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Abstract

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THE MECHANISM OF FORMATION OF FREE RADICALS DURING THE DECOMPOSITION OF HYDROPEROXIDES UNDER THE ACTION OF ORGANIC ACIDS

Pronounced chain branching in reactions of liquid-phase oxidation of hydrocarbons is associated with the accumulation in the system of hydroperoxides capable of decomposing with the formation of free radicals (^{1}). A study of the mechanism of chain branching in the oxidation reaction of *n*-decane showed that, at relatively low degrees of conversion of *n*-decane, radical formation proceeds by two parallel reactions: by monomolecular decomposition of the hydroperoxide (decomposition rate constant k_1) and by bimolecular interaction of the hydroperoxide with the initial hydrocarbon (k_2) (^{2}, ^{3}). With increasing depth of oxidation the mechanism of chain branching becomes more complex. Accumulation in the reaction mixture of one of the reaction products—organic acids—leads to a sharp increase in the rate of decomposition of the hydroperoxide into radicals (^{4}). It was suggested that, in this case, radical formation occurs upon decomposition of an intermediate complex between the hydroperoxide and the acid, formed as a result of the occurrence of intermolecular hydrogen bonds

$$\mathrm{ROOH} + \mathrm{RCOOH} \overset{K}{\rightleftarrows} [\mathrm{complex}] \xrightarrow{k_{33}} \mathrm{RO}\cdot + \mathrm{OH}\cdot + \mathrm{RCOOH}. \qquad (1)$$

In such a complex, cleavage of the $-\mathrm{O}-\mathrm{O}-$ bond in the hydroperoxide is facilitated, leading to the formation of two free radicals (^{5}). In this case the overall rate of formation of free radicals is

$$w_p = k_3[\mathrm{ROOH}]_{\mathrm{free}} + k_{33}[\mathrm{complex}] \qquad (k_3 = k_1 + k_2[\mathrm{RH}]). \qquad (2)$$

Assuming that equilibrium is established sufficiently rapidly and that the decomposition reaction of the complex does not disturb the equilibrium conditions, one may write:

$$[\mathrm{complex}] = K[\mathrm{ROOH}]_{\mathrm{free}}[\mathrm{RCOOH}]_{\mathrm{m}}; \quad [\mathrm{ROOH}]_{\mathrm{free}} = [\mathrm{ROOH}]_{\Sigma} - [\mathrm{complex}]$$

(here $[\mathrm{ROOH}]_\Sigma$ is the total concentration of hydroperoxide, $[\mathrm{ROOH}]_{\mathrm{free}}$ is the concentration of hydroperoxide not bound in the complex, and $[\mathrm{RCOOH}]_{\mathrm{m}}$ is the concentration of monomeric acid). The concentration of the complex is

$$[\text{complex}] = K[\mathrm{RCOOH}]_{\mathrm{m}}\{[\mathrm{ROOH}]_\Sigma - [\text{complex}]\} \quad \text{or}$$

$$[\text{complex}] = \frac{K[\mathrm{ROOH}]_\Sigma[\mathrm{RCOOH}]_{\mathrm{m}}}{1 + K[\mathrm{RCOOH}]_{\mathrm{m}}},$$

$$[\mathrm{ROOH}]_{\mathrm{free}} = [\mathrm{ROOH}]_\Sigma - \frac{K[\mathrm{ROOH}]_\Sigma[\mathrm{RCOOH}]_{\mathrm{m}}}{1 + K[\mathrm{RCOOH}]_{\mathrm{m}}} = \frac{[\mathrm{ROOH}]_\Sigma}{1 + K[\mathrm{RCOOH}]_{\mathrm{m}}}.$$

Substituting the values found for $[\mathrm{ROOH}]_{\mathrm{free}}$ and [complex] into equation (2), we obtain:

$$w_p/[\mathrm{ROOH}]_\Sigma = \frac{k_3 + k_{33}K[\mathrm{RCOOH}]_{\mathrm{m}}}{1 + K[\mathrm{RCOOH}]_{\mathrm{m}}}. \tag{3}$$

It follows from equation (3) that at high acid concentrations the value of $w_p/[\mathrm{ROOH}]_\Sigma$ ceases to depend on its concentration

$$w_p/[\mathrm{ROOH}]_\Sigma = k_{33}^*. \tag{4}$$

To prove the proposed mechanism of chain branching, we investigated the dependence of $w_p/[\mathrm{ROOH}]_\Sigma$ on [RCOOH] over a wide range of the concentrations of the added acid. The experiments were carried out in an oxidation cell, the design of which is described in (6). Oxidized n-decane containing hydroperoxides at a concentration of 0.1-0.08 mole/liter was poured into the cell. The cell was purged with nitrogen and placed in a thermostat heated to the specified temperature. Then α-naphthol in a solution of n-decane was introduced into the cell in an amount sufficient for complete suppression of the chain decomposition of the hydroperoxide, and caproic acid (0.5-2.0 mole/liter). During the course of the reaction, samples were taken and analyzed for α-naphthol content by the method described in (7). Figure 1 gives the dependences, constructed from experimental data, of $w_p/[\mathrm{ROOH}]_\Sigma$ on the acid concentration at

[Fig. 1 and Fig. 2 graphs]

Fig. 1. Dependence of w_p/[ROOH] on the acid concentration at temperatures of 100 (1), 110 (2), 120 (3), 140 (4), and 150° (5)

Fig. 2. Dependence of w_p/[ROOH] on $[\mathrm{RCOOH}]_{\mathrm{m}}$ at temperatures of 110 (1), 120 (2), 140 (3), and 150° (4)

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* The quantity $k_3/(1 + K[\mathrm{RCOOH}]_{\mathrm{m}})^2 \ll k_{33}$ is much smaller than k_{33}.

various temperatures. It is seen that, when large amounts of acid are added, the curve of the dependence of $w_p/[\mathrm{ROOH}]_\Sigma$ on [RCOOH] contains a section parallel to the abscissa axis, indicating that $w_p/[\mathrm{ROOH}]_\Sigma$ ceases to depend on the acid concentration. Consequently, chain branching in the interaction of hydroperoxides with an acid does indeed proceed through the intermediate formation of a complex that decomposes into free radicals.

From the values of $w_p/[\mathrm{ROOH}]_\Sigma$ on those portions of the curves in Fig. 1 where this quantity ceases to depend on [RCOOH], the rate constant for decomposition of the complex into radicals, k_{33} (equation 4), was obtained. $k_{33} = 1.18 \cdot 10^7 \exp(-16100/RT)$ min^{-1}. The intercepts cut off on the ordinate axis represent the rate constants for decomposition of the hydroperoxide into radicals without participation of the acid (k_3). The data obtained also make it possible to determine the number of organic-acid molecules participating in formation of the complex, and the equilibrium constant for formation of the complex.

Taking into account acid dimerization, the curves of Fig. 1 can be replotted in the coordinates $w_p/[\mathrm{ROOH}]_\Sigma$–$[\mathrm{RCOOH}]_\mathrm{m}$. The value $[\mathrm{RCOOH}]_\mathrm{m}$ was determined as follows:

$$2[\mathrm{RCOOH}]_\mathrm{m} \overset{k_D}{\rightleftarrows} [\mathrm{dimer}]; \qquad k_D = [\mathrm{dimer}]/[\mathrm{RCOOH}]_\mathrm{m}^2;$$

$$[\mathrm{RCOOH}]_\Sigma = [\mathrm{RCOOH}]_\mathrm{m} + 2k_D[\mathrm{RCOOH}]_\mathrm{m}^2.$$

Hence

$$[\mathrm{RCOOH}]_\mathrm{m} = \left(\sqrt{1 + 8k_D[\mathrm{RCOOH}]_\Sigma} - 1\right)/4k_D.$$

The value of k_D for caproic acid in a solution of n-decane is not available in the literature. However, on the basis of the fact that the dimerization constant does not depend strongly on the length of the carbon chain in the molecule of an organic

acids, we used the value of k_D for octanoic acid in n-heptane (^{8}). At 23°, $k_D = 5800$ l/mole. Assuming that $H = 9000$ cal • mole^{-1} (^{9}), we obtain the expression $k_D = 1.46 \cdot 10^{-3} \exp(9000/RT)$ l/mole and the values of k_D at different temperatures. The dependence of the quantity $w_p/[\mathrm{ROOH}]_\Sigma$ on $[\mathrm{RCOOH}]_\mathrm{m}$ is shown in Fig. 2. The nonlinear character of this dependence at small values of $[\mathrm{RCOOH}]_\mathrm{m}$ indicates that not one, but n, molecules of acid participate in the formation of the complex.

In this case equation (3) takes the form:

$$w_p/[\mathrm{ROOH}]_\Sigma =$$

$$= (k_3 + K \cdot k_{33}[\mathrm{RCOOH}]^n_{\mathrm{m}}) \,/\, (1 + K[\mathrm{RCOOH}]^n_{\mathrm{m}})\,. \tag{5}$$

From this one can determine the equilibrium constant K and the reaction order n (^{10}).

Let us introduce the notation:

$$\frac{w_p}{[\mathrm{ROOH}]_\Sigma}/k_3 = X; \qquad \frac{k_{33}}{k_3} = \alpha;$$

$$\frac{w_p}{[\mathrm{ROOH}]_\Sigma}\,(1 + K[\mathrm{RCOOH}]^n_{\mathrm{m}}) = k_3 + K \cdot k_{33}[\mathrm{RCOOH}]^n_{\mathrm{m}}.$$

Dividing both sides of the equation by k_3:

$$X + XK[\mathrm{RCOOH}]^n_{\mathrm{m}} =$$

$$= 1 + \alpha K[\mathrm{RCOOH}]^n_{\mathrm{m}}; \qquad (X-1)/(\alpha - X) = K(\mathrm{RCOOH})^n_{\mathrm{m}} = y,$$

$$\lg y = \lg K + n \lg[\mathrm{RCOOH}]_{\mathrm{m}}. \tag{6}$$

Fig. 3. Dependence of $\lg y$ on $\lg[\mathrm{RCOOH}]_{\mathrm{m}}$ (equation 6) at temperatures 110 (1), 120 (2), 140 (3), and 150° (4)

The dependence of $\lg y$ on $\lg[\mathrm{RCOOH}]_{\mathrm{m}}$, plotted from the experimental data, is presented in Fig. 3. From the slope of the straight lines the number of acid molecules in the complex was determined: $n = 2$, and from the value of $\lg y$ at $\lg[\mathrm{RCOOH}]_{\mathrm{m}} = 0$, the equilibrium constant K.

$$K = 5.76 \cdot 10^{-4} \exp(10\,200/RT)\ \mathrm{l}^2/\mathrm{mole}^2.$$

The values of k_3, k_{33}, K, and k_D at different temperatures are given in Table 1. Thus, the mechanism of formation of free radicals in the oxidation of paraffin hydrocarbons includes the following elementary reactions:

Table 1

t, °C	$k_3 \cdot 10^3$, min^{-1}	$k_{33} \cdot 10^2$, min^{-1}	K, l^2/mole^2	k_D, l/mole	E_3, kcal/mole	E_{33}, kcal/mole	Q, kcal/mole
150	2.80		91	62			
140	1.40		132	78.5			
120	0.30	1.48	240	136	23.8	−16.1	10.2

t, °C	$k_3 \cdot 10^3$, min^{-1}	$k_{33} \cdot 10^2$, min^{-1}	K, l^2/mole^2	k_D, l/mole	E_3, kcal/mole	E_{33}, kcal/mole	Q, kcal/mole
110	0.15	0.96	364	184			
100	0.08	0.53		260			

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{OH}\cdot,$$

$$\mathrm{ROOH} + \mathrm{RH} \rightarrow \mathrm{RO}\cdot + \mathrm{R}\cdot + \mathrm{H_2O},$$

$$\mathrm{ROOH} + \mathrm{RCOOH} \xrightarrow{K} \text{complex} \xrightarrow{k_{33}} \mathrm{RO}\cdot + \mathrm{OH}\cdot + \mathrm{RCOOH}.$$

At deep stages of oxidation, when significant quantities of organic acids accumulate in the reaction mixture, the interaction of hydroperoxide with acid with the formation of free radicals becomes the main direction of the chain-branching reaction.

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