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Abstract

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Determination of the Rate Constant of the Reaction of Atomic Oxygen with Molecular Hydrogen

The reaction of atomic oxygen with molecular hydrogen, with formation of hydroxyl radicals and hydrogen atoms,

$$O + H_2 = OH + H \qquad \text{(III)}$$

plays an essential role in the mechanism of a number of oxidation processes. However, this reaction has been studied quite inadequately, and there are no reliable data in the literature on the magnitude of its rate constant. The value of the activation energy assigned to this reaction was determined from the temperature dependence of the rate of interaction of oxygen atoms with hydrogen molecules in only one work ([1]), where the rate of formation of water was taken as this rate. It cannot, however, be certain that the obtained value $E = 6 \pm 1$ kcal/mole actually pertains precisely to the elementary reaction (III). In addition, in estimating E the authors used data referring to two temperatures out of the three at which measurements were carried out. The values of the preexponential factor calculated by various authors ([2–4]) differ greatly (from 10^{-14} to 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}).

The method we used to determine the value of the rate constant of reaction (III) is based on measuring the first ignition limit of mixtures of carbon monoxide with oxygen in the presence of small additions of hydrogen, shifting as the amount of the latter changes.

The ignition limits of mixtures of carbon monoxide and oxygen containing hydrogen, and the kinetic regularities within the ignition peninsula, can be explained with the aid of the following mechanism, based on the mechanism proposed by Buchler and Norrish ([5]), Kondrat' ev ([6]), and Enikolopyan and Nalbandyan ([7]):

$$
\begin{aligned}
H_2 + O_2 &= 2OH; && (0)\\
OH + CO &= CO_2 + H; && (I)\\
H + O_2 &= OH + O; && (II)\\
O + H_2 &= OH + H; && (III)\\
H + \text{wall} &\rightarrow \text{destruction}; && (IV)\\
O + \text{wall} &\rightarrow \text{destruction}; && (V)\\
H + O_2 + M &= H_2O + M; && (VI)
\end{aligned}
\qquad
\begin{aligned}
OH + H_2 &= H_2O + H; && (VII)\\
O + O_2 + M &= O_3 + M; && (VIII)\\
O + CO + M &= CO_2 + M; && (IX)\\
O_3 + M &= O_2 + O + M; && (X)\\
O_3 + CO &= CO_2 + O_2; && (XI)\\
O + O_3 &= 2O_2. && (XII)
\end{aligned}
$$

From the critical ignition condition ([8]), one can obtain the expression for the ignition limit

$$(O_2) = \frac{k_{IV}}{2k_{II}}\left[1 + \frac{k_{VI}(O_2)(M)}{k_{IV}}\right] \times \left[1 + \frac{k_V + k_{VIII}(O_2)(M) + k_{IX}(CO)(M) + k_{XII}(O_3)}{k_{III}(H_2)}\right], \tag{1}$$

where k_i are the rate constants of the corresponding reactions.

It is easy to show that at the first ignition limit the quantity $k_{VI}(O_2)(M)/k_{IV}$ is equal to the ratio of the first ignition limit of a mixture of carbon monoxide with oxygen to the second ignition limit of a mixture of hydrogen with oxygen. This means that at temperatures much higher than the peninsula-tip temperature of ignition, $k_{VI}(O_2)(M)/k_{IV} \ll 1$.

At pressures close to the first ignition limit, as is known, among the chain-termination reactions an essential role is played by termination reactions at the surface. Consequently, the quantities $k_{VIII}(O_2)(M)$, $k_{IX}(CO)(M)$, and $k_{XII}(O_3)$ may be neglected in comparison with k_V. This is also confirmed by comparison of the values of these quantities corresponding to the first ignition limit. Then expression (1) is rewritten in the form

$$(O_2) = \frac{k_{IV}}{2k_{II}}\left[1 + \frac{k_V}{k_{III}(H_2)}\right]. \tag{2}$$

In the case where reactions (IV) and (V) proceed in the diffusion region,

$$k_{IV} = \frac{23.2}{d^2}D_H, \qquad k_V = \frac{23.2}{d^2}D_O$$

(for a cylindrical vessel) ([3]), where D_H and D_O are the diffusion coefficients of H atoms and O atoms, respectively. Substituting these values of k_{IV} and k_V into (2), taking into account the dependence of the diffusion coefficients on temperature and pressure, and replacing the concentrations (O_2) and (H_2) by partial pressures, we obtain

$$Pp_{O2} = \frac{k^0_{IV} T^{2.5}}{2k_{II} \cdot 0.97 \cdot 10^{19}} \left(1 + \frac{k^0_V T^{2.5}}{k_{III} \cdot 0.97 \cdot 10^{19}} \frac{1}{Pp_{H2}}\right). \tag{3}$$

In this equation P, P_{O2}, and P_{H2} are, respectively, the total pressure of the mixture and the partial pressures of oxygen and hydrogen at the first ignition limit,

$$k^0_{IV} = \frac{23.2}{d^2} (D_H)^{CO} \frac{760}{(273)^{1.5}}, \tag{4}$$

$$k^0_V = \frac{23.2}{d^2} (D_O)^{CO} \frac{760}{(273)^{1.5}}, \tag{5}$$

where $(D_H)^{CO}$ and $(D_O)^{CO}$ are the diffusion coefficients of H atoms and O atoms under normal conditions.

According to (3), in the diffusion region of heterogeneous chain termination at the first limit, Pp_{O2} at constant temperature must depend linearly on $\frac{1}{Pp_{H2}}$. Hence, by measuring the first ignition limit of mixtures of carbon monoxide and oxygen with various additions of hydrogen, from the graph of the dependence of Pp_{O2} on $\frac{1}{Pp_{H2}}$ one can find

$$b = \frac{k^0_{IV} T^{2.5}}{2k_{II} \cdot 0.97 \cdot 10^{19}} \tag{6}$$

as the magnitude of the intercept cut off by the straight line on the ordinate axis, and

$$\operatorname{tg} \alpha = \frac{k^0_{VI} T^{2.5}}{2k_{II} \cdot 0.97 \cdot 10^{19}} \frac{k^0_V T^{2.5}}{k_{III} \cdot 0.97 \cdot 10^{19}}, \tag{7}$$

where α is the angle of inclination to the abscissa axis.

It follows from (6) and (7) that

$$\frac{\operatorname{tg} \alpha}{b} = \frac{k^0_V T^{2.5}}{k_{III} \cdot 0.97 \cdot 10^{19}} = \frac{k^0_V T^{2.5}}{k^0_{III} \cdot 0.97 \cdot 10^{19} \exp(-E_{III}/RT)}$$

or

$$\lg \frac{\operatorname{tg} \alpha}{bT^{2.5}} = \lg \frac{k^0_V}{k^0_{III} \cdot 0.97 \cdot 10^{19}} + \frac{E_{III}}{3RT}, \tag{8}$$

where E_{III} is the activation energy of reaction (III).

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Thus, having the values of $\operatorname{tg}\alpha$ and b at different temperatures, one can calculate E_{III} from (8), and, calculating k_V^0 from (5), determine the value of k_{III}^0. Thus, by measuring the first ignition limit of mixtures of CO and O_2 containing various additions of hydrogen in the diffusion region of heterogeneous chain termination, one can determine both the value of the activation energy and the value of the preexponential factor of the rate constant of reaction (III).

The experiments were carried out in a standard vacuum static apparatus. To determine the ignition limit, the reaction mixture from a reservoir was introduced into a transfer volume and then injected into an evacuated quartz vessel, 34 mm in diameter, heated to the required temperature.

Fig. 1. First ignition limits of mixtures $1.9\,H_2 + O_2$ (curve 1) and mixtures $2CO + O_2 + xH_2$ at values of x (in %):
2 –0.76; 3 –1.02; 4 –1.47; 5 –2.34; 6 –3.30; 7 –3.95; 8 –5.34; 9 –8.04.

Fig. 2. Dependence of Pp_{O_2} on $\dfrac{1}{Pp_{H_2}}$ for mixtures $2CO + O_2 + xH_2$ at temperatures: 1 –570°; 2 –580°; 3 –590°; 4 –600°; 5 –610°; 6 –630°; 7 –640°; 8 –650°; 9 –660°.

Treatment of the vessel surface with magnesium oxide, which strongly accelerates the destruction of active centers on the surface (9–11), ensured that heterogeneous chain termination proceeded in the diffusion region. This could be concluded from the high values of the limits, their good reproducibility, and the lowering of the limit upon dilution of the mixture with an inert gas.

Figure 1 presents the dependence of the first ignition limit on temperature for mixtures $2CO+O_2$ containing various additions of hydrogen. From the obtained values of the limits P, Pp_{O_2} and $\dfrac{1}{Pp_{H_2}}$ were calculated; the dependence between them for different temperatures is presented in Fig. 2. From this figure it is seen that, in accordance with equation (3), this dependence is linear. Taking into account that for a hydrogen-oxygen mixture $k_{\text{IV}}/2k_{\text{II}} = (O_2)_{H_2}$, where $(O_2)_{H_2}$ is the oxygen concentration at the first ignition limit of the hydrogen-oxygen ⋯ mixture, (6) can be represented in the form

$$b = p^{H_2} P_{O_2} \frac{(D_H)^{CO}}{(D_H)^{H_2}}, \tag{9}$$

where P^{H_2} and $P_{O_2}^{H_2}$ are the total pressure of the mixture and the partial pressure of oxygen at the first ignition limit of the hydrogen-oxygen mixture; $(D_H)^{CO}$ and $(D_H)^{H_2}$ are the diffusion coefficients of H atoms through a mixture of carbon

Fig. 3. Dependence of $\lg \frac{\tan \alpha}{bT^{2.5}}$ on $\frac{1}{T}$

Figure 2: Fig. 3. Dependence of $\lg \frac{\tan \alpha}{bT^{2.5}}$ on $\frac{1}{T}$

monoxide with oxygen and of hydrogen with oxygen, respectively. Thus, if the method set forth is valid, the quantity b, found from the values of the first ignition limits of CO + O_2 mixtures with various additions of hydrogen according to Fig. 2, should be determined independently from (9) from the value of the ignition limit of the hydrogen-oxygen mixture.

The values of b, determined at different temperatures by these two independent methods, differ by no more than 10%.

Thus, the validity of the method is confirmed both by the linear dependence between Pp_{O_2} and $\frac{1}{Pp_{H_2}}$, and by the agreement (to within the accuracy of determination of the diffusion coefficients of H atoms) of the values of b determined by independent routes.

Fig. 3. Dependence of $\lg \frac{\tan \alpha}{bT^{2.5}}$ on $\frac{1}{T}$

In Fig. 3 is shown the dependence of $\lg \frac{\tan \alpha}{bT^{2.5}}$ on $\frac{1}{T}$, where the quantities $\tan \alpha$ and b were determined graphically in Fig. 2. From the slope of the straight line in Fig. 3, according to expression (8), E_{III} was calculated, which proved to be 12.3 ± 0.2 kcal/mole, while from the intercept cut off by the same straight line on the ordinate axis the quantity k^0_{III} was found to be $1.55 \cdot 10^{-10}$ cm^3 molecule^{-1} sec^{-1}. For mixtures $3CO + O_2$ with various additions of hydrogen, $E_{III} = 12.0 \pm 0.2$ kcal/mole, $k^0_{III} = 1.45 \cdot 10^{-10}$ cm^3 molecule^{-1} sec^{-1} were obtained. Thus,

$$k_{III} = 1.5 \cdot 10^{-10} \exp\left(-\frac{12100 \pm 400}{RT}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}.$$

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