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Abstract

Full Text

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CHEMISTRY

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ON THE MECHANISM OF FORMATION OF CARBONYL COMPOUNDS AND ACIDS DURING EMULSION OXIDATION OF ISOPROPYLBENZENE

(Presented by Academician V. N. Kondrat' ev, 18 I 1961)

Carbonyl compounds arising in the course of oxidation of hydrocarbons and constituting products of further transformation of peroxides (or peroxide radicals) are, in most cases, formed by a radical mechanism (^{1,3}). Ketones and, especially, aldehydes are highly reactive compounds and therefore readily enter into chain reactions, giving new substances with new functions. In particular, the formation of acids, according to Rieche' s scheme (^{4}), proceeds by oxidation of ketones to α-ketohydroperoxides with their subsequent decomposition into an acid and an aldehyde:

$$\mathrm{R'—CCH_2—R'' \rightarrow R'—CCHR'' \rightarrow R'—C\left(\frac{OH}{O}\right) + R''—C\left(\frac{H}{O}\right)}.$$

The decomposition of α-ketohydroperoxides according to the above scheme is known to be catalyzed by acids (^{5}). This circumstance is evidently the reason why ketohydroperoxides have not been detected among the products of hydrocarbon oxidation. The route via dihydroperoxides (^{6}) is a second possible mechanism of acid formation.

Fig. 1. Kinetic curves of peroxide accumulation during the oxidation of isopropylbenzene. *1, 2*—0.15 mol/l, *3*—0.30 mol/l. Arrows indicate the moment of inhibitor addition.

In studying the oxidation of isopropylbenzene by the inhibition method, we encountered a new and interesting phenomenon: upon the introduction of β-naphthol, the rate of formation of carbonyl compounds and acids not only does not decrease, but increases abruptly. This, it seems to us, sheds some light on the mechanism of formation of carbonyl compounds and acids during the oxidation of hydrocarbons.

The emulsion oxidation of isopropylbenzene was carried out at a phase ratio of 1 : 1 (the aqueous phase was a 0.1 N solution of sodium carbonate) in a steel thermostated autoclave at a pressure of 10 atm and 105°. During the process, samples were taken in which peroxides were determined iodometrically, carbonyl compounds by the hydroxylamine method, and acids by titration of one phase. During the reaction, an inhibitor—β-naphthol—was introduced.

When an inhibitor is introduced into the reaction mixture, the accumulation of the total amount of peroxides not only ceases, but their concentration decreases (Fig. 1), which indicates the chain character of their formation, as well as the molecular mechanism of consumption of peroxide compounds.

The kinetic curves for the accumulation of carbonyl compounds are presented in Fig. 2. From the observed fact that the reaction accelerates upon introduction of an inhibitor, it follows unambiguously that, in this case, the formation of carbonyl compounds proceeds by a molecular mechanism, while their consumption proceeds by a radical chain mechanism. After the end of the inhibition period, intensive consumption of the carbonyl compounds begins.

The kinetic curve for acid formation also shows a break, but of a somewhat different character (Fig. 3). After introduction of the inhibitor, the acid concentration increases sharply to a certain value and subsequently remains constant. Such a picture may be a consequence of the formation of acids from ketohydroperoxides. The inhibitor retards the chain processes of ketohydroperoxide formation, as a result of which acid accumulation proceeds until the ketohydroperoxide has been completely consumed, after which it stops. When the reaction leaves the inhibition period, the formation of ketohydroperoxide and its decomposition with formation of acids again begin, as does the consumption of acids by a chain mechanism. Since at first the ketohydroperoxide concentration is low, these processes compensate one another, which leads to constancy of the acid concentration in the system for a period longer than the inhibition period.

Table 1

Depth of oxidation C_{GHP}, mol/l	ΔC_{GHP}, mol/l	Sum of increases of carbonyls and acids ΔC, mol/l	$\Delta C_{\text{GHP}}/\Delta C$
0.3	0.25	0.24	1.04
0.8	0.34	0.33	1.03
1.25	0.43	0.425	1.01

According to the Rieche scheme, upon decomposition of ketohydroperoxides (and also upon decomposition of dihydroperoxides), carbonyl and acid are formed in equivalent amounts. In the case of oxidation of isopropylbenzene, the amount of carbonyl compounds formed during the inhibition period of the reaction is several times greater than the amount of acids formed. It is natural to assume that the route of formation of carbonyl compounds through a single act of decomposition of the ketohydroperoxide into an acid and an aldehyde is not the only one. It is quite possible that the formation of carbonyl compounds and acids proceeds by the following mechanism of decomposition of the ketohydroperoxide formed during oxidation of acetophenone:

$$\mathrm{C_6H_5{-}CO{-}CH_2OOH} \xrightarrow{(1)} \mathrm{C_6H_5C(=O)OH + HCOH}$$

$$\mathrm{C_6H_5{-}CO{-}CH_2OOH} \xrightarrow{(2)} \mathrm{C_6H_5COC(=O)H + H_2O}$$

The formation of phenylglyoxal by route (2) is quite possible. Methylglyoxal, for example, is formed during the oxidation of acetone, as indicated in the work of E. T. Denisov (^{7}).

A second possible route for the formation of carbonyl compounds is, apparently, the molecular decomposition of cumene hydroperoxide:

$$\mathrm{C_6H_5C(CH_3)_2OOH} \longrightarrow [\ \text{cyclic transition complex}\ ] \longrightarrow \mathrm{C_6H_5COCH_3 + CH_3OH}$$

To confirm the above, it is useful to compare the consumption of hydroperoxides during the inhibition period with the total formation of carbonyl compounds and acids. The corresponding data are given in Table 1. We see that the amount formed during inhibition of the reac-

of carbonyl compounds and acids corresponds well to the amount of hydroperoxides that have undergone molecular decomposition.

Thus, in the emulsion oxidation of isopropylbenzene, an intermediate compound is kinetically manifested (evidently, α-ketohydroperoxide, $\mathrm{C_6H_5COCH_2OOH}$), which, upon decomposition, forms an acid and a carbonyl compound. When

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

oxidation processes proceeding in homogeneous systems are inhibited, the phenomenon under consideration may not be observed, since the formation of acids in the course of the reaction leads to a strong decrease in the concentration of the intermediate ketohydroperoxide. In the case of oxidation in a weakly alkaline emulsion, with constant neutralization of the acidic products in the aqueous phase (pH > 7), the concentration of the ketohydroperoxide can reach values that are analytically detectable, which, in our view, accounts for the phenomenon considered.

Fig. 2. Kinetic curves for the accumulation of carbonyl compounds during the oxidation of isopropylbenzene. The arrows indicate the moments at which the inhibitor was introduced.

Fig. 3. Kinetic curves for the accumulation of acids during the oxidation of isopropylbenzene. The arrows indicate the moments at which the inhibitor was introduced.

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REFERENCES

1. E. T. Denisov, *ZhFKh*, **33**, 1198 (1959).
2. Z. K. Maizus, I. P. Skibida, N. M. Emanuel, V. N. Yakovleva, *Kinetics and Catalysis*, **1**, 55 (1960).
3. J. H. Raley, F. F. Rust, W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).
4. A. Rieche, *Angew. Chem.*, **50**, 520 (1937); **70**, 251 (1958).
5. W. Pritzkow, *Ber.*, **88**, 572 (1955).
6. K. I. Ivanov, V. K. Savinova, V. I. Zhakhovskaya, *DAN*, **59**, 905 (1948).
7. E. T. Denisov, *Izv. AN SSSR, OKhN*, 1956, No. 5, 812.