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1962

SovietRxiv

Abstract

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FORMATION OF FREE RADICALS IN THE INTERACTION OF HYDROPEROXIDE WITH CYCLOHEXANONE

(Presented by Academician V. N. Kondrat' ev, 4 IV 1962)

Among the various chain reactions, processes of oxidation by molecular oxygen are distinguished by one characteristic feature—a pronounced branching of the chains (^{1}). Therefore the question of the elementary reactions of pronounced chain branching occupies one of the central places in the study of the mechanism of oxidation of organic compounds both in the gas and in the liquid phase. In liquid-phase oxidation of hydrocarbons, the branching agent is a hydroperoxide. At present three elementary reactions for the formation of free radicals from hydroperoxide are known (^{2}, ^{3}):

$$\mathrm{ROOH} \to \mathrm{RO}\cdot + \cdot\,\mathrm{OH}, \qquad 2\mathrm{ROOH} \to \mathrm{RO}\cdot + \mathrm{H_2O} + \mathrm{RO_2}\cdot,$$

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

Of great interest is the search for new, as yet unknown chain-branching reactions. Recently, in studying the mechanism of pronounced chain branching in oxidizing cyclohexanol, V. V. Kharitonov and I established the following reaction for the formation of free radicals. Cyclohexanone and hydrogen peroxide, formed during the oxidation of cyclohexanol, reversibly add to one another with formation of oxycyclohexyl hydroperoxide, which decomposes into free radicals much faster than hydrogen peroxide. The question naturally arises whether a similar mechanism of chain branching is realized in hydrocarbon oxidation processes through interaction of hydroperoxides with ketones. The present work was carried out in order to test this assumption.

As objects of investigation we took tert-butyl hydroperoxide (distilled in vacuum) and cyclohexanone (distilled in vacuum); chlorobenzene served as solvent (purified with sulfuric acid and distilled). The rate of formation of free radicals was measured from the consumption of the inhibitor—α-naphthylamine. The experiments were carried out as follows. Chlorobenzene and cyclohexanone containing the inhibitor (total volume 20 ml) were introduced into a glass reactor with a reflux condenser, heated to the specified temperature. After 5 min of warming, the oxygen flow was switched on and tert-butyl hydroperoxide was introduced. During the experiment (after 1–2 min), samples were withdrawn and analyzed for hydroperoxide content (iodometrically) and for inhibitor content by the azo-coupling reaction with sulfanilic acid p-sulfophenyldiazonium in methyl alcohol solution, followed by colorimetric analysis of the dye formed. The azo-coupling reaction was carried out in a neutral medium, where hydroperoxide does not interfere with the analysis. The first experiments showed that from cyclohexanone, even in the presence of inhibitor, α-ketohydroperoxide is formed, decomposing extremely rapidly into free radicals. Therefore the rate of formation of free radicals from tert-butyl hydroperoxide could be measured from inhibitor consumption only in the initial period of the reaction, when α-ketohydroperoxide had not yet accumulated in appreciable amount. In this case the inhibitor concentration was chosen small, so that its consumption could be measured with sufficient accuracy over a short time interval. At the inhibitor concentrations used in this work ($1—20 \cdot 10^{-4}$ mol/l), the rate of inhibitor consumption did not depend on its concentration. Consequently, the inhibitor was consumed only by

reactions with free radicals, and all peroxide radicals perished as a result of reaction with the inhibitor. The error in determining the rate of amine consumption did not exceed 5%. It was assumed that, in the reaction with one amine molecule, one radical disappeared.

Fig. 1. Dependence of W_i on the hydroperoxide concentration in chlorobenzene (1) and cyclohexanone (2) at 120°.

Fig. 2. Dependence of the rate constant for peroxide decomposition into radicals on the ketone content. 1—126°, 2—120°, 3—115°, 4—110°.

Figure 1 shows the dependence of the rate of formation of free radicals (W_i) on the hydroperoxide concentration in chlorobenzene and in cyclohexanone (120°). In both solvents the rate W_i is directly proportional to the hydroperoxide concentration: $W_i = k_i[\mathrm{ROOH}]$; in cyclohexanone the hydroperoxide decomposes into free radicals 7 times faster than in chlorobenzene.

Table 1

Decomposition of tert-butyl hydroperoxide into free radicals in cyclohexanone—chlorobenzene mixtures

T-ra, °C	Ketone introduced, vol. %	[InH]·10^4, mol/l	[ROOH], mol/l	$W_i \cdot 10^8$, mol/l·sec	$K_i \cdot 10^6$, sec^{-1}	T-ra, °C	Ketone introduced, vol. %	[InH]·10^4, mol/l	[ROOH], mol/l	$W_i \cdot 10^8$, mol/l·sec	$K_i \cdot 10^6$, sec^{-1}
110	0	0,95	0,041	1,40	0,34	120	0	5	0,123	11,0	0,90
110	0	0,50	0,042	1,27	0,30	120	0	2,5	0,130	12,1	0,93
110	1,04	0,98	0,042	3,1	0,74	120	0	2,5	0,083	8,3	1,00
110	2,7	1,08	0,042	4,3	1,02	120	0	2,5	0,050	5	1,00
110	5,0	2,10	0,035	5,6	1,60	120	5	2,63	0,050	13,7	2,74

Fig. 3 graph

Figure 1: Fig. 3 graph

Fig. 4 graph

Figure 2: Fig. 4 graph

T-ra, °C	Ketone introduced, vol. %	[InH]·10^4, mol/l	[ROOH], mol/l	$W_i\cdot 10^8$, mol/l·sec	$K_i\cdot 10^6$, sec^{-1}	T-ra, °C	Ketone introduced, vol. %	[InH]·10^4, mol/l	[ROOH], mol/l	$W_i\cdot 10^8$, mol/l·sec	$K_i\cdot 10^6$, sec^{-1}
110	10	2,20	0,040	7,3	1,81	120	10	3,03	0,043	16,0	3,72
110	15	2,96	0,040	8,2	2,05	120	20	3,26	0,042	20,8	4,95
110	20	3,03	0,040	8,6	2,15	120	40	3,72	0,036	21,0	5,84
110	30	3,14	0,039	11,0	2,82	120	70	4,41	0,043	26,0	6,05
110	50	3,37	0,037	9,8	2,64	120	100	11,5	0,047	30,5	6,50
110	100	3,94	0,032	8,7	2,72	126	100	21,7	0,108	67,0	6,20
115	0	1,80	0,080	4,0	0,50	126	0	1,9	0,040	5,7	1,63
115	2,5	1,95	0,042	5,5	1,31	126	0	1,8	0,07	11,7	1,67
115	5	2,0	0,040	7,2	1,80	126	5	2,0	0,040	18,8	4,7
115	10	2,2	0,039	11,0	2,82	126	10	2,1	0,040	24,1	6,0
115	20	2,3	0,040	12,9	3,22	126	20	2,33	0,020	14,6	7,3
115	95	3,8	0,040	17,0	4,25	126	40	2,75	0,020	17,1	8,5
						126	97,5	3,90	0,020	21,4	10,7

The strong accelerating effect of cyclohexanone on W_i indicates its interaction with the hydroperoxide. The results of experiments on measuring W_i are given in Table 1 and in Fig. 2.

With an increase in the cyclohexanone content in the mixture, W_i first increases linearly, then its growth slows and stops. If the hydroperoxide reacted with the ketone bimolecularly, W_i would increase linearly with increasing ketone concentration. The experimental dependence of

$$k_i = \frac{W_i}{[\mathrm{ROOH}]}$$

on the ketone content agrees well with the following mechanism of free-radical formation:

Fig. 3. Dependence of $\dfrac{k_1}{k_i - k_1}$ on the reciprocal ketone concentration: 1—120°, 2—115°

Fig. 4. Temperature dependence of the constants. 1—$\lg k_2$, 2—$\lg k_1$, 3—($\lg K-6$)

$$\mathrm{ROOH} \xrightarrow{k_1} \mathrm{RO}\cdot + \cdot\mathrm{OH}, \qquad \mathrm{ROOH} + \text{ketone} \overset{k}{\rightleftarrows} X, \qquad X \xrightarrow{k_2} \text{free radicals.}$$

The rate of formation of free radicals in such a system is

$$W_i = k_1[\mathrm{ROOH}] + k_2(X),$$

$$[X] = K[\text{ketone}][\mathrm{ROOH}], \qquad W_i = (k_1 + k_2K[\text{ketone}])[\mathrm{ROOH}].$$

Iodometric analysis determines the total concentration of peroxide. Therefore

$$k_i = \frac{W_i}{[\text{peroxide}]} = \frac{(k_1 + k_2K[\text{ketone}])[\mathrm{ROOH}]}{[\mathrm{ROOH}] + [X]} = \frac{k_1 + k_2K[\text{ketone}]}{1 + K[\text{ketone}]}. \qquad \text{(I)}$$

When there is little ketone ($[\text{ketone}] < 1/K$), $k_i \approx k_1 + k_2K[\text{ketone}]$; when there is much ketone ($K[\text{ketone}] > 1$), $k_i \approx k_2$, which is also observed experimentally. Peroxide X apparently has the following structure:

cyclohexane ring C(OH)(OOR)

just as hydrogen peroxide with cyclohexanone gives the peroxide

cyclohexane ring C(OH)(OOH) (4)

and peracids add to cyclohexanone with formation of the peroxide

cyclohexane ring C(OH)(OOC(O)R).

From the experimental data one can calculate k_1, k_2, and K at different temperatures and determine the activation energy for decomposition of the two forms of peroxide into free radicals and the heat of addition of tert-butyl hydroperoxide to cyclohexanone, Q. Formula (I) can be rewritten in the following form ($\alpha = k_2/k_1$):

$$\frac{k_1}{k_i - k_1} = \frac{1}{(\alpha-1)K}\,\frac{1}{[\text{ketone}]} + \frac{1}{\alpha - 1}. \qquad \text{(II)}$$

Plotting the graph

$$\frac{k_1}{k_i - k_1} = f\left([\text{ketone}]^{-1}\right)$$

we obtain a straight line (Fig. 3)

$$\frac{k_1}{k_i - k_1} = \frac{a}{[\text{ketone}]} + b,$$

whence we find a and b, which are related to k_2 and K by the relations: $K = \frac{b}{a}$; $k_2 = k_1\left(\frac{1}{b} + 1\right)$. The constant k_1 is found from experiments in pure chlorobenzene. The results of calculating k_1, k_2, and K are given in Table 2; the dependence of the constants on reciprocal temperature is shown in Fig. 4. The error in determining the activation energies does not exceed 2 kcal/mol.

Table 2

Values of k_1, k_2, and K at different temperatures

Temp., °C	$k_1 \cdot 10^7$, mol/l · sec	$k_2 \cdot 10^6$, mol/l · sec	K, l/mol
100	3.2	3.0	1.3
115	5.0	4.35	1.0
120	9.5	7.3	0.83
126	16.5	11.7	0.69

$$E_1 = 33 \text{ kcal/mol.} \qquad E_2 = 26 \text{ kcal/mol.} \qquad Q = 11 \text{ kcal/mol.}$$

The formation of the peroxide

cyclohexylidene structure bearing OOR and OH

takes place with liberation of 11 kcal/mol of heat. This peroxide decomposes into free radicals with a lower activation energy (26 kcal/mol instead of 33) and approximately 10 times faster (at 100°) than tert-butyl hydroperoxide. The rate constants of decomposition into radicals and the equilibrium constant have the following form:

$$k_1 = 1.8 \cdot 10^{12} \exp(-33000/RT) \text{ sec}^{-1},$$

$$k_2 = 1.8 \cdot 10^{9} \exp(-26000/RT) \text{ sec}^{-1},$$

$$K = 6.9 \cdot 10^{-7} \exp(11000/RT) \text{ l/mol.}$$

The results obtained indicate that, in reactions of liquid-phase oxidation of hydrocarbons, alongside the previously known mechanisms, the following mechanism of chain branching apparently also occurs: hydroperoxide adds to a ketone in a reversible reaction with formation of a peroxide form that decomposes more rapidly into free radicals. In this reaction the chains branch with the participation of two intermediate products (ketone and hydroperoxide), in contrast to the previously known branching reactions, in which the chains were branched by only one product (hydroperoxide). The results of the present work explain the accelerating effect of ketones on the oxidation of hydrocarbons. It is obvious that combined additions of ketone and hydroperoxide to an oxidizing hydrocarbon should exert a stronger initiating effect than additions of ketone alone or hydroperoxide alone.

I express my deep gratitude to L. N. Denisova for assistance in carrying out the experiments.

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Received
30 III 1962

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