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Yu. A. ALEKSANDROVA, HUANG YU-LI, A. N. PRAVEDNIKOV

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Abstract

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Yu. A. ALEKSANDROVA, HUANG YU-LI, A. N. PRAVEDNIKOV
and Academician S. S. MEDVEDEV

REACTIONS OF OXYGEN-CONTAINING RADICALS OF THE TYPE RO •

The oxidation of hydrocarbons, in particular of carbon-chain polymers, proceeds through the stage of formation of hydroperoxide compounds, which decompose under the reaction conditions with the formation of radicals of the type RO • ; accordingly, the study of reactions involving these radicals is of great interest. The study of such reactions has been carried out mainly on model systems, in which RO • radicals were formed as a result of the decomposition of dialkyl peroxides. It was found that, in the decomposition of di-tert-butyl peroxide in hydrocarbon solvents, the main reaction products are acetone, tert-butyl alcohol, and methane; for their formation the following scheme was proposed:

$$(\mathrm{CH_3})_3\mathrm{CO}\cdot \xrightarrow{k_1} (\mathrm{CH_3})_2\mathrm{C}=\mathrm{O} + \cdot\mathrm{CH_3}; \quad \text{(I)}$$

$$(\mathrm{CH_3})_3\mathrm{CO}\cdot + \mathrm{R'H} \xrightarrow{k_2} (\mathrm{CH_3})_3\mathrm{COH} + \mathrm{R'}\cdot; \quad \text{(II)}$$

$$\cdot\mathrm{CH_3} + \mathrm{R'H} \xrightarrow{k_3} \mathrm{CH_4} + \mathrm{R'}\cdot\,. \quad \text{(III)}$$

According to this scheme, the ratio between the concentrations of acetone a and tert-butyl alcohol b is

$$\frac{a}{b} = \frac{k_1}{k_2}\frac{1}{[\mathrm{R'H}]}$$

(where [R′H] is the concentration of the solvent). Brook (^{1,2}), using this equation and data on the formation of acetone and tert-butyl alcohol at 135°, calculated the values of

$$\frac{k_1}{k_2}\frac{1}{[\mathrm{R'H}]}$$

Fig. 1. Dependence of the molar ratio of acetone to tert-butyl alcohol on the initial peroxide concentration. 1—120°, 2—135°, 3—150°.

Figure 1: Fig. 1. Dependence of the molar ratio of acetone to tert-butyl alcohol on the initial peroxide concentration. 1—120°, 2—135°, 3—150°.

for the reaction of tert-butoxy radicals in various solvents. The values he found lie within the range from 0.05 to 0.5, which indicates that reaction (I) proceeds at an appreciable rate. It may be supposed that, in the case of polymers, this reaction will lead to cleavage of C—C bonds in the polymer molecules and, consequently, to a decrease in molecular weight. The activation energy $E_1 - E_2 \simeq$ 8 kcal/mol, found in the same work, indicates that with increasing temperature the role of this reaction will increase.

An investigation of the decomposition products of di-tert-butyl peroxide at 195° showed (^{3}) that at this temperature the yield of acetone is $\sim$ 12 times greater than the yield of tert-butyl alcohol, which indicates an activation energy higher than that found by Brook.

If one proceeds from the scheme given above, the data obtained indicate that at these temperatures almost all tert-butoxy radicals decompose with cleavage of the C—C bond, which is in contradiction with the literature data on the thermooxidative destruction of carbon-chain polymers (^{4}).

The data presented above give grounds for believing that the formation of acetone in the decomposition of di-tert-butyl peroxide occurs not only as a re-

as a result of reaction (I), but also as a result of some other reaction whose rate depends strongly on temperature. Such a reaction may be the interaction of the radicals RO· with one another. At low temperatures, when the concentration of RO· radicals is low, the rate of this reaction is relatively small, as indicated by the data obtained by Bruk. However, when the temperature is raised (or when the peroxide concentration is significantly increased), the concentration of RO· radicals in the system and, consequently, the rate of this reaction will increase greatly, which in turn will lead to higher yields of acetone as compared with the yield of tert-butyl alcohol.

Fig. 1. Dependence of the molar ratio of acetone to tert-butyl alcohol on the initial peroxide concentration. 1—120°, 2—135°, 3—150°.

In order to test this assumption, we investigated the decomposition of di-tert-butyl peroxide in isopropylbenzene solution at 120—150° over the concentration range 4—16 wt.%. The concentrations of the reaction products were determined by means of infrared spectra: acetone, by absorption in the region 1714 cm^{-1}; tert-butyl alcohol, in the region 3000 cm^{-1}; peroxide, in the region 878 cm^{-1} (and also iodometrically); methane was determined volumetrically.

The data presented in Fig. 1 show that the value of the ratio a/b increases as the peroxide concentration increases. This indicates that the order of the reactions of formation of these compounds with respect to the peroxide concentration is not equal to unity.

In addition, the yield of methane, as is seen from Table 1, is lower than the yield of acetone, and this difference is the greater, the higher the initial peroxide concentration C_{initial}.

Table 1

Amount of acetone and methane formed during decomposition of the peroxide at 135°

C_{initial}, mol/l	a, mol/l	m, mol/l	m/a
0.268	0.101	0.0846	0.838
0.356	0.130	0.1035	0.796
0.818	0.352	0.264	0.75

The formation of acetone in the interaction of two RO· radicals may be represented by the following scheme:

$$(\mathrm{CH_3})_3\mathrm{CO}\cdot + (\mathrm{CH_3})_3\mathrm{CO}\cdot \xrightarrow{k_4} (\mathrm{CH_3})_2\mathrm{C} = \mathrm{O} + \mathrm{CH_3} - \mathrm{O} - \mathrm{C}(\mathrm{CH_3})_3. \qquad \text{(IV)}$$

In this case the total rate of acetone formation is

$$\frac{da}{dt} = k_1[\mathrm{RO}\cdot] + k_4[\mathrm{RO}\cdot]^2. \qquad (1)$$

The rate of peroxide decomposition is

$$\frac{dC}{dt} = -k_{cDC}. \qquad (2)$$

Dividing (1) by (2), we obtain

$$\frac{da}{dC} = -\frac{k_1}{k_c}\frac{[\mathrm{RO}\cdot]}{C} + \frac{k_4}{k_c}\frac{[\mathrm{RO}\cdot]^2}{C}. \qquad (3)$$

The concentration of RO· radicals in the system will be determined by the stationarity condition

$$k_{cC} = k_1[\mathrm{RO}\cdot] + k_4[\mathrm{RO}\cdot]^2 + k_5[\mathrm{RO}\cdot][\mathrm{R}'\cdot]. \qquad (4)$$

Approximately, the concentration of RO· may be represented by the equation

Fig. 2. Determination of α. 1 –120°, 2 –135°, 3 –150°

Figure 2: Fig. 2. Determination of α. 1 –120°, 2 –135°, 3 –150°

$$[\mathrm{RO}\cdot] = k_{aC}^{\alpha}, \tag{5}$$

where the value α is determined by the ratio of the rate constants for chain termination of first and second order with respect to the concentration of RO· radicals and the concentration of RO· radicals. Substituting (5) into (3), we obtain:

$$\frac{da}{dC} = -\frac{k_1 k_a}{k_c} C^{\alpha-1} - \frac{k_4 k_a^2}{k_c} C^{2\alpha-1}. \tag{6}$$

We integrate this equation within the limits from $a = 0,\ C = C_{\text{init}}$ to $a = a,\ C = C_{\text{final}}$:

$$a = \frac{k_1 k_a}{k_c \alpha} \left(C_{\text{init}}^{\alpha} - C_{\text{final}}^{\alpha}\right) + \frac{k_4 k_a^2}{k_c \cdot 2\alpha} \left(C_{\text{init}}^{2\alpha} - C_{\text{final}}^{2\alpha}\right). \tag{7}$$

The main quantity of reaction products is formed with a comparatively small change in the concentration of radicals in the system. Therefore, as an approximation, the value α may be taken as constant throughout the reaction, and it may be determined from data on methane formation during peroxide decomposition:

$$\frac{dM}{dt} = k_1[\mathrm{RO}\cdot]. \tag{8}$$

Dividing (8) by (2) and taking (5) into account, we obtain

$$\frac{dM}{dC} = -\frac{k_1 k_a}{k_c} C^{\alpha-1}. \tag{9}$$

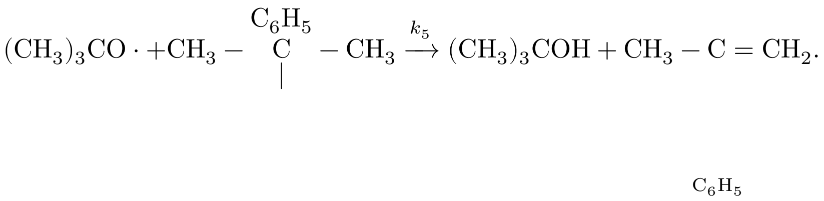
Integrating this equation within the limits from $M = 0,\ C = C_{\text{init}}$ to $M = M,\ C = 0$ and taking the logarithm of the resulting expression, we obtain

$$\lg M = \lg \frac{k_1 k_a}{k_c \alpha} + \alpha \lg C_{\text{init}}. \tag{10}$$

Fig. 2. Determination of α. 1 –120°, 2 –135°, 3 –150°

It is seen from Fig. 2 that the experimental points lie satisfactorily on the straight lines described by this equation. The slopes of these straight lines correspond to the following values of α: at 120°, $\alpha = 0.94$; at 135°, $\alpha = 0.86$; at 150°, $\alpha = 0.81$. As was to be expected, the role of the second-order termination reaction increases with increasing temperature.

In principle, alcohol may also be formed by a second-order reaction with respect to the concentration of RO$\cdot$ and R$'\cdot$ radicals.



$$(CH_3)_3CO\cdot + CH_3 - \overset{C_6H_5}{\underset{|}{C}} - CH_3 \xrightarrow{k_5} (CH_3)_3COH + CH_3 - \underset{C_6H_5}{C} = CH_2. \quad (V)$$

In this case

$$\frac{db}{dt} = k_2[\mathrm{RO}\cdot][\mathrm{R'H}] + k_5[\mathrm{RO}\cdot][\mathrm{R'}\cdot]. \qquad (11)$$

Taking into account that

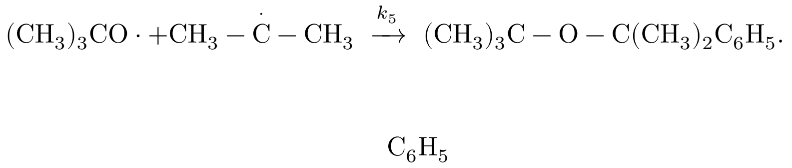
$$[\mathrm{R'}] = (n - [\mathrm{RO}\cdot]) = kC^{1/2} - k_a C^{\alpha},$$

where n is the total concentration of free radicals, by an analogous route we obtain:

$$\frac{b}{M} = \frac{k_2}{k_1}[\mathrm{R'H}] + \frac{k_5 k_a}{k_1(\alpha + 1/2)} \frac{C_{\text{init}}^{\alpha+1/2} - C_{\text{final}}^{\alpha+1/2}}{C_{\text{init}}^{\alpha} - C_{\text{final}}^{\alpha}} - \frac{k_5 k_a}{2k_1}\left(C_{\text{init}}^{\alpha} + C_{\text{final}}^{\alpha}\right). \qquad (12)$$

However, plotting the experimental data in the coordinates b/M–C gives a straight line parallel to the abscissa axis. This indicates that the alcohol is formed only by a first-order reaction. Interaction of radicals,

RO$\cdot$ and R$'\cdot$ apparently leads not to the formation of an alcohol, but to the formation of an ether:



$$(CH_3)_3CO\cdot + CH_3 - \underset{C_6H_5}{\dot{C}} - CH_3 \xrightarrow{k_5} (CH_3)_3C - O - C(CH_3)_2C_6H_5. \quad (VI)$$

Thus, the equation for b may be written in the form

$$b = \frac{k_2 k_a}{k'_c \alpha} \, [\mathrm{R'H}] \, (C^{\alpha}_{\text{init}} - C^{\alpha}_{\text{final}}). \tag{13}$$

Dividing (7) by (13), we obtain

$$\frac{a}{b} = \frac{k_1}{k_2} \frac{1}{[\mathrm{R'H}]} + \frac{k_4 k_\alpha}{2k_2 [\mathrm{R'H}]} \, (C^{\alpha}_{\text{init}} + C^{\alpha}_{\text{final}}). \tag{14}$$

Fig. 3. Determination of the ratio of the constants k_1/k_2:
1—at 120°, 2—at 135°, 3—at 150°

Fig. 4. Determination of activation energies.
1—k_1/k; 2—$\frac{k_4 k_\alpha}{2k_2}$

Plotting the experimental data in the coordinates $\frac{a}{b}[\mathrm{R'H}]$—$(C^{\alpha}_{\text{init}} + C^{\alpha}_{\text{final}})$ gives straight lines, whose slope is $k_4 k_\alpha / 2k_2$, and whose intercept on the ordinate axis is k_1/k_2 (Fig. 3).

The activation energy $E_1 - E_2$ is equal to $\sim$ 7 kcal/mole, while the activation energy of the processes characterized by the expression $\frac{k_4 k_\alpha}{2k_2}$ and representing reactions leading to the formation of acetone as a result of a reaction of second order with respect to the concentration of RO· radicals is equal to $\sim$ 17.5 kcal/mole (Fig. 4).

Thus the formation of acetone during the decomposition of di-*tert*-butyl peroxide in hydrocarbon solvents at temperatures of the order of 200° is to a considerable extent associated with the bimolecular reaction (IV), and not with monomolecular decomposition of RO· radicals.

In the case of high polymers, reaction (IV) should lead to a sharp change in the molecular-weight distribution, which indeed occurs at deep stages of polyethylene oxidation; moreover, this change is accompanied by the appearance of ether bridges between macromolecules (^{5}).

Research Physicochemical Institute
named after L. Ya. Karpov

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