RATE CONSTANTS AND MECHANISM OF REACTIONS OF OXYGEN ATOMS WITH ETHANOL AND PROPIONALDEHYDE

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There is no information in the literature on measurements of the rate constants of reactions of oxygen atoms with ethanol and propionaldehyde. Nor is there any information on the mechanism of these reactions. There are studies on measurements of the rate constants and studies on the mechanism of the reactions of oxygen atoms with lower homologs of these compounds: with methanol [1] and acetaldehyde [2-4]. A study of the mechanism of the reactions of oxygen atoms with CH₃OH and CH₃CHO indicated that although in the reaction with alcohol there is virtually a single reaction, proceeding with the formation of CH₂O and H₂O, in the reaction with CH₃CHO several reaction directions are possible [2-4]. Among the main directions are: the reaction producing acetic acid, as well as the reaction yielding formaldehyde, proceeding with cleavage of the C–C bond. In this work we measured the rate constants of the reactions of oxygen atoms with C₂H₅OH and C₂H₅CHO. Experiments were conducted directed toward elucidating the mechanism of these reactions.

EXPERIMENTAL

The experiments were conducted on a jet-type vacuum apparatus, a description of which is given in [5]. A high-voltage discharge in molecular oxygen served as the source of oxygen atoms. At the end of the experiment, the reaction products, frozen out in a trap cooled with liquid nitrogen, were analyzed. The acid was analyzed by titration with alkali with phenolphthalein; the amount of aldehyde was determined by titration with hydroxylamine hydrochloride. Formaldehyde was determined separately from the other aldehydes on a photoelectrocolorimeter after the reaction with chromotropic acid. In certain experiments, an analysis was made for carbon monoxide. In these cases, the stream of gas passed through the trap cooled by liquid nitrogen and thence through a tube filled with I₂O₅ and heated to 150°C. The carbon monoxide was oxidized to CO₂ on the I₂O₅. The CO₂ formed was frozen out in a second trap, cooled with liquid nitrogen, and was analyzed at the end of the experiment. The rate constants of the reactions of oxygen atoms were determined by the method published in [5, 6]. To determine the rate constant of the reaction of oxygen atoms with a molecule of the substance, it was necessary to measure the final concentration of the primary product (or sum of the primary products) as a function of the initial concentration of the starting material. If the final concentration of the sum of primary products is measured, then the rate constant of the reaction of the oxygen atom with the initial molecule is determined from the formula

$$\frac{1}{\Sigma_k} = \frac{a}{(O)₀} + \frac{[k_3 + k_4^M(0)₀]}{k(0)₀^2} \frac{a}{(O)₀}$$  \hspace{1cm} (1)$$

where Σ_k is the final concentration of the sum of primary products; (O)₀ is the initial concentration of oxygen atoms; (A)₀ is the initial concentration of the starting material; M is the concentration of the third particle; k₃ is the rate constant of linear destruction of oxygen atoms; k₄ is the rate constant of quadratic destruction of oxygen atoms; k is the reaction rate constant sought; a is a constant [5]. The rate constant of the reaction k is determined from the segment a/(O)₀ = b, intercepted on the Y-axis and the slope of the straight line in coordinates 1/Σ_k versus 1/(A)₀. The rate constant of the destruction of oxygen atoms, which enters into the value of the slope of the straight line (1), is measured for each value of k. A detailed description of the determination of the rate constant of the destruction of oxygen atoms is given in [7, 8].

In the reaction of oxygen atoms with ethanol, the main reaction products are aldehydes (formaldehyde and acetaldehyde). Figure 1 presents the dependence of the reciprocal of the final concentration of total
aldehydes upon the reciprocal of the initial ethanol concentration \([p = 4 \text{ mm Hg}; t = 70^\circ; k_0 = 125 \text{ sec}^{-1}\) (linear destruction of atoms predominates)]. From the graph of Fig. 1 we obtained a value of the rate constant for the reaction with \(\text{C}_2\text{H}_5\text{OH}\) at the temperature \(70^\circ\); \(k = 3.25 \times 10^{-14} \text{ cm}^3 \cdot \text{sec}^{-1} \cdot \text{molecule}^{-1}\). In the reaction of oxygen atoms with propionaldehyde, one of the main primary products is an acid. To determine the rate constant of the reaction of oxygen atoms with propionaldehyde, we measured the dependence of the final acid concentration on the original concentration of propionaldehyde. As was shown in [5], the summary rate constant of the reaction of \(\text{O} + \text{RH}\) can be measured according to any primary (or secondary) products, as well as according to their sum.

Figure 2 presents a graph of the dependence of the reciprocal of the final acid concentration on the reciprocal of the initial propionaldehyde concentration \([p = 4 \text{ mm}; t = 150^\circ; k_0 = 140 \text{ sec}^{-1}\). The rate constant for this temperature \(k = 6.2 \times 10^{-14} \text{ cm}^3 \cdot \text{sec}^{-1} \cdot \text{molecule}^{-1}\). For other temperatures, values of the reaction rate constants were obtained analogously.

Table 1 gives values of the rate constants of the reactions of oxygen atoms with ethanol and propionaldehyde, measured at different temperatures.

From Fig. 3 (straight line 1) we obtained the activation energy of the reaction of oxygen atoms with ethanol, which was equal to 4000 cal/mole. The following expression is obtained for the rate constant of the reaction of \(\text{O} + \text{C}_2\text{H}_5\text{OH}\):

\[
k_{\text{C}_2\text{H}_5\text{OH}} = 1.05 \times 10^{-14} e^{-rac{4000}{RT}} \text{ cm}^3\text{sec}^{-1}\cdot\text{molecule}^{-1}.
\] (2)

On the basis of straight line 2 (Fig. 3) we obtained the activation energy of the reaction of oxygen atoms with propionaldehyde, equal to 2850 \(\pm\) 250 cal/mole. The following expression was obtained for the rate constant of the reaction \(\text{O} + \text{C}_3\text{H}_5\text{CHO}\):

\[
k_{\text{C}_3\text{H}_5\text{CHO}} = 1.75 \times 10^{-12} e^{-rac{2850}{RT}} \text{ cm}^3\text{sec}^{-1}\cdot\text{molecule}^{-1}.
\] (3)

In order to draw conclusions on the mechanism of the reactions, we performed analyses of the reaction products.

Table 2 gives the results of an analysis of the principal reaction products of oxygen atoms with ethanol. In addition to aldehydes and carbon monoxide, an acid is detected in the reaction products, the amount of which is ten times smaller than the total aldehydes. As can be seen from Table 2, somewhat more acetaldehyde is obtained than formaldehyde; the amount of CO is approximately equal to the amount of \(\text{CH}_2\text{O}\). Acetaldehyde evidently is formed according to a reaction analogous to the formation of \(\text{CH}_2\text{O}\) from \(\text{CH}_3\text{OH}\) [1]

\[
\text{O} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + 100 \text{ kcal}.
\] (4)

The formation of formaldehyde is one of the characteristic reactions of oxygen atoms. It might be said that with each compound possessing C and H atoms, a molecule of \(\text{CH}_2\text{O}\) is formed in the reaction with