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Abstract

Full Text

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DETERMINATION OF THE RATE CONSTANT OF THE REACTION OF ATOMIC OXYGEN WITH ETHANE

(Presented by Academician V. N. Kondrat' ev, July 4, 1962)

There are very few works devoted to the reaction of atomic oxygen with ethane. Harteck and Kopsch ([1]) showed that oxygen atoms interact with ethane even at room temperature. The activation energy, estimated from the amount of ethane that entered into reaction (assuming a steric factor equal to 0.1), is about 7 kcal/mole. This reaction was also studied by Avramenko and Kolesnikova ([2]), and comparatively recently by Myorad and Noyes ([3]); however, in these works the rate constant was not determined.

To determine the rate constant of this reaction we used the method of shifting the lower self-ignition limit of mixtures of carbon monoxide with oxygen in the presence of small additions of various substances that can serve as hydrogen donors ([4]). It was shown earlier ([5,6]) that, in dilute flames of carbon monoxide with oxygen, in the presence of small amounts of hydrogen in the reacting system, high concentrations of atomic hydrogen and oxygen arise. If it is assumed that, in the case of small additions of ethane as a hydrogen donor to a mixture of CO with O_2, the lowering of the ignition limit occurs as a result of the reaction $O + C_2H_6 = OH + C_2H_5$, then the mechanism of CO combustion near the first self-ignition limit may be represented as the following set of elementary reactions:

Fig. 1. Dependence of the lower self-ignition limit of mixtures of concentration C_2H_6 (in vol. %) on temperature and on x:

1–x = 0.0225, 2–x = 0.0389, 3–x = 0.0555, 4–x = 0.074, 5–x = 0.097, 6–x = 0.141, 1′–x = 0.252, 2′–x = 0.345, 3′–x = 0.50

$$OH + CO = CO_2 + H \tag{1}$$

$$H + O_2 = OH + O \tag{2}$$

$$O + C_2H_6 = OH + C_2H_5 \tag{3}$$

$$H + \text{wall} = \text{destruction} \tag{4}$$

$$O + \text{wall} = \text{destruction} \tag{5}$$

$$H + C_2H_6 = H_2 + C_2H_5 \tag{6}$$

The substitution reaction ([6]), leading to the replacement of the active H atom by the less active radical C_2H_5, should be regarded as a chain-termination reaction ([7–9]).

The scheme does not take into account the destruction of OH radicals, since (OH) $\ll$ (H) and (O), because the rate constant of reaction (2) is much smaller than the rate constant of reaction (1) ([4,10,11]), and the concentration of carbon monoxide is much greater than the concentration of ethane. The scheme under consideration also does not take into account chain-termination reactions occurring in triple collisions, since near the first limit the rate of heterogeneous chain termination is much greater than the rates of termination occurring in the gas phase.

On the basis of the mechanism given above, it should be expected that the effect of ethane on the first ignition limit of CO with O_2 will be twofold. With small additions of ethane, the increase in the concentration of the latter in the reacting mixture will accelerate the reaction and lower the ignition limit. With large

additions an increase in the ethane concentration will inhibit the reaction and raise the limit.

On the basis of the scheme presented for the combustion of carbon monoxide and the critical condition for self-ignition, it is not difficult to derive an equation for the lower limit, which may be written in the following form

$$(O_2) = \frac{k_4}{k_2}\left[1 + \frac{k_6(C_2H_6)}{k_4}\right]\left[1 + \frac{k_5}{k_3(C_2H_6)}\right], \tag{A}$$

Fig. 2. Dependence of the lower self-ignition limit on the ethane content in a mixture of $2CO + O_2$ at different temperatures: 1–640°, 2–630°, 3–650°

Figure 2: Fig. 2. Dependence of the lower self-ignition limit on the ethane content in a mixture of $2CO + O_2$ at different temperatures: 1–640°, 2–630°, 3 –650°

where (O_2) and (C_2H_6) are the concentrations of oxygen and ethane at the limit; k_i are the rate constants of the corresponding elementary processes. The dual action of ethane on the self-ignition limit of CO with O_2 is clearly seen from equation (A). At very small additions of (C_2H_6), as this addition increases the limiting oxygen concentration will decrease, while at relatively large additions of ethane, as the magnitude of the addition increases, the oxygen concentration at the limit will rise.

Fig. 2. Dependence of the lower self-ignition limit on the ethane content in a mixture of $2CO + O_2$ at different temperatures: 1–640°, 2–630°, 3–650°.

Analysis of equation (A) shows that if the dependence of (O_2) on (C_2H_6) is found experimentally over a sufficiently wide temperature range and the values of the constants k_4, k_5, and k_6 are used, then the rate constant of reaction (3)

$$O + C_2H_6 = OH + C_2H_5$$

can be determined. The value of the constant k_6 is taken from literature data ([7,9]); the constants k_4 and k_5 can be calculated if reactions (4) and (5) are made to proceed in the diffusion region, as was done in work ([4]). If the dependence of the diffusion coefficients on temperature and pressure is taken into account and one passes from concentrations to pressures, equation (A) is rewritten as:

$$\frac{pp_{O2}}{1+\beta} = \frac{k_4^0 \cdot T^{2.5}}{10^{19} \cdot k_2}\left[1 + \frac{k_5^0 \cdot T^{2.5}}{k_3 \cdot 10^{19} \cdot pp_{C2H_6}}\right], \tag{B}$$

where p is the total pressure of the mixture, and p_{O2} and p_{C2H_6} are the partial pressures of oxygen and ethane, respectively, at the lower self-ignition limit. The expressions denoted by k_4^0 and k_5^0 are:

$$k_{het}^0 = \frac{23.2}{d^2}\frac{760}{(273)^{1.5}}D_{760}^{273}, \tag{V}$$

where D_{760}^{273} is the diffusion coefficient of the corresponding atoms (H or O) under normal conditions, and $d = 55$ mm is the diameter of the reaction vessel:

$$\beta = \frac{k_6 \cdot 10^{19} \cdot pp_{O2}}{k_4^0 \cdot T^{2.5}}.$$

It follows from equation (B) that, at each given temperature, $\frac{pp_{O2}}{1+\beta}$ must be linearly related to $\frac{1}{pp_{C2H_6}}$. In equation (B) the slope is equal to

$$\operatorname{tg}\alpha = \frac{k_4^0 \cdot T^{2.5}}{10^{19} \cdot k_2} \cdot \frac{k_5^0 \cdot T^{2.5}}{10^{19} \cdot k_3}. \tag{G}$$

Denoting the intercept cut off on the ordinate axis by

$$b = \frac{k_4^0 \cdot T^{2.5}}{10^{19} \cdot k_2},$$

we obtain:

$$\lg \frac{\operatorname{tg}\alpha}{b \cdot T^{2.5}} = \lg \frac{k_5^0}{k_3^0 \cdot 10^{19}} + \frac{E_3}{2.3 \cdot R} \cdot \frac{1}{T}, \tag{D}$$

where E_3 and k_3^0 are the activation energy and the pre-exponential factor of the rate constant of reaction (3).

From the slope of the straight line in the coordinates $\lg \frac{\operatorname{tg}\alpha}{b \cdot T^{2.5}} \left(\frac{1}{T}\right)$, it is possible to determine the is-

···the sought value E_3 of the activation energy of reaction (3), and from the intercept cut off by this straight line on the ordinate axis, and from k_5^0, calculated by (B), the pre-exponential factor k_3^0.

A check on the correctness of the reaction scheme for CO oxidation in the presence of small additions of ethane may be, as was shown in work ([1]), the condition:

$$b = \frac{k_4^0 \cdot T^{2.5}}{10^{19} \cdot k_2} = 2\,\frac{D_H^{CO}}{D_H^{H_2}} \cdot p^{H_2} p_{O_2}^{H_2}, \tag{E}$$

where p^{H_2} is the total pressure of the mixture, $p_{O_2}^{H_2}$ is the partial pressure of oxygen at the first limit of ignition of the hydrogen–oxygen mixture, and D_H^{CO} and $D_H^{H_2}$ are the diffusion coefficients of H atoms in the mixtures $2CO + O_2$ and $2H_2 + O_2$, respectively.

Results of experiments and discussion

The experimental procedure has been described earlier ([1]). To ensure the occurrence of reactions (4) and (5) in the diffusion region, the reactor ($d = 55$ mm) was coated with magnesium oxide. It had previously been noted that, below the

lower ignition limit in a heated reaction vessel coated with magnesium oxide, after admission of the mixture a slow pressure drop is observed, which in the present case had to be taken into account in order to establish the correct value of the limits at different temperatures.

Fig. 3. Dependence of

$$\frac{pp_{O_2}}{1+\beta} \quad \text{on} \quad \frac{1}{pp_{C_2H_6}}$$

at different temperatures, °C: 1–590, 2–610, 3–620; 4–630, 5–640, 6–650, 7–660.

In Fig. 1 a series of curves is given for the dependence of the lower ignition limit of $2CO + O_2$ on temperature in the presence of different additions of ethane. From Fig. 1 it is seen that, as the ethane content is increased to 0.14% in the mixture (curves 1–6), the lower limit decreases. However, with a further increase in the concentration of ethane in the mixture (curves 1′–3′) the reverse phenomenon occurs–an increase of the limit. The dual action of ethane is seen more clearly from Fig. 2, which gives curves for the dependence of the lower limit on the ethane concentration, obtained for 3 temperatures. All of them have a clearly expressed minimum at a definite ethane concentration, different at different temperatures.

Table 1

T, °C	b, mm^2	$1.4 \cdot p^{H_2} \times p^{H_2}_{O_2}$, mm^2	T, °C	b, mm^2	$1.4 \cdot p^{H_2} \times p^{H_2}_{O_2}$, mm^2
590	25	29.6	650	17	20.4
610	21.5	25.5	660	16.5	19.6
630	19	22.5			

In Fig. 3 the dependence is presented of

$$\frac{pp_{O_2}}{1+\beta} \quad \text{on} \quad \frac{1}{pp_{C_2H_6}}$$

for 7 temperatures, obtained on the basis of the experimental data shown in Fig. 1. To determine the value of β, use was made of k_6, determined in work ([9]). In accordance with requirement (B), the experimental data fit well on straight lines. These lines cut off on the ordinate axis segments "b," which, as noted above, must satisfy equality (E).

Table 1 gives the values of b, obtained from the intercepts in Fig. 3 for different temperatures. Alongside are given the corresponding values of $p^{H_2} \cdot p^{H_2}_{O_2}$, deter-

Fig. 4. Dependence of $\lg \frac{\operatorname{tg}\alpha \cdot 10^9}{b \cdot T^{2.5}}$ on $1/T \cdot 10^3$ for mixtures $2CO + O_2 + xC_2H_6$.

Figure 3: Fig. 4. Dependence of $\lg \frac{\operatorname{tg}\alpha \cdot 10^9}{b \cdot T^{2.5}}$ on $1/T \cdot 10^3$ for mixtures $2CO + O_2 + xC_2H_6$.

obtained by an independent measurement of the lower flammability limit of the hydrogen-oxygen mixture (1) and multiplied by the correction factor. As we see, the discrepancy is comparatively small, and, consequently, the limiting condition (E) is also satisfied. From the slopes of the straight lines in Fig. 3 the values of $\operatorname{tg}\alpha$ were calculated for different temperatures, as well as the dependence of

$$\lg \frac{\operatorname{tg}\alpha}{T^{2.5} \cdot b}$$

on $1/T$, which is shown in Fig. 4. In accordance with equation (E), all the points fit well on a straight line. From its slope we find $E_3 = 7500 \pm 600$ cal/mole and, from the intercept cut off on the ordinate axis, $k_3^0 = 1.4 \pm 0.5 \cdot 10^{-10}$ cm$^3 \cdot$ molecule$^{-1} \cdot$ sec^{-1}. Thus, in general for the rate constant of reaction (3) we have:

$$k_3 = (1.4 \pm 0.6) \cdot 10^{-10} \exp\left(\frac{-7500 \pm 600}{RT}\right) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}. \quad (\,)$$

Fig. 4. Dependence of $\lg \frac{\operatorname{tg}\alpha \cdot 10^9}{b \cdot T^{2.5}}$ on $1/T \cdot 10^3$ for mixtures $2CO + O_2 + xC_2H_6$.

According to equation ( ):

$$\lg \frac{b}{T^{2.5}} = \lg \frac{k_4^0}{k_2^0 \cdot 10^{19}} + \frac{E}{2.3RT},$$

where E_2 and k_2^0 are the activation energy and pre-exponential factor of the rate constant of reaction (2). The dependence of $\lg \frac{b}{T^{2.5}}$ on $1/T$ is indeed linear. From the slope of the straight line and the intercept it cuts off on the ordinate axis, we find

$$k_2 = (0.65 \pm 0.3) \cdot 10^{-10} \exp\left(\frac{-15000 \pm 600}{RT}\right) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1},$$

i.e., a value very close to those known from the literature ([4,12]). The agreement obtained again confirms the correctness of the above-proposed mechanism of CO combustion in the presence of ethane. The value of k_3 can also be determined by another method, if the critical concentration of ethane is known that produces

the maximum decrease in the lower flammability limit of carbon monoxide at a given temperature (Fig. 2).

Indeed, differentiating expression (A) with respect to (C_2H_6) and setting it equal to zero, after transformation we obtain:

$$k_3 = \frac{k_4 \cdot k_5}{k_6 (C_2H_6)^2_{\min}}. \tag{3}$$

The values of k_3 determined from (3) for different temperatures are in good agreement with the value of k_3 calculated from ( ). Thus, at 923°K the value of k_3 from (3) is $3.5 \cdot 10^{-12}$ cm$^3 \cdot$ molecule$^{-1} \cdot$ sec^{-1}, while from ( ) it is $2.5 \cdot 10^{-12}$ cm$^3 \cdot$ molecule$^{-1} \cdot$ sec^{-1}.

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