3.2 \cdot 10^{-3}$ M, the appearance of ROOR required a dose of 1.2–$1.3 \cdot 10^{20}$ eV/ml, at which $[\mathrm{ROOH}] \approx 2.2 \cdot 10^{-3}$ M. The character of the dependence of the concentration of radiation-oxidation products on dose leads to the conclusion that, after a certain concentration is reached, the hydroperoxide begins to be converted, under the action of the radiolysis products of isooctane, into dialkyl peroxide and alcohol. In the presence of such a process, competing with the formation of ROOH from the same radiolysis products and O_2, irradiation of isooctane containing, in addition to O_2, hydroperoxide introduced beforehand should lead, depending on the ratio of their concentrations, to an increase, constancy, or decrease in the ROOH concentration and to different yields of ROOR. The data given in Table 1, obtained at a constant concentration $[O_2] = 0.8 \cdot 10^{-3}$ M and increasing initial concentrations of isooctyl hydroperoxide, confirm this assumption.

Table 1

$[\mathrm{ROOH}]_0$, $M \cdot 10^3$	$G(\mathrm{ROOH})^*$, molecules/100 eV	$G(\mathrm{ROOR})$, molecules/100 eV	$G(\mathrm{ROH})$, molecules/100 eV	$G\left(R\overset{\overset{O}{\|}}{C}R'\right)$, molecules/100 eV
0	1.07	0	1.15	1.08
0.41	0.66	0	—	—
1.10	0.21	0.30	1.53	—
2.05	−0.09	0.45	—	—
2.75	−0.24	0.54	—	—
6.12	−0.55	0.96	1.96	1.32

* The negative sign of $G(\mathrm{ROOH})$ corresponds to a decrease in [ROOH] during irradiation.

Analogous results were obtained with *n*-heptane.

The pathway considered for the formation of dialkyl peroxides is further confirmed by the radiolysis of solutions of isooctyl hydroperoxides in isooctane and of *n*-heptyl hydroperoxides in *n*-heptane in the absence of O_2 (saturation with N_2). Irradiation leads to decomposition of the hydroperoxide and to the appearance of dialkyl peroxide and alcohol. Carbonyl compounds are not formed in this case. Figure 3 gives the radiation yield of its decomposition as a function of

Fig. 3

Figure 3: Fig. 3

the ROOH concentration. The course of this dependence is characteristic of the scavenging by ROOH, as acceptor, of radicals arising during radiolysis of the solvent. The process can be represented by the following sequence of reactions:

Fig. 3. Dependence of the radiation yield of the decomposition reaction of isooctyl hydroperoxide on its concentration

$$\mathrm{RH} \rightsquigarrow \dot{\mathrm{R}}, \tag{A}$$

$$\dot{\mathrm{R}} + \mathrm{ROOH} \rightarrow \dot{\mathrm{R}}\mathrm{O} + \mathrm{ROH}, \tag{4}$$

$$2\dot{\mathrm{R}}\mathrm{O} \rightarrow \mathrm{ROOR}. \tag{5}$$

According to this scheme, the disappearance of 1 molec. ROOH should correspond to the formation of 1 molec. ROH and 0.5 molec. ROOR. As is seen from the data of Table 2, the experimental data satisfactorily correspond to the proposed mechanism.

Table 2

	[ROOH], $M \cdot 10^3$	G(−ROOH), molec/100 eV	G(ROOR), molec/100 eV	G(ROH), molec/100 eV
Isooctane	0.18	0.77	–	–
Isooctane	1.35	1.71	0.83	1.50
Isooctane	2.58	1.94	1.10	1.83
Isooctane	5.60	2.20	1.25	2.14
n-Heptane	0.50	1.26	0.67	–
n-Heptane	1.64	1.65	0.80	1.45
n-Heptane	5.20	2.50	1.32	2.57

In the presence of oxygen, the radicals $\dot{\mathrm{R}}$ first of all form peroxy radicals

$$\dot{\mathrm{R}} + \mathrm{O}_2 \rightarrow \dot{\mathrm{R}}\mathrm{O}_2, \tag{1}$$

which then are converted into hydroperoxides, carbonyl compounds, and alcohols, the corresponding reactions being

$$\dot{\mathrm{R}}\mathrm{O}_2 + \mathrm{RH} \rightarrow \mathrm{ROOH} + \dot{\mathrm{R}}, \tag{2}$$

$$\dot{R}O_2 \rightarrow \text{carbonyl compounds (isomerization and decomposition)} \quad (3)$$

do not show a temperature dependence in the range considered ([10,11]), despite the fact that they require a certain activation energy ([12]). This circumstance leads to the conclusion that those radicals $\dot{R}O_2$ which are capable of carrying out these reactions possess a sufficient excess of energy transmitted to them by the primary radicals $\dot{R}$ ([13,3]). When ROOH reaches a concentration comparable with that of O_2, competition begins to appear between reactions (4) and (1) for the radicals $\dot{R}$. The necessity of considering radicals differing in their energy state complicates the appli-

the use of the usual scheme of competing reactions for the kinetic treatment of experimental data in order to obtain the corresponding reaction constants.

The data obtained in the present work and earlier[14], characterizing the structure of hydroperoxides, carbonyl compounds, and alcohols formed during the liquid-phase radiation oxidation of hydrocarbons, show that the major part of these products retains the carbon skeleton of the original hydrocarbon, i.e., that it is chiefly the radical arising upon abstraction of one hydrogen atom that is used. Evidently, only this radical has a sufficiently long lifetime to participate in reactions (1)–(3), while fragment radicals recombine or disproportionate in the cage before interacting with oxygen.

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