THE MECHANISM OF CHAIN INITIATION IN OXIDIZING CYCLOHEXANOL

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. T. DENISOV

THE MECHANISM OF CHAIN INITIATION IN OXIDIZING CYCLOHEXANOL

(Presented by Academician V. N. Kondrat' ev, May 31, 1961)

Liquid-phase oxidation as a chain process begins with the formation of free radicals in the initial substance containing dissolved oxygen. The mechanism of reactions of this kind has not yet been studied, although the investigation of such reactions is of considerable scientific interest. In the literature on the oxidation of hydrocarbons, the prevailing opinion is that at the initial moment of oxidation free radicals are formed by the reaction

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}. \quad (1)$$

However, calculation has shown that this reaction can provide a much lower rate of formation of free radicals than the rates observed experimentally ([1]). In this connection, for liquid-phase oxidation a trimolecular reaction of free-radical formation was proposed as energetically more favorable ([1]):

$$RH + O_2 + RH \rightarrow 2R^{\bullet} + H_2O_2. \quad (2)$$

Along with the initial substance and the oxygen dissolved in it, various impurities may take part in the formation of free radicals, in particular peroxide, which is slowly formed at room temperature. A final answer to the question of the mechanism of formation of free radicals in the initial oxidizing substances can be provided only by experiment.

In the present work the mechanism of formation of free radicals in cyclohexanol in the presence of oxygen was studied with the aid of an inhibitor (α-naphthol). The inhibitor was consumed only by reaction with free radicals, so that the rate of its consumption characterized the rate of formation of free radicals. Two peroxide radicals perish on one molecule of inhibitor (naphthol) ([2]):

$$InH + RO_2^{\bullet} \rightarrow In^{\bullet} + ROOH,$$

$$In^{\bullet} + RO_2^{\bullet} \rightarrow InOOR.$$

Therefore the rate of radical formation is $W_0 = 2(-d[\mathrm{InH}]/dt)$. The presence of the inhibitor retarded the accumulation of peroxide, which decomposes into free radicals, and in experiments with the inhibitor it was possible, for a fairly long time, to follow the formation of radicals only at the expense of the initial cyclohexanol and the oxygen dissolved in it.

Cyclohexanol was chosen as the object of investigation because a systematic study of the mechanism of its oxidation is currently being carried out ([3]). The experiments were performed in a quartz cylindrical reactor with a reflux condenser and a capillary tube through which oxygen was fed into the reactor. The reactor was heated to the specified temperature, cyclohexanol (20 ml) with α-naphthol dissolved in it (10^{-3}–$1.5 \cdot 10^{-4}$ mol/l) was introduced into it, and after 5 min of warming the flow of oxygen was turned on.

at a rate of 0.2 ml/sec. During the course of the experiment, samples of cyclohexanol were taken from the reactor and analyzed for their content of α-naphthol by the method developed in [4]. To the sample containing α-naphthol, a solution of diazotized sulfanilic acid in methyl alcohol and a small amount of alcoholic alkali were added; the amount of dye formed was determined colorimetrically with a green light filter. The inhibitor concentration was determined with an accuracy of $\pm 0.7\%$.

Fig. 1. Kinetics of the consumption of α-naphthol in cyclohexanol at 121° (1) and accumulation of peroxide in the presence of the inhibitor (2) (the scale for peroxide concentration is reduced by a factor of 100).

Fig. 1 shows the kinetic curve for inhibitor consumption in cyclohexanol at 121°. During the first 100 min, the inhibitor is consumed at a constant rate; then the rate of its consumption increases, which is associated with peroxide accumulation. α-Naphthol is a reducing agent, and it may be expected to react not only with free radicals but also with dissolved oxygen. Special experiments showed that in chlorobenzene in the presence of oxygen at 121° α-naphthol is not consumed. Consequently, under the conditions of the experiments performed, inhibitor consumption occurs only through reaction with free radicals. The rate of formation of free radicals in oxidizing cyclohexanol, determined from the initial slope of the kinetic curve for inhibitor consumption, is equal to $8.3 \cdot 10^{-9}$ mol/l · sec (at 121°). It is seen from Fig. 1 that measurement of inhibitor consumption in the oxidizing substance gives more reliable values of W_0 than W_0 determined as the ratio

$$W_0 = 2[\mathrm{InH}]_0/t_{\mathrm{inh}},$$

where t_{inh} is the period of inhibition caused by the inhibitor at its concentration $[\mathrm{InH}]_0$. In the latter case, a more or less strong overestimation of W_0 occurs because of peroxide accumulation during the inhibition period. Measurement of the initial rate of inhibitor consumption made it possible to determine W_0 with an accuracy of $\pm 0.5 \cdot 10^{-9}$ mol/l · sec.

Fig. 2. 1 —dependence of the rate of formation of free radicals in cyclohexanol on the partial pressure of oxygen at 111°; 2 —the same, in the presence of oxygen, on the concentration of cyclohexanol at 121°; 3 —the same, but in an atmosphere of nitrogen; 4 —dependence of the rate of radical formation in the interaction of cyclohexanol with oxygen at 121° on the square of the cyclohexanol concentration.

In order to clarify the mechanism of radical formation in the cyclohexanol plus oxygen system, it is necessary to establish the relationship between W_0 and the oxygen concentration (or its partial pressure), between W_0 and the cyclohexanol concentration, and between W_0 and temperature. The dependence of W_0 on the concentration of dissolved oxygen was determined in experiments at 111° with an α-naphthol concentration of $2.5 \cdot 10^{-4}$ mol/l; from experiment to experiment the partial pressure of oxygen was varied by diluting it with nitrogen at a total pressure of 1 atm. With an increase in the partial pressure of oxygen

W_0 increases linearly: $W_0 = W_0' + a \cdot P_{O_2}$ (Fig. 2). The fact that, in the absence of dissolved oxygen, $W_0 \neq 0$ indicates the formation of radicals by a reaction not involving oxygen (apparently owing to impurities contained in cyclohexanol, which decompose with the formation of free radicals). The linear increase of W_0 with increasing P_{O_2} indicates the formation of free radicals by a reaction involving one molecule of oxygen. It may be assumed that W_0' is supplied by traces of peroxide formed in cyclohexanol during storage. Iodometric analysis showed that the initial cyclohexanol contains $1.6 \cdot 10^{-4}$ mole/liter of peroxide. The rate constant for decomposition of the peroxide formed during oxidation of cyclohexanol into free radicals at 111° is approximately $6 \cdot 10^{-7}$ $\sec^{-1}$ (3). Consequently, the peroxide can provide a rate of formation of free radicals equal to 10^{-10} mole/liter $\cdot$ sec, which amounts to only 5% of W_0' and 1.4% of W_0 at 1 atm P_{O_2}. Replacing the quartz-glass reactor by a Pyrex-glass reactor does not change the rate of formation of free radicals, which indicates the homogeneous character of their formation. Further experiments showed that W_0' varies from one series of experiments to another (each series of experiments was carried out with one solution of α-naphthol in cyclohexanol) and is associated with accidental impurities entering the cyclohexanol.

The dependence of the rate of formation of free radicals on the concentration of cyclohexanol was studied in experiments with dilution of cyclohexanol by chlorobenzene at 121° and an α-naphthol concentration of $1.5 \cdot 10^{-4}$ mole/liter. The results of the experiments are presented in Table 1 and in Fig. 2. As is seen from Fig. 2, W_0' decreases with decreasing concentration of cyclohexanol, and in pure chlorobenzene it is equal to 0.

It is seen from Fig. 2 that $W_0' \sim [RH]$, while $W_0^{O_2} \sim [RH]^2$. In order to determine more precisely the reaction order with respect to cyclohexanol, it is necessary to plot $\lg W_0^{O_2}$ as a function of $\lg[RH]$, determine the reaction order with respect to cyclohexanol from the slope of the straight line, and introduce a correction for the change in the concentration of dissolved oxygen as cyclohex-

anol is diluted

Table 1

t, °C	O_2 content in the mixture, %	cyclohexanol content, mole %	W_0	W_0'	$W_0^{O_2}$
111	1	100	2.0		
111	1	100	1.7		
111	21	100	3.0		
111	41	100	4.4		
111	41	100	4.8		
111	55	100	5.1		
111	100	100	7.1	2.0	5.1
121	100	100	8.2	2.3	5.9
121	100	90	7.2	2.1	5.1
121	100	90	6.7	2.1	4.6
121	100	80	5.4	1.8	3.6
121	100	80			3.2
121	100	70	4.8	1.4	3.2
121	100	60	3.1	1.4	1.7
121	100	50	3.1	1.2	1.9
121	100	25	1.2	0.6	0.6
121	100	10	0.5	0.2	0.3
121	100	0.0	0.0	0.0	0.0
121	1	90		2.1	
121	1	50		1.4	
121	1	10		0.2	
111	100	100			4.3
121	100	100	15.7	8.8	6.9
130.5	100	100	20	10	10

Units for W_0, W_0', and $W_0^{O_2}$: mole % $\cdot l^{-1}$ $\cdot sec^{-1}$ $\cdot 10^9$.

with chlorobenzene. For the range of changes in $[RH]$ from 9.6 to 5.8 mol/l,

$$\Delta \lg W_0^{O_2} / \Delta \lg [RH] = 2.3 \pm 0.2.$$

When cyclohexanol is diluted with chlorobenzene, the partial pressure of oxygen decreases because the vapor pressure of chlorobenzene is higher than that of cyclohexanol. The concentration of oxygen dissolved in heated cyclohexanol was determined in an autoclave apparatus at 110° and an oxygen pressure of 10 atm. Under these conditions, 0.095 ± 0.010 mol O_2 dissolves in one liter of cyclohexanol. Therefore, it is necessary to take into account the change in the

concentration of dissolved oxygen only as a consequence of the change in the partial pressure of oxygen:

$$W_0^{O_2} = k[RH]^n P_{O_2}, \qquad \Delta \lg W_0^{O_2} = n\,\Delta \lg[RH] + \Delta \lg P_{O_2},$$

whence

$$n = \frac{\Delta \lg W_0^{O_2}}{\Delta \lg[RH]} - \frac{\Delta \lg P_{O_2}}{\Delta \lg[RH]} = 2.3 - \frac{\Delta \lg P_{O_2}}{\Delta \lg[RH]}.$$

At 120° in pure cyclohexanol $P_{O_2} = 560$ mm Hg; in pure chlorobenzene $P_{O_2} = 225$ mm Hg; in a 50% mixture of cyclohexanol with chlorobenzene one may take $P_{O_2} = 393$ mm Hg, whence

$$\Delta \lg P_{O_2}/\Delta \lg[RH] = 0.15/0.30 = 0.5, \qquad n = 2.3 - 0.5 = 1.8 \pm 0.3,$$

i.e., practically $n = 2$. This is evidence that in cyclohexanol free radicals are formed by the reaction of one oxygen molecule with two cyclohexanol molecules, i.e., in the case of cyclohexanol the trimolecular mechanism of chain initiation proposed in work (1) is realized.

Knowing the solubility of oxygen in cyclohexanol, one can determine the absolute value of the rate constant of reaction (2). At 111° and a total pressure of 1 atm, $P_{O_2} = 630$ mm Hg; the concentration of dissolved oxygen is then $7.9 \cdot 10^{-3}$ mol/l, the concentration of cyclohexanol in the liquid phase is 9.6 mol/l. $W_0^{O_2} = 5.1 \cdot 10^{-9}$ mol/l $\cdot$ sec, whence $k = 0.7 \cdot 10^{-8}$ l^2/mol$^2 \cdot$ sec. Experiments at different temperatures made it possible to find the activation energy of reaction 2, equal to 12 ± 2 kcal/mol. However, the true activation energy is somewhat higher, since with increasing temperature the vapor pressure of cyclohexanol increases and the partial pressure of oxygen and its concentration in the liquid phase decrease. At 111° $P_{O_2} = 630$ mm Hg; at 130°—490 mm Hg. This temperature dependence corresponds to an activation energy of 4 kcal/mol. Consequently, the true activation energy for the trimolecular reaction of formation of free radicals is 16 kcal/mol. The rate constant of this reaction has the form

$$k = 8.3 \cdot \exp(-16000/RT)\ \text{l}^2/\text{mol}^2 \cdot \text{sec}.$$

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
24 V 1961

CITED LITERATURE

1. E. T. Denisov, DAN, **130**, 1055 (1960).

2. C. E. Boozer, G. S. Hammond, C. E. Hamilton, J. N. Sen, J. Am. Chem. Soc., **77**, 3233 (1955).

3. E. T. Denisov, V. V. Kharitonov, ZhFKh, **35**, 444 (1961).

4. D. G. Knorre, Z. K. Maizus, N. M. Emanuel' , DAN, **123**, 123 (1958).

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