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Abstract

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DETERMINATION OF THE RATE CONSTANTS OF THE REACTIONS OF H AND O ATOMS WITH THE NH_3 MOLECULE

The elementary reactions of H and O atoms with ammonia have been poorly studied, and the available literature data on them are contradictory.

Böhm and Bonhoeffer (^{1}) found that at room temperature hydrogen atoms almost do not react with ammonia. Dixon (^{2}) observed the occurrence of a slow reaction under conditions in which preheated ammonia was fed into a jet of hydrogen atoms drawn out of a discharge, and gave an estimate of the lower limit of the activation energy, 8.5 kcal/mole. Schiavello and Volpi (^{3}) found the rate constant of the reaction $H + NH_3 = H_2 + NH_2$ at 150° to be $1.66 \cdot 10^{-17}$ cm^3/molecule • sec and estimated the interval of possible values of the activation energy as 10–15 kcal/mole.

The reaction of atomic oxygen with ammonia has been studied by a number of authors. Garteck and Kopsch (^{4}) observed in this reaction the formation of a small amount of nitrous acid. Avramenko, Kolesnikova, and Kuznetsova (^{5}) studied the interaction of oxygen atoms with ammonia in the range 348–458° K. According to their data, the reaction proceeds without activation energy, with a rate constant of $1.84 \cdot 10^{-14}$ cm^3/molecule • sec.

Uong and Potter (^{6}) showed that the main products of the reaction are water and nitric oxide. For the rate constant of the reaction they obtained the value

$$k = (5 \pm 2.5) \cdot 10^{-12} e^{-(4800 \pm 1500)/RT} \ \text{cm}^3/\text{molecule} \cdot \text{sec}.$$

From this brief review it is clear that there are no unambiguous data in the literature on the rate constants of the elementary reactions of H and O atoms with NH_3, and that the available studies were carried out chiefly at comparatively low temperatures.

In the present work we describe the results of experiments to determine the rate constants of the above-mentioned reactions at high temperatures (590–690°) by the method of ignition limits ($^{7-9}$). Previously, in a rarefied flame of $2CO + O_2 + NH_3$, by the EPR method at a temperature of 670°, a volumetric jet velocity of 53.4 cm^3/min ($v_l = 5.4$ m/sec), and a pressure of 8 mm Hg, signals of H and O* atoms were registered; their concentration reached 10^{14} particles/cm^3.

At small ammonia contents in the reacting mixture, the concentration of active centers increased with increasing NH_3. The first self-ignition limits of the mixtures $2H_2+O_2+NH_3$ and $2CO+O_2+NH_3$, measured in a quartz vessel ($d = 80$ mm, $l = 195$ mm), as a function of the NH_3 concentration are presented in Figs. 1 and 2. The vessel for transferring the loss of active centers into the diffusion region was coated with magnesium oxide. The regularities obtained are well explained by generally accepted schemes for the combustion of hydrogen ($^{10-12}$) and carbon monoxide ($^{13-15}$).

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* The work on detecting H and O atoms by the EPR method was carried out jointly with V. V. Azatyan.

For combustion of $H_2 + O_2 + NH_3$

$$OH + H_2 = H_2O + H; \tag{I}$$

$$H + O_2 = OH + O; \tag{II}$$

$$O + H_2 = OH + H; \tag{III}$$

$$H + \text{wall} \rightarrow \text{termination}; \tag{IV}$$

$$H + NH_3 = H_2 + NH_2; \tag{VI}$$

$$NH_2 + O_2 = OH + HNO; \tag{VII}$$

$$NH_2 + O_2 \rightarrow \text{products}. \tag{VIII}$$

For combustion of $CO + O_2 + NH_3$

$$OH + CO = CO_2 + H; \tag{Ia}$$

$$H + O_2 = OH + O; \tag{II}$$

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

$$\mathrm{O} + \mathrm{NH_3} = \mathrm{OH} + \mathrm{NH_2}; \tag{IIIa}$$

$$\mathrm{H} + \text{wall} \rightarrow \text{termination}; \tag{IV}$$

$$\mathrm{O} + \text{wall} \rightarrow \text{termination}; \tag{V}$$

$$\mathrm{H} + \mathrm{NH_3} = \mathrm{H_2} + \mathrm{NH_2}; \tag{VI}$$

$$\mathrm{NH_2} + \mathrm{O_2} = \mathrm{OH} + \mathrm{HNO}; \tag{VII}$$

$$\mathrm{NH_2} + \mathrm{O_2} \rightarrow \text{products}. \tag{VIII}$$

The inhibiting action of an ammonia additive in the $H_2 + O_2$ mixture is associated with reaction (VI), which competes with the branching reaction (II). As a result of elementary act (VI), the more reactive hydrogen atom is replaced by the less reactive NH_2 radical. The dual action of ammonia on the ignition limit of $CO + O_2$ can be explained by reactions (IIIa) and (VI). Reaction (IIIa) is the elementary act that realizes the branching process (II). The inhibiting action of large concentrations of NH_3 is due to reaction (VI).

Fig. 1. Dependence of the first ignition limits of mixtures $2H_2 + O_2 + xNH_3$ on temperature. Values of x in %:
1 –0.0; 2 –2.5; 3 –5.0; 4 –7.5; 5 –10.

Fig. 2. Dependence of the first ignition limits for mixtures $2CO + O_2 + xNH_3$ on temperature. Values of x in %:
1 –0.5; 2 –0.75; 3 –1.5; 4 –3.5; 5 –4.5; 6 –6.0; 7 –9.0; 8 –12.0.

Reaction (VII) has been introduced into the combustion schemes of H_2 and CO. This reaction takes into account the possibility of occasional regeneration of an active center–the carrier of the chain oxidation of hydrogen with oxygen and of carbon monoxide with oxygen. From the combustion schemes given, one can obtain expressions for the lower self-ignition limits ([7,9,10,11]). To eliminate the

Fig. 3

Figure 3: Fig. 3

ratio $k_{\mathrm{VII}}/k_{\mathrm{VIII}}$ from the equation for the lower limit of the mixture $2\mathrm{CO} + \mathrm{O}_2 + \mathrm{NH}_3$, following (^{9,16}), this ratio, obtained from the limit equation for the mixture $E\mathrm{H}_2 + \mathrm{O}_2 + \mathrm{NH}_3$, was substituted into it:

$$P^{\mathrm{H}_2} \cdot P^{\mathrm{H}_2}_{\mathrm{O}_2} = \frac{(k^0_{\mathrm{IV}})^{\mathrm{H}_2}_{\mathrm{NH}_3} T^{2.5}}{2k_{\mathrm{II}} \cdot 10^{19}} + \frac{k_{\mathrm{VI}} P^{\mathrm{H}_2} \cdot P^{\mathrm{H}_2}_{\mathrm{NH}_3} k_{\mathrm{VIII}}}{2k_{\mathrm{II}} \left[k_{\mathrm{VIII}} + k_{\mathrm{VII}}\right]}. \tag{1}$$

The resulting equation has the form:

$$\frac{P^{\mathrm{CO}} \cdot P^{\mathrm{CO}}_{\mathrm{O}_2}}{\beta + P^{\mathrm{CO}} \cdot P^{\mathrm{CO}}_{\mathrm{NH}_3}} = \frac{k_{\mathrm{VI}}}{k_{\mathrm{VI}}/b^{\mathrm{H}_2} - k_{\mathrm{II}}} \left[1 + \frac{(k^0_{\mathrm{V}})^{\mathrm{CO}}_{\mathrm{NH}_3} T^{2.5}}{10^{19} k_{\mathrm{IIIa}} P^{\mathrm{CO}} \cdot P^{\mathrm{CO}}_{\mathrm{NH}_3}}\right], \tag{2}$$

where

$$\beta = \frac{(k^0_{\mathrm{IV}})^{\mathrm{CO}}}{(k^0_{\mathrm{IV}})^{\mathrm{H}_2}} \frac{a^{\mathrm{H}_2}}{b^{\mathrm{H}_2}}.$$

The indices CO and H_2 indicate that the quantities refer to the mixtures $2\mathrm{CO} + \mathrm{O}_2$ and $2\mathrm{H}_2 + \mathrm{O}_2$, respectively; $P^{\mathrm{H}_2}_{\mathrm{O2}}$, $P^{\mathrm{CO}}_{\mathrm{O2}}$, $P^{\mathrm{H}_2}_{\mathrm{NH3}}$, and $P^{\mathrm{CO}}_{\mathrm{NH3}}$ are the partial pressures, respectively, of oxygen and ammonia; P^{H_2} and P^{CO} are the total pressures at the limits of the corresponding mixtures; a^{H_2}, a^{CO} and b^{H_2}, b^{CO} are the intercepts and angular coefficients of equations (1) and (2), respectively. $(k^0_{\mathrm{IV}})^{\mathrm{H}_2}_{\mathrm{NH3}}$ and $(k^0_{\mathrm{V}})^{\mathrm{CO}}_{\mathrm{NH3}}$ are quantities constant for a given vessel and mixture composition, determined from the known formulas (8).

Fig. 3. Dependence of $P^{\mathrm{H}_2} \cdot P^{\mathrm{H}_2}_{\mathrm{O2}}$ on $P^{\mathrm{H}_2} P^{\mathrm{H}_2}_{\mathrm{NH3}}$ for mixtures $2\mathrm{H}_2 + \mathrm{O}_2 + x\mathrm{NH}_3$ at temperatures: 1 –690°; 2 –760°; 3 –650°; 4 –630°; 5 –610°; 6 –590°; 7 – 570°.

The numerical values of a^{CO} and b^{CO} make it possible to determine k_{IIIa} from the condition

$$\lg \frac{b^{\mathrm{CO}}}{a^{\mathrm{CO}} T^{2.5}} = \lg \frac{(k^0_{\mathrm{V}})^{\mathrm{CO}}_{\mathrm{NH3}}}{k^0_{\mathrm{IIIa}} \cdot 10^{19}} + \frac{E_{\mathrm{IIIa}}}{2.303RT}. \tag{3}$$

The expression for a^{CO} can be written in the form:

$$\lg \left(\frac{1}{b^{\mathrm{H}_2}} - \frac{1}{a^{\mathrm{CO}}}\right) = \lg \frac{k^0_{\mathrm{II}}}{k^0_{\mathrm{VI}}} - \frac{E_{\mathrm{II}} - E_{\mathrm{VI}}}{2.303RT}. \tag{4}$$

Let us first consider how the experimental data satisfy equation (1). Figure 3 presents the dependence of $P^{\mathrm{H}_2} \cdot P^{\mathrm{H}_2}_{\mathrm{O2}}$ on $P^{\mathrm{H}_2} \cdot P^{\mathrm{H}_2}_{\mathrm{NH3}}$ at various temperatures. According to (1), the intercepts a^{H_2} must satisfy the condition:

$$a^{\mathrm{H}_2} = P^{\mathrm{H}_2} \cdot P^{\mathrm{H}_2}_{\mathrm{O2}} \frac{(D_{\mathrm{H}})^{\mathrm{H}_2}_{\mathrm{NH3}}}{(D_{\mathrm{H}})^{\mathrm{H}_2}} = \frac{(k^0_{\mathrm{IV}})^{\mathrm{H}_2}_{\mathrm{NH3}} T^{2.5}}{2k_{\mathrm{II}} \cdot 10^{19}}. \tag{5}$$

$(D_{\mathrm{H}})^{\mathrm{H}_2}_{\mathrm{NH3}}/(D_{\mathrm{H}})^{\mathrm{H}_2} = 0.96$ is a small correction that takes into account the change in the diffusion coefficient of the H atom with change in the mixture composition. In our case the mixture contained, on average, about 6% NH_3.

Table 1 gives a series of values of the intercepts a^{H_2} and of the product $P^{\mathrm{H}_2} \cdot P^{\mathrm{H}_2}_{\mathrm{O2}}(D_{\mathrm{H}})^{\mathrm{H}_2}_{\mathrm{NH3}}/(D_{\mathrm{H}})^{\mathrm{H}_2}$ at various temperatures.

For the calculation of k_{IIIa} (k'_{IIIa} and k_{IIIa}), equation (2) was used. In Fig. 4, in the coordinates $C+m$, $\dfrac{1}{P^{\mathrm{CO}} \cdot P^{\mathrm{CO}}_{\mathrm{NH3}}}$ $\left(C = \dfrac{P^{\mathrm{CO}} \cdot P^{\mathrm{CO}}_{\mathrm{O2}}}{\beta + P^{\mathrm{CO}} \cdot P^{\mathrm{CO}}_{\mathrm{NH3}}}\right)$, a series of straight lines is presented, obtained in accordance with equation (2). According to (3), in the coordinates $\lg \dfrac{b^{\mathrm{CO}}}{a^{\mathrm{CO}} T^{2.5}}$, $\dfrac{1}{T}$, a straight line was constructed, from the slope of which the activation energy of reaction (IIIa) was determined:

$$E_{\mathrm{IIIa}} = 10\,000 \pm 500 \text{ cal/mol}$$

from the intercept on the ordinate axis,

Table 1

T, °C	a^{H_2}, mm^2	$P^{\mathrm{H}_2} \cdot P^{\mathrm{H}_2}_{\mathrm{O2}} \dfrac{(D_{\mathrm{H}})^{\mathrm{H}_2}_{\mathrm{NH3}}}{(D_{\mathrm{H}})^{\mathrm{H}_2}}$, mm^2
610	6.7	6.5
650	5.2	5.0
690	4.3	3.9

calculated with $k^0_V = 0.018$ mm/sec • deg$^{3/2}$, is

$$k^0_{\mathrm{IIIa}} = (0.32 \pm 0.10) \cdot 10^{-10}.$$

On the whole, the following value was obtained for the rate constant:

$$k_{\mathrm{IIIa}} = (0.32 \pm 0.10) \cdot 10^{-10} e^{-(10000 \pm 500)/RT} \text{ cm}^3/\text{molecule} \cdot \text{sec}.$$

In accordance with equation (4), the difference in activation energies between reactions (II) and (VI) was determined:

$$E_{\mathrm{II}} - E_{\mathrm{VI}} = 2300 \pm 200 \text{ cal/mol},$$

and the preexponential factor

$$K^0_{\mathrm{VI}} = (0.68 \pm 0.18) \cdot 10^{-10}.$$

In equation (4) the rate constant of the branching reaction

$$\mathrm{H} + \mathrm{O_2} = \mathrm{OH} + \mathrm{O},$$

determined by us from measurements of the lower limit of the mixture $2\mathrm{H_2} + \mathrm{O_2}$, was used. It proved to be equal to

$$k_{\mathrm{II}} = (1.38 \pm 0.18) \cdot 10^{-10} e^{-(16000 \pm 600)/RT} \text{ cm}^3/\text{molecule} \cdot \text{sec}$$

and is in agreement with data known from the literature (^{8,17}).

Fig. 4. Dependence of $C \leftrightarrow m$ on $1/P^{\mathrm{CO}}_{\mathrm{NH_3}}$, $P^{\mathrm{CO}}_{\mathrm{NH_3}}$, at temperatures: 1–690°; $m = -1$; 2–670°; $m = -0.5$; 3–650°; $m = 0$; 4–630°; $m = 0.5$; 5–610°; $m = 1.0$; 6–590°; $m = 1.5$; 7–570°; $m = 2$.

Since $E_{\mathrm{II}} = 16000 \pm 600$ cal/mol, for the activation energy of the reaction

$$\mathrm{H} + \mathrm{NH_3} = \mathrm{H_2} + \mathrm{NH_2}$$

we have

$$E_{\mathrm{VI}} = 13700 \pm 600 \text{ cal/mol}.$$

For the rate constant of reaction (VI), the following value was obtained:

$$k_{\mathrm{VI}} = (0.68 \pm 0.18) \cdot 10^{-10} e^{-(13700 \pm 600)/RT} \text{ cm}^3/\text{molecule} \cdot \text{sec}.$$

It should be noted that if k_{VI} is calculated from equation (1) under the assumption $k_{\mathrm{VII}}/k_{\mathrm{VIII}} \ll 1$, using data on the ignition of mixtures $2\mathrm{H_2} + \mathrm{O_2} + \mathrm{NH_3}$, it practically coincides with the value determined by the method described in the present work. Substitution of the value of k_{VI} into the equation for the lower self-ignition limit of $2\mathrm{CO} + \mathrm{O_2} + \mathrm{NH_3}$, derived under the assumption $k_{\mathrm{VII}}/k_{\mathrm{VIII}} \ll 1$, leads to the same value of k_{IIIa} as was obtained with allowance for reaction

(VIII). The preservation of the values of k_{IIIa} and k_{VI} indicates that, in the systems studied, the NH_2 radicals evidently disappear mainly without regenerating new active centers. It follows from this that they most likely disappear on the walls of the reaction vessel.

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