G. E. ZAIKOV, Z. K. MAIZUS

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G. E. ZAIKOV, Z. K. MAIZUS

ON THE INFLUENCE OF THE POLARITY OF THE MEDIUM ON THE ACTIVATION ENERGY OF THE CHAIN-PROPAGATION REACTION IN THE OXIDATION OF ETHYL ALCOHOL AND METHYL ETHYL KETONE

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In studying the mechanism of oxidation of polar organic substances in the liquid phase, it was established that the rate and direction of the process (the composition of the reaction products) depend to a considerable extent on the polarity of the medium (^{1}). These observations make it possible to pose in a new way the question of controlling oxidation processes, since, by carrying out the reaction in appropriate solvents and changing the dielectric constant of the medium, one can promote greater selectivity of the process. In the oxidation of ethyl alcohol and methyl ethyl ketone, the interaction of the peroxide radical, which carries the oxidation chain ($\mathrm{RO}_2^\bullet$), with methyl ethyl ketone or ethyl alcohol (RH) is an interaction of two dipoles (^{1}). When these substances are diluted with a nonpolar solvent—benzene—the rate of interaction of $\mathrm{RO}_2^\bullet$ with the initial substance decreases. Since the total rate of conversion of $\mathrm{RO}_2^\bullet$ radicals is composed of the rate of decomposition of these radicals

$$\mathrm{RO}_2^\bullet \xrightarrow{w_1} \mathrm{R'O}^\bullet + \mathrm{R''HO} \tag{1}$$

and the rate of the reaction

$$\mathrm{RO}_2^\bullet + \mathrm{RH} \xrightarrow{w_2} \mathrm{ROOH} + \mathrm{R}^\bullet, \tag{2}$$

a decrease in the value of w_2 leads to an increase in the relative amount of products of decomposition of the $\mathrm{RO}_2^\bullet$ radical in the oxidized mixture. This makes it possible to understand the experimentally observed change in the composition of the reaction products with changing polarity of the medium.

In the present work, the influence of the dielectric constant of the medium on the activation energy of the chain-propagation reaction in the oxidation of methyl ethyl ketone and ethyl alcohol was studied. The experiments were carried out at a pressure of 50 atm in an autoclave-type apparatus described in (^{2}). Figure 1 gives the kinetic curves for the consumption of methyl ethyl ketone at temperatures of 100, 122, and 145° and molar ratios methyl ethyl ketone : benzene = 2 : 1, 1 : 1, and 1 : 2. From these curves the values of the maximum reaction rates ($w_{\max}$) were obtained. From analogous curves for the oxidation of ethyl alcohol, the values of $w_{\max}$ were obtained at temperatures of 145, 200, and 232° and molar ratios alcohol : benzene = 8 : 1, 2 : 1, and 1 : 1. The dependence of $\lg w_{\max}$ on $1/T$ in experiments without dilution and with various dilutions of methyl ethyl ketone and ethyl alcohol with benzene is shown in Fig. 2, from which it is seen that, as the amount of benzene in the mixture increases, the activation energies of the oxidation processes of ethyl alcohol and methyl ethyl ketone increase.

A change in the dielectric constant of the medium has an analogous effect on the activation energy of the elementary chain-propagation reaction (E_2) in these processes. The value of E_2 was determined experimentally. It is known that the following expression can be written for the rate of oxidation (^{3})

$$w = \frac{k_2}{\sqrt{k_5}}[\mathrm{RH}]\sqrt{w_i}. \tag{3}$$

Here k_2 is the rate constant of the chain-propagation reaction, k_5 is the rate constant of chain termination, $[RH]$ is the concentration of the oxidized substance, and w_i is the rate of chain initiation. The rate of initiation was determined from the rate of consumption of α-naphthol introduced at the moment corresponding to the maximum oxidation rate. Substituting the obtained values of w_i and the known quantities $[RH]$ and w into equation (3), we obtain the value $k_2/\sqrt{k_5}$. The dependence $\lg k_2/\sqrt{k_5}$ on $1/T$ gives the values of E_2 (since it may be assumed that $E_5 \simeq 0$ (4)). By this method the values of E_2 were determined for the oxidation process of ethyl alcohol and methyl ethyl ketone at different dilutions with benzene (Fig. 3). From consideration of Table 1, in which all the obtained values of E_2 are collected, it follows that the value E_2, like E, increases as the oxidized substance is diluted with benzene, i.e., as the dielectric constant of the medium decreases.

From the standpoint of the general concepts developed for ionic reactions, where interaction of the ion–ion or ion–dipole type takes place, an increase in the polarity of the medium may either decrease the activation energy or increase it ($^{6-9}$). In cases where the activated complex is more polar than the initial substances, a decrease in the dielectric constant of the medium decreases the solvation of the activated complex more than the solvation of the initial substances, which leads to an increase in the activation energy of the reaction. In oxidation processes of me-

Fig. 1. Kinetic curves of oxidation of methyl ethyl ketone at 145° (1), 122° (2), and 100° (3). A—without solvent; , , and —at molar ratios methyl ethyl ketone : benzene 2 : 1, 1 : 1, and 1 : 2.

Figure 1

Figure 1: Figure 1

Table 1

Activation energies E and E_2 (kcal/mol) in the oxidation of solutions of methyl ethyl ketone and ethyl alcohol in benzene

Substance	Without solvent E	Without solvent E_2	8:1 E	8:1 E_2	2:1 E	2:1 E_2	1:1 E	1:1 E_2	1:2 E	1:2 E_2
Ethyl alcohol	5.7	4.5	9.1	6.9	11.8	9.2	17.5	14.3	17.5	–
Methyl ethyl ketone	11.6	6.6	–	–	12.8	7.8	14.2	9.2	15.09	9.9

til ethyl ketone and ethyl alcohol, the dipole moment of the activated complex of the limiting stage of the process (chain-propagation reaction 2) is much larger [5] than the dipole moments of the reacting substances (Table 2).

Table 2

Value of the dipole moments of the initial substances and of the activated complex of the chain-propagation reaction in the oxidation of ethyl alcohol and methyl ethyl ketone at different temperatures [5]

	Ethyl alcohol	Ethyl alcohol	Ethyl alcohol	Ethyl alcohol	Methyl ethyl ketone	Methyl ethyl ketone	Methyl ethyl ketone
	145°	170°	200°	232°	100°	122°	145°
$\mu_{\mathrm{RH}} \cdot 10^{18}$ CGSE	1.7	1.7	1.7	1.7	2.75	2.75	2.75
$\mu_{\mathrm{RO}_{12}} \cdot 10^{18}$ CGSE	2.3	2.3	2.3	2.3	4.4	4.4	4.4
$\mu^{*} \cdot 10^{18}$ CGSE	14.9	12.0	11.5	11.3	8.4	8.4	8.4

Fig. 2

Figure 2: Fig. 2

A decrease in the dielectric constant of the medium leads to an increase in the activation energy of the reaction. Thus, ideas concerning the influence of the polarity of the medium on the activation energy of ionic reactions prove applicable for explaining the influence of the polarity of the medium on the activation energy of radical reactions observed in the present work.

Fig. 2. Dependence of $\lg w_{\max}$ on $1/T$ in the oxidation of ethyl alcohol (left scale) and methyl ethyl ketone (right scale) without solvent (1, 5) and in benzene solutions at molar ratios ethyl alcohol : benzene 8 : 1 (2); 2 : 1 (3) and 1 : 1 (4) and methyl ethyl ketone : benzene 2 : 1 (6); 1 : 1 (7) and (1 : 2) (8)

A change in the dielectric constant of the medium affects the constants of the elementary reactions of chain propagation and chain termination in different ways. From Fig. 3 it is seen that the ratio of the constants $k_2/\sqrt{k_5}$ in the oxidation of ethyl alcohol decreases, while in the oxidation of methyl ethyl ketone it increases with decreasing dielectric constant of the medium.

In a recently published work [5] it was shown that the experimental values of w_2 (the rate of the reaction $RO_2\cdot + RH$), obtained in the oxidation of ethyl alcohol and methyl ethyl ketone at different dilutions with the nonpolar substance—benzene, fall well on straight lines in the coordinates

$\lg w_2 - \dfrac{\varepsilon - 1}{2\varepsilon + 1}$ (ε is the dielectric constant of the medium) at all temperatures studied. The equations of these straight lines may be written in the form

$$\lg w_2 = a + b\,\frac{\varepsilon - 1}{2\varepsilon + 1}.$$

The quantity a (the intercept cut off by the straight lines on the ordinate axis) is the value of $\lg w_2^0$ at $\varepsilon = 1$, when electrostatic interaction between molecules is completely absent. The experimental values of the quantities a and b are as follows:

	Ethyl alcohol	Ethyl alcohol	Ethyl alcohol	Ethyl alcohol	Methyl ethyl ketone	Methyl ethyl ketone	Methyl ethyl ketone
Temperature, °C	145	170	200	232	100	122	145
a	−9.0	−4.2	−2.6	−2.1	0.21	0.66	1.14
b	22.8	12.0	9.2	8.3	1.71	1.56	1.37

Plotting the dependence of a on $1/T$ (Fig. 3), we obtained for methyl ethyl ketone an activation energy $E = 15.1$ kcal/mol. From this there may be obtained

the true activation energy of the reaction $\mathrm{RO}_2^\bullet + \mathrm{RH}$ under conditions where polar factors play no role: $E_2^0 = E - \frac{1}{2}E_i = 15.1 - 5 = 10.1$ kcal/mole ($E_i = 10$ kcal/mole was determined from experimental data by formula (3)). The agreement of the values E_2^0 and E_2 at high dilution of methyl ethyl ketone with benzene serves as another confirmation of the correctness of our ideas about the reaction $\mathrm{RO}_2^\bullet + \mathrm{RH}$ as an interaction of two dipoles. In the oxidation of ethyl alcohol, the temperature dependence $\lg w_2^0$ does not obey the Arrhenius law. This was to be expected, since in this case the decrease in the rate of reaction (2) upon dilution with benzene is associated not only with a decrease in the dielectric constant of the medium, but also with a decrease in the degree of association of the alcohol molecules. A change in the polarity of the medium affects not only the activation energy, but also the pre-exponential factor in the expression for the rate constant of the chain-propagation reaction in the oxidation of methyl ethyl ketone and ethyl alcohol. Indeed, the rate of oxidation of methyl ethyl ketone upon dilution with benzene decreases by only a factor of 1.5. Meanwhile, an increase in the activation energy of this reaction from 6.6 to 9.9 kcal/mole should have led to a decrease in the rate of this reaction by at least a factor of 10^2. Similarly, the increase in the activation energy of the chain-propagation reaction for ethyl alcohol should have reduced the rate of its oxidation by $5 \cdot 10^5$ times. In the experiment, however, only a tenfold decrease in the oxidation rate of ethyl alcohol is observed upon its dilution with benzene. These discrepancies between the calculated and experimental values of the rates indicate that in the systems considered there is a so-called compensation effect. As the dielectric constant of the medium decreases, not only does the activation energy of chain propagation increase, but so does the pre-exponential factor in the expression for the rate constant of this reaction.

Fig. 3. Dependence of $\lg \frac{k_2}{\sqrt{k_5}}$ on $1/T$ in the oxidation of ethyl alcohol (left scale) and methyl ethyl ketone (right scale) without solvent $(1, 5)$ and in benzene solutions at molar ratios ethyl alcohol : benzene 8 : 1 (2); 2 : 1 (3) and 1 : 1 (4) and methyl ethyl ketone : benzene 1 : 2 (6). Straight line 7 is the dependence of $\lg w_2^0$ on $1/T$ in the oxidation of methyl ethyl ketone

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Institute of Chemical Physics
Academy of Sciences of the USSR

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