COUPLED OXIDATION OF BENZENE AND ETHANOL BY MOLECULAR OXYGEN

D.I. Metelitsa and V.N. Tyukalo

In the couple oxidation of aliphatic alcohols and aromatic compounds of the benzene series, the latter are hydroxylated by the HO₂⁻ radical, formed in the interaction of peroxy radicals of alcohol with hydrogen peroxide [1]. When the oxidation of aliphatic alcohols is coupled with benzene, the rate of accumulation of phenol and its concentration increase in the sequence: t-BuOH, MeOH, EtOH and i-PrOH, corresponding to the oxidizability of the alcohols. The purpose of this work was to study the kinetics of the coupled oxidation of benzene and ethanol, leading to phenol and acetic acid.

EXPERIMENTAL SECTION

The experiments were conducted in an autoclave at 110-215°C and an air pressure of 50 atm. A 150-ml portion of a mixture of ethanol (absolute) and benzene (cryoscopic) in a glass cylinder was inserted into a steel autoclave and mixed with air at a rate of no less than 60 liters/h. Acetaldehyde was determined by the method of gas-liquid chromatography on an LKhM-7A instrument with a 0.2 × 195 cm column, containing Tween-50 (10%) and apiezon-N (10%) on celite-545; temperature of evaporator 100°C, column temperature 54°C, flame-ionization detector. Acetic acid and ethyl acetate were determined together after saponification of ethyl acetate according to the procedure of [2]. Hydrogen peroxide was determined iodometrically. Phenol was determined by the method of gas-liquid chromatography on an instrument with a 0.2 × 200 cm column, containing polyethylene glycol adipate (20%) on celite; temperature of evaporator 250°C, column temperature 154°C.

Autooxidation of Mixtures of Benzene and Ethanol. The kinetics of the accumulation of the oxidation products is shown in Fig. 1. As a rule, the oxidation products are formed with autocatalysis; therefore, the process is characterized by the values of the maximum rate of accumulation of phenol \( w_{\text{PhOH}} \) and its maximum concentration \( [\text{PhOH}]_{\text{max}} \). The optimum ratio of the reagents in a mixture of benzene with ethanol according to \( w_{\text{PhOH}} \) and according to \( [\text{PhOH}]_{\text{max}} \) is a 4:1 ratio (by volume), which corresponds to 72.3 mole % benzene in solution. As can be seen from the dependence of \( w_{\text{PhOH}} \) and \( [\text{PhOH}]_{\text{max}} \) on the composition of the mixture to be oxidized (Fig. 2), the two quantities are correlated.

Mixtures of benzene (72.3 mole %) with ethanol were oxidized at various temperatures. From Table 1 it follows that 200°C is the optimum temperature of oxidation of mixtures of this composition.

<table>
<thead>
<tr>
<th>T., °C</th>
<th>( w_{\text{PhOH}} ) ( \times 10^6 ) moles/liter·sec</th>
<th>( w_{\text{PhOH}} ) ( \times 10^6 ) moles/liter·sec</th>
<th>( [\text{PhOH}]_{\text{max}} ) M</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>0.24</td>
<td>0.83</td>
<td>0.021</td>
</tr>
<tr>
<td>200</td>
<td>1.84</td>
<td>1.25</td>
<td>0.035</td>
</tr>
<tr>
<td>215</td>
<td>40.7</td>
<td>1.33</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Initiation of the Oxidation of Mixtures of Benzene and Ethanol. Cumyl peroxide (CP), recrystallized from ethanol, was used as the initiator. To establish the rates of initiation by CP in mixtures of ethanol with benzene (4:1 by volume), we determined the rate constant of initiation in the interval 115-144°C, using \( \alpha \)-naphthol as the inhibitor. It was assumed that one molecule of \( \alpha \)-naphthol is consumed according to the reaction with two radicals, i.e., the coefficient of inhibition \( f = 2 \). Experiments with the introduction...
of an inhibitor, the solution of which was dropped into the autoclave after heating, were conducted in an atmosphere of argon (48 atm). Figure 3 shows the temperature dependence of the rate constant of initiation $k_1$, from which the value of $k_1$ is obtained in general form:

$$k_1 = 1.2 \times 10^{14} \text{ exp} \left(-37 \ 000/RT\right) \text{ sec}^{-1}.$$  

The rate constant of initiation obtained agrees with the constants of the decomposition of CP, known in the literature [3, 4].

The use of an initiator ensures a constant rate of accumulation of oxidation products at the initial stages of the reaction. Initiated oxidation of mixtures of benzene and ethanol (4:1) at 135° showed that the initial rates of accumulation of all the oxidation products are directly proportional to the CP concentration in the interval 0.025-0.100 M, i.e., under these conditions (72.3 mole% benzene), there is a linear termination of chains (Fig. 4).

Under our conditions of initiated oxidation of mixtures of ethanol with benzene (4:1) (excess alcohol), using CP in the interval 115-144°, the termination of the chains is quadratic [1], and the rate of oxidation of the components is described by the formulas

$$W_0^{\text{EtOH}} = k_2/\sqrt{k_5} \left[\text{EtOH}\right]_0 V \sqrt{W_1},$$

$$W_0^{\text{PhOH}} = k_2/\sqrt{k_5} \left[\text{C}_6\text{H}_5\right]_0 V \sqrt{W_1},$$

where $k_2$ is the rate constant of chain propagation; $k_5$ is the rate constant of chain termination; $W_1$ is the rate of initiation. The results of the initiated oxidation of mixtures of ethanol with benzene (4:1) at various temperatures are given in Table 2.

From the data of Table 2 and the equations cited above, knowing $[\text{EtOH}]_0 = 13.70$ and $[\text{C}_6\text{H}_5]_0 = 2.25$ M, we can calculate $k_2/\sqrt{k_5}$ and $k_2'/\sqrt{k_5}$. From the temperature dependences of the quantities (see Fig. 3), we obtained these quantities in general form (liters/mole-sec)$^{1/2}$

$$k_2/\sqrt{k_5} = 1.8 \times 10^7 \text{ exp} \left(-20 \ 000 \pm 2000/RT\right),$$

$$k_2'/\sqrt{k_5} = 3.5 \times 10^9 \text{ exp} \left(-18 \ 000 \pm 2000/RT\right).$$

RESULTS AND DISCUSSION

On the basis of the mechanism assumed for the oxidation of alcohols [5] and our experimental results of this work and [1], the mechanism of the initiated oxidation of ethanol—benzene mixtures can be represented as follows: