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OXIDATION OF CYCLOHEXANOL BY OZONIZED OXYGEN

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Gas initiation of liquid-phase oxidation reactions was proposed and carried out by N. M. Emanuel' and co-workers ([1]-[3]). The present work is devoted to the study of the oxidation of cyclohexanol by ozonized oxygen. The results of the work shed light on the mechanism of ozone oxidation of aliphatic compounds in the liquid phase.

The experiments were carried out as follows. Cyclohexanol in an amount of 25-30 ml was oxidized in a glass reactor while bubbling oxygen containing 0.3 ± 0.03% ozone through it, at a rate of 6.7 ± 0.7 l/hr and at temperatures of 50-100°. During the course of oxidation, samples of the oxidized cyclohexanol were taken and analyzed for the content of cyclohexanone, peroxide, acids, and esters. During the experiment the ozone concentration before and after the reactor was systematically determined with the aid of KI. As a result of oxidation, cyclohexanone, hydrogen peroxide, adipic acid, and complex esters are formed. The kinetics of accumulation of cyclohexanone and peroxide at the beginning of the reaction are linear; at a considerable depth of oxidation (~10%) the concentrations of ketone and peroxide pass through a maximum. Table 1 gives data on the composition of the products after 2 hours of oxidation. The products of ozonized oxidation differ from those of thermal oxidation at 120° by a high content of acids and esters (10-20% instead of 1-2%). Comparison of the amount of ozone absorbed with the oxygen content in the oxidation products shows (Table 1) that at 50° oxygen is not involved in the oxidation, whereas at higher temperatures it is undoubtedly incorporated into the reaction. In the calculation it was assumed that all three oxygen atoms from the absorbed ozone pass into the oxidation products.

Table 1

Yield of products and incorporation of oxygen in the oxidation of cyclohexanol by ozone

Temp., °C	Peroxide	Ketone	Acid + ester	Yield of products per absorbed O_3, mol.%	Incorporation of O_2 per 1 molecule absorbed O_3
50	51	64	36	137	−0.04

Temp., °C	Peroxide	Ketone	Acid + ester	Yield of products per absorbed O_3, mol.%	Incorporation of O_2 per 1 molecule absorbed O_3
60	49	55	45	173	0.33
70	73	73	27	190	0.45
80	51	84	16	310	0.94
80	54	80	$ $0	310	1.03
90	61	83	17	333	1.13
100	69	69	31	290	1.25

Table 2

Rate of chain initiation and their length in the oxidation of cyclohexanol by ozone

Temp., °C	v	$v - v_{O_3}$	v_v (calculated)	W_0	ν
		10^{-6} mol/l · sec			
50	11	0.0	1.1	0.003	370
60	12.5	1.5	2.0	0.005	400
70	12	1.0	4.0	0.009	450
80	19	8	6.3	0.012	520
90	23	12	10	0.016	620
100	27	16	16	0.025	640

The incorporation of oxygen into the reaction indicates a chain mechanism of oxidation. To check this assumption, experiments were carried out with the introduction of an inhibitor—hydroquinone—into the oxidation reaction. Hydroquinone, introduced in an amount of 10-40 mmol/l, retards oxidation.

cyclohexanol by ozonized oxygen. At 50-60°, the inhibition is incomplete; at higher temperatures the reaction practically stops for some time (Fig. 1). A comparison of oxidation by ozone with thermal oxidation showed that the inhibitor is consumed mainly by reaction with ozone. Therefore, the rate of its consumption cannot in any way serve as a criterion for the rate of chain initiation. Experiments with the introduction of an inhibitor, although they prove the presence of a chain mechanism, do not answer the question of whether all the cyclohexanol is oxidized by the chain route or only some part of it. The results of our work on the thermal oxidation of cyclohexanol help to clarify this question. The rate of the chain oxidation reaction is equal to:

$$v_\nu = \frac{k_2}{\sqrt{k_6}}[\mathrm{RH}]\sqrt{W_0},$$

where the constants k_2 and k_6 refer, respectively, to the reactions $\mathrm{RO}_2^\bullet + \mathrm{RH}$ and $\mathrm{RO}_2^\bullet + \mathrm{RO}_2^\bullet$. The activation energy for the rate v_ν is

$$E = E_2 + \tfrac{1}{2}E_0 > E_2 = 7.7 \text{ kcal/mol}.$$

Let us assume that cyclohexanol is oxidized only by the chain route. It is known from experiment that at 50°

$$v = 11 \cdot 10^{-6} \text{ mol/l} \cdot \text{s},$$

and at 100°

$$v = 27 \cdot 10^{-6} \text{ mol/l} \cdot \text{s}.$$

Such a change in v with temperature corresponds to $E = 4$ kcal/mol, whereas it should be $E > 7.7$. Thus, the involvement of oxygen in the oxidation and the slowing of the reaction by an inhibitor indicate a chain mechanism of the reaction, while the assumption that the reaction is exclusively chain in nature contradicts the data on the thermal oxidation of cyclohexanol. It remains to assume that cyclohexanol is oxidized by ozonized oxygen by two mechanisms: a chain mechanism—with rate v_ν, and a non-chain mechanism—with rate v_{O_3}, equal to the rate of entry of ozone into the reactor. v_{O_3} is independent of temperature. At low temperatures $v \approx v_{O_3}$; with increasing temperature v_ν increases (see Table 2).

(Figure: Figure 1)

Fig. 1. Kinetics of oxidation of cyclohexanol by ozonized oxygen with introduction of an inhibitor during the course of the reaction (the moment of introduction is indicated by an arrow).
1—hydrogen peroxide, 2—cyclohexanone, 3—acids.

The temperature dependence of v_ν corresponds to an activation energy

$$E = 13 \pm 2 \text{ kcal/mol},$$

which agrees well with the data for thermal oxidation. Alongside v_ν, the experimentally obtained values of v_ν calculated from the value of v_ν at 90°C and $E = 13$ kcal/mol are given. Since

$$v_\nu = \frac{k_2}{\sqrt{k_6}}(\mathrm{RH})\sqrt{W_0},$$

and

$$k_2 k_6^{-1/2} = 320\, e^{-7700/RT}$$

(from experiments on the thermal oxidation of cyclohexanol), the chain-initiation rate can be found from this:

$$W_0 = \frac{v_\nu^2 k_6}{k_2^2 (\mathrm{RH})^2}$$

and

$$\nu = \frac{v_\nu}{W_0}.$$

These quantities are given in Table 2, from which it is seen that

$$W_0 \approx 10^{-8} \text{ mol/l} \cdot \text{s}, \qquad \nu \approx 400\text{-}600;$$

with increasing temperature W_0 and ν increase. This leads to the fact that, as the temperature rises, v_ν becomes greater than v_{O_3}. If W_0 is compared with the rate of entry of ozone into the reactor, it turns out that only 0.1% of the ozone is consumed for chain initiation; practically all the ozone reacts with cyclohexanol without formation of free radicals. W_0 is small because ozone rapidly enters into reaction with cyclohexanol and its concentration is low. The ozone concentration can be estimated as follows. Let us assume that Henry' s coefficient for the dissolution of ozone in the alcohol is the same as for oxygen,

$$10^{-2} \text{ mol/l} \cdot \text{atm}.$$

The partial pressure of O_3 at the outlet of the reactor is 10^{-4} atm, whence

$$[\mathrm{O_3}] \approx 10^{-6} \text{ mol/l}.$$

The activation energy for initiation of chains by ozone is $E_0 = 2(E - E_2) = 2(13 - 7.7) = 11$ kcal/mole. Consequently, chain initiation through decomposition of the ozone molecule into an atom and an oxygen molecule does not play any significant role, since in this case E_0 would be close to 25 kcal/mole. In the liquid phase, the formation of free radicals apparently occurs by a bimolecular reaction of O_3 and RH:

$$\mathrm{RH} + \mathrm{O_3} \rightarrow \mathrm{R}\cdot + \mathrm{O_2} + \mathrm{HO}\cdot - q,$$

for which $E_0 \approx q = Q - 100 + 25 = Q - 75$, where Q is the energy of rupture of the $R - H$ bond. For cyclohexanol $Q < 90$, whence $E_0 < 15$, which agrees well with the value $E_0 = 11$ kcal/mole obtained experimentally. The rate constant for chain initiation, assuming $[O_3] = 10^{-6}$ mole/l, is

$$k = 6 \cdot 10^3 e^{-11000/RT} \text{ l/mole} \cdot \text{sec}.$$

Interesting data were obtained by us concerning the mechanism of the reaction of ozone with cyclohexanone. Upon introduction of an inhibitor at 100°, a decrease in the concentration of cyclohexanone is observed, which indicates a non-chain mechanism for the interaction of ozone with cyclohexanone (in thermal oxidation it is consumed only by the chain pathway). A special experiment on the oxidation of cyclohexanone by ozonized oxygen at 80° with the introduction of an inhibitor showed that cyclohexanone is oxidized by a non-chain pathway with the formation of acids (the inhibitor does not retard the reaction). It is possible that oxidation proceeds by the reaction of ozone with the enol form of the ketone:

$$\text{cyclohexanone} \rightleftharpoons \text{enol form} \xrightarrow{O_3} \text{ozonide} \longrightarrow \text{dicarboxylic acids}$$

In the oxidation reaction of cyclohexanol at 80°, the maximum concentration of ketone is 0.75 mole/l, whence it follows that ozone reacts 20 times faster with cyclohexanone than with cyclohexanol.

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CITED LITERATURE

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