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Reactions of $C_2H_5O_2$ and C_2H_5 Radicals on Acidic and Basic Surface

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Abstract: The analysis and discussion of the kinetic data obtained by studying the effect of the nature of the reactor surface (H_3BO_3, KCl) on the oxidation of C_2H_5CHO allowed us to provide experimental evidence for the heterogeneous reaction of $C_2H_5O_2$ radicals with aldehyde and the heterogeneous formation of ethylene and hydroperoxide through the involvement of C_2H_5 radicals. In this context, elucidating the possibility of heterogeneous reactions involving $C_2H_5O_2$ and C_2H_5 radicals is important for advancing our understanding of the oxidation and ignition reactions of aldehydes. It was also concluded that the interaction of peroxy radicals with an organic compound is more general and not limited to CH_3O_2 radicals.

Key Words: reaction mechanism, radicals, oxidation and ignition reactions, surface

1. Introduction

The possibility, of heterogeneous interactions between CH_3O_2 radicals with aldehydes and hydrocarbons has been established in recent studies [1−9]. However, there is no direct evidence of such heterogeneous reactions concerning $C_2H_5O_2$ and C_2H_5 radicals. In this study, we sought to provide such evidence by analyzing and discussing the kinetic data obtained from the investigation of the influence of the reaction vessel surface (H_3BO_3, KCl) on the oxidation process of propionaldehyde at atmospheric pressure in air flow [10,11]. This reaction proceeds *via* a chain degenerate branching mechanism [12].

$$C_2H_5CO_3H \rightarrow C_2H_5CO_2 + OH \quad (1)$$
$$C_2H_5CO_2 \rightarrow C_2H_5 + CO_2 \quad (2)$$
$$C_2H_5 + O_2 \rightarrow C_2H_5O_2 \quad (3)$$

Eq. 1-3, where the branching stage at relatively low temperatures, involves the heterogeneous radical decay of $C_2H_5CO_3H$ (Eq. 1). The leading active centers in this process are $C_2H_5CO_3$ radicals (Eq. 1-3). As the oxidation process develops, the contribution of $C_2H_5O_2$ radicals, formed as a result of the heterogeneous decay of peracid, increases (Eq. 1).

Based on the dependence of the yields of such reaction products as ethylene and ethyl hydroperoxide on the nature of the reactor surface [10,11], it was possible to identify their heterogeneous formation with the participation of C_2H_5 radicals (Eq. 2, 3).

Gas-phase oxidation reactions of aldehydes, proceeding *via* a chain degenerate branching mechanism, are a source of valuable oxygen-containing compounds. Depending on the nature of the reaction vessel, both the rate and the direction of the process can change [12]. For example, during the oxidation of C_2H_5CHO in the boric acid-treated reactor, peroxypropionic acid ($C_2H_5CO_3H$) can be formed with high selectivity (80%), while in the potassium chloride-treated reactor, the selectivity for propionic acid ($C_2H_5CO_2H$) is 90%.

The heterogeneous reactions of peroxy radicals such as CH_3O_2 play a crucial role in the combustion of $CH_3CHO + O_2$ mixtures, initiated by peroxy radicals formed during the heterogeneous radical decay of RCO_3H [13].

Thus, investigating the possibility of heterogeneous reactions involving $C_2H_5O_2$ (Eq. 3) and C_2H_5 (Eq. 2) radicals is essential for understanding the mechanism of oxidation and combustion reactions of aldehydes.

2. Results and Discussion

Reaction of $C_2H_5O_2$ Radical with Aldehyde on Solid Surface

Figures 1 and 2 demonstrate the kinetic curves of the consumption of C_2H_5CHO and the accumulation of some reaction products including peroxy radicals, $C_2H_5CO_3H$ and $C_2H_5O_2H$, obtained in the aforementioned two reactors at 291°C [11].

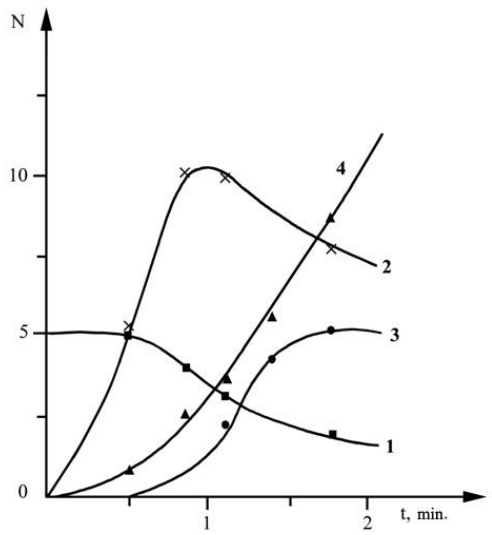

Fig. 1. Kinetic Curves of C_2H_5CHO Consumption (1) and of Accumulation of Peroxy Radicals (2), RCO_3H (3), RO_2H (4) at T = 291°C in the Reactor, Treated by Boric Acid. $[C_2H_5CHO] = N \times 10^{17}$, [radical] = $N \times 10^{12}$, $[RCO_3H]$ and $[RO_2H] = N \times 10^{16}$ part.cm^{-3}.

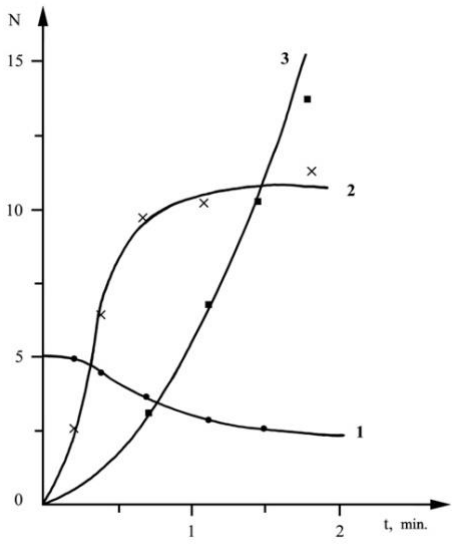

Fig. 2. Kinetic Curves of C_2H_5CHO Consumption (1) and of Accumulation of Peroxy Radicals (2), RO_2H (3) at T = 291°C in a Reactor Treated by KCl. $[C_2H_5CHO] = N \times 10^{17}$, [radical] = $N \times 5 \times 10^{11}$, $[RO_2H] = N \times 2 \times 10^{16}$ part.cm^{-3}.

Table 1 shows the concentrations of reaction products at 291°C and 1 minute of reaction time in reactors treated by boric acid and potassium chloride.

Table 1. Concentrations of Reaction Products at 291°C and t = 1 min (reaction time) in Reactors Treated by Boric Acid and Potassium Chloride; $[C_2H_5CHO]_0 = 5 \times 10^{17}$ part.cm^{-3}

Surface	KCl (part.cm^{-3})	H_3BO_3 (part.cm^{-3})
$[C_2H_5CHO]_t$	3×10^{17}	3.6×10^{17}
$[RCO_3H]$	–	1.5×10^{16}
$[RO_2H]_t$	1.07×10^{17}	3.2×10^{16}
$[RCO_3 + RO_2]_t$	5.2×10^{12}	1.02×10^{13}
$[C_2H_4]_t$	2.3×10^{16}	–
$[CO_2]_t$	2.04×10^{17}	3×10^{16}

This data indicates that the process characteristics strongly depend on the nature of the surface. This applies both to the composition of the reaction products and to the absolute values of products concentrations. Notably, $C_2H_5CO_3H$ is absent in the reactor treated with KCl. This is attributed to a higher rate of heterogeneous radical decay of the peracid on the KCl surface in compared to the H_3BO_3 surface [14]. The high yield of CO_2, formed during the decay of peracid in the reactor, further supports this. Consequently, the process in the KCl-treated reactor begins earlier than in the H_3BO_3-treated reactor, and even at t = 1 min the aldehyde consumption is 1.4 times greater than that in a boric acid-treated reactor. It is noteworthy that the concentration of peroxy radicals in the volume is less by approximately 2 times. This clearly indicates that a significant portion of the aldehyde in the KCl-treated reactor is consumed on the reactor surface. The yield of hydroperoxide is almost three times higher than in the reactor treated with boric acid.

Apparently, a significant contribution to the formation of hydroperoxide is linked to the heterogeneous interaction of $C_2H_5O_2$ radicals with propionaldehyde. The presence of ethylene in the KCl-treated reactor and its absence in the boric-acid reactor, also suggests that more C_2H_5 radicals were formed in the first reactor. It is important to note that the reactions of C_2H_5 radicals are the source of both ethylene and $C_2H_5O_2$ radicals.

Regarding the H_3BO_3 surface, since it is known that the rate of $C_2H_5CO_3H$ heterogeneous radical decomposition on this surface is much slower than that on the KCl surface, it is evident that the amount of formed $C_2H_5O_2$ radicals on the H_3BO_3 surface should be significantly lower. Therefore, the yield of hydroperoxide is also lower.

A comparison of the kinetic curves for the accumulation of peroxy radicals in both reactors and, considering the significant

amounts of $C_2H_5CO_3H$ in the boric acid-treated reactor, shows that the ratio of $C_2H_5CO_3$ and $C_2H_5O_2$ radical concentrations is higher in the boric acid-treated reactor.

Analysis of the kinetic data on propionaldehyde oxidation depending on the nature of the surface, reliably indicates the possibility of heterogeneous interaction between $C_2H_5O_2$ radicals and aldehyde-C_2H_5CHO. Thus, we conclude that the interaction of peroxy radicals with organic compounds is more general and is not limited to CH_3O_2 radicals.

Heterogeneous Reaction Pathways of C_2H_5 Radicals on a Solid Surface

This work presents data on the heterogeneous formation of several reaction products, such as C_2H_4 and $C_2H_5O_2H$, during the low-temperature oxidation of propionaldehyde. These results were obtained by analyzing the kinetic patterns of the process in reactors treated with boric acid and potassium chloride [10].

Fig. 3 and 4 illustrate the kinetics of peroxy radicals formation and the initial aldehyde consumption while the concentrations of some reaction products for a fixed reaction time are shown in the Table 2.

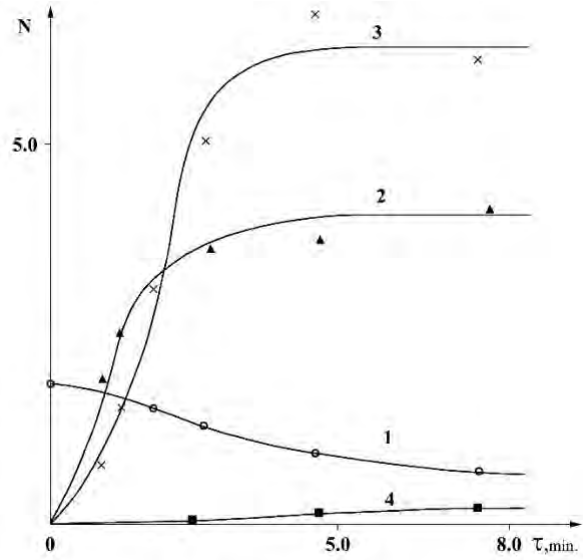

Fig. 3. Kinetic Curves of C_2H_5CHO (1) Consumption and of Peroxy Radicals (2), $C_2H_5CO_3H$ (3), C_2H_4, CO (4) Accumulation at 175°C in a Boric Acid Treated Reactor. $[C_2H_5CHO] = N \times 10^{18}$, $[RCO_3H] = N \times 2 \times 10^{16}$, $[RO_2] = N \times 4 \times 10^{12}$, $[C_2H_4] = N \times 10^{17}$, part.cm^{-3}.

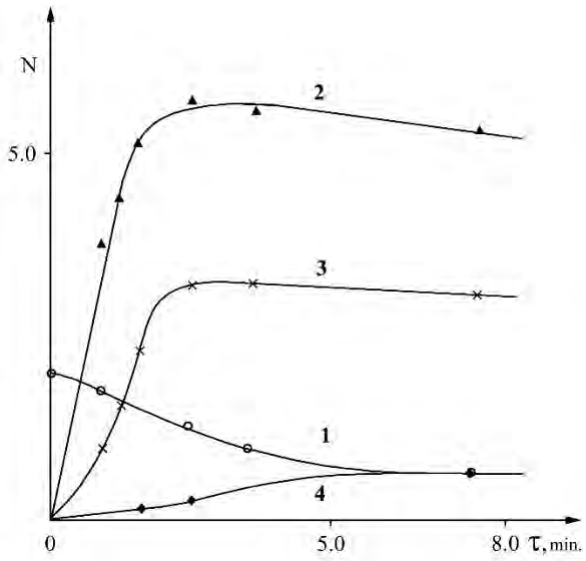

Fig. 4. Kinetic Curves of C_2H_5CHO (1) Consumption and of Peroxy Radicals (2), $C_2H_5CO_3H$ (3), $C_2H_5O_2H$ (4) Accumulation at 175°C in a Reactor Treated by KCl. $[C_2H_5CHO] = N \times 10^{18}$, $[RCO_3H] = N \times 2 \times 10^{16}$, $[RO_2] = N \times 4 \times 10^{12}$, $[C_2H_5O_2H] = N \times 10^{17}$, part.cm^{-3}.

Table 2. The Concentrations of the Reaction Products at 175°C and at Reaction Time t = 5 min in Reactors Treated by H_3BO_3 and KCl; $[C_2H_5CHO]_0 = 1.9 \times 10^{18}$ part.cm^{-3}

Surface	KCl (part.cm^{-3})	H_3BO_3 (part.cm^{-3})
$[C_2H_5CHO]_t$	7.5×10^{17}	9.3×10^{17}
$[C_2H_5CO_3H]_t$	6.2×10^{16}	1.3×10^{17}
$[C_2H_5CO_2H]_t$	8.4×10^{17}	3.9×10^{17}
$[RO_2]_t$	2.1×10^{13}	1.6×10^{13}
$[C_2H_4]_t$	-	1.7×10^{16}
$[CO_2]_t$	8.5×10^{16}	6×10^{16}
$[CH_3CHO]_t$	1.8×10^{17}	9.3×10^{15}

Comparison of the results obtained in the two reactors reveals that the rate of the process in the potassium chloride-treated reactor is higher than in the boric acid-treated reactor, while the yield of $C_2H_5CO_3H$ product responsible for the branching is much lower. This was not unexpected, as the rate of heterogeneous radical decay of peracids is greater in a reactor treated with potassium chloride [14].

The data indicates that the concentration of peroxy radicals such as $C_2H_5CO_3$ and $C_2H_5O_2$ [10] in the given volume, correlates

with the rate of oxidation in these reactors, and is higher in the reactor treated by potassium chloride.

An important feature of the process is the detection of ethylene and the absence of hydroperoxide in the boric acid-treated reactor. Conversely, in the potassium chloride-treated reactor, hydroperoxide is detected while ethylene is absent. This suggests that there are heterogeneous pathways for the formation of these compounds. Possible pathways for the formation of these compounds are:

1. $RCO_3H \rightarrow RCO_2 + OH \rightarrow R + CO_2 + OH$
2. $R + O_2 \rightarrow RO_2$
3. $RO_2 + RCHO \rightarrow RO_2H + RCO$
4. $R \rightarrow C_2H_4 + H$
5. $R + O_2 \rightarrow C_2H_4 + HO_2$, where R is a C_2H_5 radical

It is noteworthy that comparison of the yields of ethylene and hydroperoxide with those obtained during the oxidation of C_2H_5CHO in the same reactors at 291°C [11], reveals that the concentration of hydroperoxide is higher in the reactor treated with potassium chloride, although a certain amount of it is also already registered in the reactor treated with boric acid. As for ethylene, it is formed at higher temperatures in the potassium chloride-treated reactor. The obtained data show that the competition between reactions 2. and reactions 4. and 5. favor of 2. on the KCl surface.

3. Conclusion

Thus, this study allows us to conclude that the heterogeneous reactions of $C_2H_5O_2$ and C_2H_5 radicals play a crucial role in the gas-phase oxidation of C_2H_5CHO, contributing to the formation of several reaction products.

Declaration of competing interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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