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Abstract

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THE REACTION OF THE ISOPROPYL RADICAL WITH THE OXYGEN MOLECULE

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There is no information in the literature on works devoted to the study of the direct interaction of isopropyl radicals with molecular oxygen. Studies of the photochemical oxidation of hydrocarbons can in no way be regarded as studies in which the direct interaction of aliphatic radicals and oxygen is investigated, since light acts not only on the hydrocarbons but also on oxygen ([1]), as well as on oxidation products, thereby forming new radicals and atoms, such as H and O. For this reason, in the photochemical method the reaction products are not separated into primary, secondary, quadratic, etc., and therefore it is difficult to draw unambiguous conclusions about the reaction mechanism. This applies especially to mercury-sensitized reactions.

We set ourselves the task of investigating the products of the reaction of the isopropyl radical with the oxygen molecule under the purest possible conditions, in which the action of light on the reaction products occurring under the conditions of photochemical experiments, as well as the formation of H and O atoms, would be excluded. For this purpose we used a method already employed by us ([2,3]) in studying the reactions of the ethyl radical with the oxygen molecule.

Experiment and discussion

The isopropyl radicals were obtained by us through the action of H atoms, drawn by a jet from a discharge in H_2, on propylene. A conical nozzle between the discharge and the reaction vessel made it possible to separate the zone in which H atoms were formed from the zone of the reaction

$$H + C_3H_6 \rightarrow \text{iso-}C_3H_7.$$

The surface of the reaction vessel was coated with KCl. The preferential formation of the isopropyl radical in the interaction

$$H + C_3H_6$$

was shown by the work of Bradley, Melville, and Robb ([4]). To avoid possible quadratic reactions

$$H + C_3H_7 \rightarrow CH_3 + C_2H_5$$

propylene was fed into the reaction zone in an amount of 0.3–0.5 mm Hg, which exceeded the concentration of hydrogen atoms by more than an order of magnitude. Special experiments–placing in the jet mirrors coated with soot–showed that, at such propylene feeds, hydrogen atoms were no longer detected at a distance of 2 cm from the point of mixing, which indicates their rapid reaction with propylene. In order to obtain reliable information on the reactions of aliphatic radicals with the oxygen molecule, the absence of H atoms in the zone where the radicals are mixed with the oxygen molecule is very important.

Therefore, in our experiments molecular oxygen was fed into the reaction zone at a distance of 2 or more centimeters from the nozzle. Feeding oxygen at such distances guaranteed the absence of interaction between H atoms and the O_2 molecule. It should be noted that such a guarantee is obtained only when there is no back diffusion of oxygen, which depends on the velocity of the carrier-gas jet and the oxygen concentration. The absence of H atoms in the reaction zone is important because, under jet conditions and at low tempe-

temperatures and pressures, as was shown by the authors of [5], the reaction of formation of oxygen atoms on the wall

$$H + O_2 + \text{wall} \rightarrow OH + O,$$

which makes its own contribution to the reaction products, takes place.

The presence of parallel reactions of oxygen atoms with hydrocarbons and of aliphatic radicals with molecular oxygen does not make it possible to obtain an unambiguous answer either about the reaction products or about the reaction mechanism.

Among the oxygen-containing products of the reaction of the isopropyl radical with the oxygen molecule, one might expect hydroperoxide, acetone, acetic and formic aldehydes, and isopropyl alcohol. The reaction products, together with propylene, were collected in a trap cooled with liquid nitrogen and then analyzed. Peroxide was determined polarographically and by titration of the liberated J_2 after addition of a KJ solution in an acid medium. Hydrogen peroxide was absent in our experiments. Acetone was determined by the furfural method. Aldehydes were analyzed by the polarographic method; in addition, formaldehyde was determined by means of a sensitive reaction (a solution of hydrochloric-acid phenylhydrazine + a solution of red blood salt + HCl). Isopropyl alcohol was detected qualitatively by reaction with *m*-nitrobenzaldehyde.

Table 1

Rate of O_2 feed, $1 \cdot 10^{-17}$ mol/sec	Rate of peroxide accumulation, $1 \cdot 10^{-16}$ mol/sec	Rate of acetone accumulation, $1 \cdot 10^{-16}$ mol/sec	Formation of aldehydes
5.48	0.31	0.1	Not detected
6.4	0.36	0.1	Not detected
8.2	0.29	0.1	Not detected

The results of analysis of the reaction products in several experiments are presented in Table 1. The experiments were carried out at a total pressure $P_{\text{ob}} = 8$ mm and a temperature of 150°. The propylene feed rate was $4.15 \cdot 10^{18}$ mol/sec. Oxygen was fed at a distance of 3 cm from the point of mixing of H atoms with propylene. Under these experimental conditions, peroxide, acetone, and isopropyl alcohol are found as products of the reaction of isopropyl radicals. Careful searches for aldehydes (formic and acetic) gave a negative result. Since peroxide is found in the reaction products, the formation of peroxy radicals iso-$C_3H_7O_2$ is beyond doubt. Assuming the occurrence of isomerization of the peroxy radical, one should expect the formation of a CH_3O radical and acetaldehyde; however, aldehydes are not formed under the conditions of our experiments. It could be thought that the reason for the absence of aldehydes was an insufficiently high temperature at which the iso-$C_3H_7O_2$ radical can decompose. Therefore, in order to study the properties of isopropylperoxy radicals at a temperature higher than 150°, a new temperature regime of the apparatus was created. First, at a distance of 9 cm from the nozzle in the reaction vessel, a temperature of 150° was maintained (under these conditions the iso-$C_3H_7O_2$ radical is formed, since peroxide is found in the reaction products), and then over the next 25 cm of the reaction vessel a temperature of 350° was maintained.

It was assumed that the peroxy radical formed in the 150° temperature zone would decompose as soon as it entered the zone at 350°, and that we would observe corresponding changes in the reaction products. In fact, such changes in the reaction products were observed experimentally, but not at all those that we expected. The results of the experiments under the new temperature conditions are set out in Table 2. These experiments were carried out at $P_{\text{ob}} = 8$ mm Hg. The propylene feed rate and the place where molecular oxygen was fed into the reaction zone were the same as in the experiments presented in Table 1.

As is seen from Table 2, the increase in temperature led to a decrease in the yield of peroxide by approximately a factor of 10; the decrease in acetone was insignificant, and at the same time aldehydes did not appear, despite our careful searches and expectations. Since raising the temperature to 350° led to ⋯

Table 2

Rate of O_2 supply, $1 \cdot 10^{-17}$ mol/sec	Rate of peroxide accumulation, $1 \cdot 10^{-16}$ mol/sec	Rate of acetone accumulation, $1 \cdot 10^{-16}$ mol/sec	Formation of aldehydes	Formation of isopropyl alcohol
5.5	0.03	0.08	Not detected	Not detected
6.5	0.03	–	Not detected	Not detected
5.5	–	0.08	Not detected	Not detected

leads to decomposition of the iso-$C_3H_7O_2$ radical (as evidenced by the sharp decrease in peroxide yield), but since aldehydes are not formed, an increase in isopropyl alcohol or acetone could have been expected. However, isopropyl alcohol was likewise not detected at this temperature, whereas at 150° the alcohol is detected, and the yield of acetone also decreases. This experimental fact indicates that at relatively low temperatures (150°) the iso-$C_3H_7O_2$ radical forms peroxide and alcohol in parallel reactions. It is natural to assume the following steps for the formation of these products:

$$\begin{array}{l} CH_3 - \underset{\underset{O - O}{|}}{CH} - CH_3 + H_2,\ (RH) \rightarrow CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 + OH \\ \qquad\qquad\qquad\qquad\qquad\qquad\downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad CH_3 - \underset{\underset{O - OH}{|}}{CH} - CH_3 + R \end{array}$$

Decomposition of the isopropylperoxy radical entails the disappearance of peroxide and alcohol as reaction products. Since aldehydes are also not formed in this case, it remains to assume that decomposition of the peroxy radical proceeds back to the isopropyl radical and molecular oxygen

$$\text{iso-}C_3H_7O_2 \rightarrow \text{iso-}C_3H_7 + O_2.$$

Explaining the disappearance of peroxide at 350° by decomposition of the peroxide itself contradicts experiment, since decomposition of the peroxide should not have been accompanied by disappearance of isopropyl alcohol.

As for the formation of acetone under the conditions of our experiments, we believe that it is formed on the surface, analogously to the way acetaldehyde is formed in the interaction of the ethyl radical with oxygen ([2,6]). However, while we were able to prove the formation of acetaldehyde on the KCl surface from C_2H_5 and O_2 by the fact that, by treating the reaction vessel and coating with KCl, we obtained only one hydroperoxide as the reaction product, in the case of the iso-$C_3H_7O_2$ reaction coating the vessel with KCl leads to disappearance of acetone from the reaction products. The absence of acetaldehyde formation in the reaction of iso-$C_3H_7 + O_2$ and the decomposition of the iso-$C_3H_7O_2$ radical with increasing temperature without the appearance of aldehydes and isopropyl alcohol provide grounds to assume that, if iso-$C_3H_7O_2$ radicals are formed, their further route of transformation consists either in the formation of hydroperoxide or in decomposition without formation of aldehydes and alcohols.

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