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Abstract

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DETERMINATION OF THE RATE CONSTANTS OF ELEMENTARY REACTIONS OF ATOMIC HYDROGEN AND OXYGEN WITH ETHYLENE

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The reactions of atomic hydrogen and oxygen with ethylene are the most important stages of the hydrogenation and chain oxidation of unsaturated hydrocarbons. Many works are known in the literature devoted to these reactions and to the determination of their rate constants ($^{1-9}$). Most of them were carried out at low temperatures, and the values of the constants and activation energies obtained by different authors agree poorly with one another. Only in the work of N. N. Tikhomirova and V. V. Voevodskii (^{6}) was the rate constant of atomic hydrogen with ethylene determined at high temperatures (550-650°). In it, in comparison with analogous studies carried out at low temperatures, the highest activation energy was obtained, which indicates a possible change in the mechanism of the reaction of interaction of H with ethylene. If at low temperatures it is undoubted that hydrogen atoms add to ethylene, forming ethyl radicals, then at high temperatures the process of hydrogen abstraction from the ethylene molecule by the reaction $H + C_2H_4 = H_2 + C_2H_3$ is more probable.

Our work, undertaken with the aim of determining the rate constants of atomic hydrogen and oxygen with ethylene in the temperature region 570-660°, is based on measurements of the first limits of self-ignition of hydrogen-oxygen mixtures and mixtures of carbon monoxide with oxygen (^{10,12}) in the presence of small additions of ethylene. The mechanism of hydrogen combustion above the first self-ignition limit in the presence of small additions of ethylene may be represented by the following sequence of elementary reactions:

$$\begin{array}{rl}
\mathrm{OH} + \mathrm{H_2} = \mathrm{H_2O} + \mathrm{H}; & \text{(I)} \\
\mathrm{H} + \mathrm{O_2} = \mathrm{OH} + \mathrm{O}; & \text{(II)} \\
\mathrm{O} + \mathrm{H_2} = \mathrm{OH} + \mathrm{H}; & \text{(III)} \\
\mathrm{H} + \text{wall} \to \text{destruction}; & \text{(IV)} \\
\mathrm{H} + \mathrm{C_2H_4} = \mathrm{H_2} + \mathrm{C_2H_3}; & \text{(VI)} \\
\mathrm{C_2H_3} + \mathrm{O_2} = \text{destruction}; & \text{(VII)} \\
\mathrm{C_2H_3} + \mathrm{O_2} = \mathrm{C_2H_2O} + \mathrm{OH}. & \text{(VIII)}
\end{array}$$

In this scheme it is taken into account that hydrogen atoms, along with destruction at the wall of the reaction vessel (reaction (IV)), may perish in the volume as a result of reaction (VI). In this case new, although comparatively less reactive, radicals C_2H_3 arise, which then perish mainly by reaction (VII), but sometimes may, as a result of reaction (VIII), regenerate the OH radical, which is one of the carriers of the chain oxidation of hydrogen.

From the scheme given, taking into account the condition of the ignition limit, one can obtain the following equation of the lower limit, relating the oxygen concentration (O_2) at the limit to the ethylene concentration (C_2H_4)

$$[\mathrm{O_2}] = \frac{(k_4)_{\mathrm{H_2}}}{2k_2} + \frac{k_6[\mathrm{C_2H_4}]}{2k_2}\,\frac{1}{1 + k_8/k_7}. \qquad (1)$$

where k_i are the rate constants of the corresponding elementary reactions.

It follows from equation (1) that as the concentration of ethylene in the reacting mixture increases, the limiting concentration of oxygen will increase.

At constant temperature, in the coordinates $[\mathrm{O_2}]$, $[\mathrm{C_2H_4}]$, expression (1) is the equation of a straight line cutting off on the ordinate axis a ···

zone, numerically equal to $[O_2]_{\mathrm{H2}} = (k_4)_{\mathrm{H2}}/2k_2$ (13), with the tangent of the angle of inclination

$$\operatorname{tg}\alpha = \frac{k_6}{2k_2}\,\frac{1}{1 + k_8/k_7}. \qquad (2)$$

In the case $k_8 = 0$ it is not difficult, knowing k_2 and determining from experimental data the angle of inclination α, to calculate k_6. Since, however, in the general case $k_8 \neq 0$, an independent determination of the ratio is necessary:

$$\frac{k_8}{k_7} = \frac{k_6}{2k_2\operatorname{tg}\alpha} - 1. \qquad (3)$$

For this purpose one may use the condition for the first ignition limit of a mixture of carbon monoxide with oxygen in the presence of small additions of ethylene. The combustion mechanism of such mixtures may be written as the following sequence of elementary reactions:

$\mathrm{OH + CO = CO_2 + H}$ (I)
$\mathrm{H + O_2 = OH + O}$ (II)
$\mathrm{O + C_2H_4 = OH + C_2H_3}$ (III)
$\mathrm{H + wall \rightarrow death}$ (IV)
$\mathrm{O + wall \rightarrow death}$ (V)
$\mathrm{H + C_2H_4 = C_2H_3 + H_2}$ (VI)
$\mathrm{C_2H_3 + O_2 \rightarrow death}$ (VII)
$\mathrm{C_2H_3 + O_2 = C_2H_2O + OH}$ (VIII).

The equation of the first ignition limit, after replacing the concentrations $[O_2]$ and $[C_2H_4]$ by partial pressures and substituting the value $k_8/k_7 = k_6/2k_2 \operatorname{tg}\alpha - 1$, in the case of the death of H and O atoms on the surface in the diffusion region, takes the form

$$\frac{Pp_{O_2}}{Pp_{C_2H_4} + \dfrac{(k_4^0)^{\mathrm{CO}}T^{2.5}}{10^{19}\cdot 2k_2 \operatorname{tg}\alpha}} = \frac{1}{\dfrac{1}{\operatorname{tg}\alpha} - \dfrac{k_2}{k_6}}\left[1 + \frac{(k_5^0)^{\mathrm{CO}}T^{2.5}}{k_3\cdot 10^{19}Pp_{C_2H_4}}\right], \tag{4}$$

where P is the pressure at the first ignition limit of carbon monoxide in the presence of ethylene, and p_{O_2} and $p_{C_2H_4}$ are, respectively, the partial pressures of oxygen and ethylene at this limit. At constant temperature, in the coordinates $Pp_{O_2}\xi;\ 1/Pp_{C_2H_4}$, where

$$\xi = \frac{1}{Pp_{C_2H_4} + \dfrac{(k_4^0)^{\mathrm{CO}}T^{2.5}}{10^{19}\cdot 2k_2 \operatorname{tg}\alpha}},$$

expression (4) is the equation of a straight line cutting off on the ordinate axis the segment

$$b = \frac{1}{1/\operatorname{tg}\alpha - k_2/k_6} \tag{5}$$

with angular coefficient

$$\operatorname{tg}\gamma = \frac{1}{1/\operatorname{tg}\alpha - k_2/k_6}\,\frac{(k_5^0)^{\mathrm{CO}}T^{2.5}}{k_3\cdot 10^{-19}}. \tag{6}$$

It follows from (6) and (7) that

$$\lg\frac{\operatorname{tg}\gamma}{bT^{2.5}} = \lg\frac{(k_5^0)^{\mathrm{CO}}}{k_3^0\cdot 10^{19}} + \frac{E}{2.3R}\,\frac{1}{T}. \tag{7}$$

In the coordinates $\lg \frac{bT^{2.5}}{\operatorname{tg}\gamma}$; $1/T$, according to expression (7), it is not difficult to find E_3 from the angle of inclination, and from the segment cut off on the ordinate axis, k_3^0, since the value k_5^0 is known (10,12).

Thus, from the displacement of the ignition limit of mixtures of carbon monoxide with oxygen and hydrogen with oxygen in the presence of small additions of ethylene, the rate constant of reaction (III) can be determined.

Substituting in (3) the value of k_6 from (5), we have $k_8/k_7 = b/2(b - \operatorname{tg}\alpha) - 1$. Substituting this value into equation (1), with replacement of the concentrations $[O_2]$ and $[C_2H_4]$ by pressures, and also taking into account that the death of H atoms by reaction (IV) occurs in the diffusion region, we obtain the following condition for the lower ignition limit of a hydrogen-oxygen mixture in the presence of ethylene:

$$Pp_{O_2} = \frac{(k_4^0)^{\mathrm{H_2}} T^{2.5}}{2k_2 \cdot 10^{19}} \left(1 + \frac{k_6 \cdot 10^{19} Pp_{C_2H_4}}{(k_4^0)^{\mathrm{H_2}} T^{2.5}} \frac{2(b - \operatorname{tg}\alpha)}{b} \right). \tag{8}$$

In the coordinates $Pp_{\mathrm{O_2}}$; $Pp_{\mathrm{C_2H_4}}$, expression (8) represents the equation of a straight line cutting off on the ordinate axis a segment

$$a = \frac{(k_4^0)^{\mathrm{H_2}} T^{2.5}}{2k_2 \cdot 10^{19}} \tag{9}$$

with angular coefficient

$$\operatorname{tg}\alpha = \frac{(k_4^0)^{\mathrm{H_2}} T^{2.5}}{2k_2 \cdot 10^{19}} \frac{k_6 \cdot 10^{19}}{(k_4^0)^{\mathrm{H_2}} T^{2.5}} \frac{2(b - \operatorname{tg}\alpha)}{b}. \tag{10}$$

From (10) and (11) we obtain

$$\lg \frac{\operatorname{tg}\alpha T^{2.5}}{a} = \lg \frac{k_6^0 \cdot 10^{19}}{(k_4^0)^{\mathrm{H_2}}} \frac{2(b - \operatorname{tg}\alpha)}{b} - \frac{E_6}{2.3R} \frac{1}{T}. \tag{11}$$

In the case where the ratio $\frac{b - \operatorname{tg}\alpha}{b}$ changes little with temperature, in the coordinates $\lg \frac{\operatorname{tg}\alpha T^{2.5}}{a}$; $\frac{1}{T}$ we obtain a straight line, from whose slope one can find E_6, and from the segment cut off on the ordinate axis, k_6^0.

The experimental procedure has been described earlier (10).

Figs. 1 and 2 present plots of the first self-ignition limits of the mixtures $2H_2 + O_2 + nC_2H_4$ and $2CO + O_2 + nC_2H_4$. From Fig. 1 it is seen that, as the ethylene content in the hydrogen-oxygen mixture increases, the limit rises. In the mixture

Fig. 1 and Fig. 2 plots

Figure 1: Fig. 1 and Fig. 2 plots

Figure 3

Figure 2: Figure 3

of carbon monoxide with oxygen, however, an increase in the concentration of ethylene leads at first to a gradual lowering of the lower ignition limit (Fig. 2), and then, in accordance

Fig. 1. Dependence of the first ignition limits on temperature for mixtures $2H_2 + O_2$, (1) and $2H_2 + O_2 + nC_2H_4$, where n (in %) = 0.41 (2); 0.675 (3); 0.93 (4); 1.41 (5); 1.87 (6); 2.3 (7)

Fig. 2. Dependence of the first ignition limits on temperature for mixtures $2CO + O_2 + nC_2H_4$, where n (in %) = 0.036 (1); 0.053 (2); 0.066 (3); 0.088 (4); 0.12 (5); 0.16 (6)

with the combustion mechanism of CO considered above, the limit begins to rise. The lowering of the lower self-ignition limit of the mixture $2CO + O_2$ in the presence of small additions of ethylene is direct confirmation of the decisive role of reaction (3) in the combustion mechanism of carbon monoxide.

Figure 3 presents the dependence of Pp_{O_2} on $Pp_{C_2H_4}$, calculated for the mixtures $2H_2 + O_2 + nC_2H_4$ at different temperatures. From this plot it is seen that, in accordance with the requirements of the theory, the dependence is linear in character.

From the slope of the straight lines obtained, the values of $\operatorname{tg}\alpha$ and $\operatorname{tg}\gamma$ for different temperatures and the corresponding values of the intercepts a and b were determined. In accordance with equations (VII) and (XI), straight lines were obtained.

From the slope of the straight lines and the intercepts cut off by them on the ordinate axis, the values of the activation energies E_3 and E_6, as well as the pre-exponential factors k_3^0 and k_6^0, were found.

Fig. 3. Dependence of Pp_{O_2} on $Pp_{C_2H_4}$ for mixtures $2H_2 + O_2 + nC_2H_4$, at different temperatures.
1–600°C, 2–610°, 3–620°, 4–630°, 5–640°, 6–650°, 7–660°, 8–670°, 9–680°.

The rate constant of the reaction of atomic hydrogen with ethylene is

$$k_6 = (1.5 \pm 0.5) \cdot 10^{-11} e^{-\frac{7200 \pm 500}{RT}} \text{ cm}^3/\text{molecule} \cdot \text{sec}.$$

The rate constant of the reaction of atomic oxygen with ethylene is

$$k_3 = (2.3 \pm 0.8) \cdot 10^{-1} e^{-\frac{8100 \pm 500}{RT}} \text{ cm}^3/\text{molecule} \cdot \text{sec.}$$

The value we found, $E_6 = 7200$ cal, for the activation energy of atomic hydrogen with ethylene is in good agreement with $E_6 = 6600$, determined by Tikhomirova and Voevodskii (^{6}). Despite the difference in methods, almost identical activation energies were obtained in the same temperature range, 550–660°. The value we determined for the activation energy of the reaction of atomic hydrogen with ethylene differs considerably from the corresponding quantities obtained at low temperatures. Evidently, as noted above, at high temperatures the mechanism of interaction changes. If at low temperatures the reaction of addition of atomic hydrogen to ethylene predominates, then at high temperatures the reaction leading to the formation of the vinyl radical and molecular hydrogen predominates.

It should be noted that the activation energy determined at low temperatures for the reaction of atomic oxygen with ethylene ($^{7-9}$) is also considerably lower than that obtained by us.

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