Determination of the Rate Constant for the Reaction $NH_3+O\rightarrow NH_2+OH$

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Synopsis. The rate constant for the reaction $NH_3+O\rightarrow NH_2+OH$ was determined by the comparison of the calculated ammonia consumption rates with those observed in shock tube experiments in the range of 1690—2310 K, for NH_3-N_2O-Ar mixtures. The rate constant can be represented by the expression $k=3.1\times10^{12}\exp(-25.5\ \mathrm{kJ}/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$.

The rate constants for the reaction $NH_3+O\rightarrow NH_2+OH$ were measured at low temperatures below 1000 K by several researchers,[1,2] but those at high temperatures have not been measured accurately. The rate constants at higher temperatures in the range of 1690—2310 K were determined using the shock tube technique in this experiment.

Experimental

The shock tube consisted of a 2 m driver section and a 3.6 m experimental section. These were made of 46 mm inside diameter precision-bore stainless steel tubing. The shock velocity was measured by two piezogauges with a time counter. An observation section was placed at a position of 3 m apart from the diaphragm. Here, the change of absorption of NH_3 at 220 nm behind the incident shock wave was monitored by using an optical system consisting of a D_2 lamp, a monochromator, and a photomultiplier. Simultaneously at the same location, the infra-red emission of N_2O at 4.52 μm was measured with an InSb detector through an infra-red filter (half width: 0.18 μm). These signals were displayed on an oscilloscope and photographed. The composition of the gas mixtures, the temperature and the pressure range of incident shock waves are shown in Table 1. The shock parameters were calculated from the incident shock velocities.

Results and Discussion

Typical profiles of NH_3 and N_2O concentration change with reaction time behind the incident shock wave are shown in Fig. 1. In order to compare the profiles with those obtained by computer simulation, elementary reactions shown in Table 2 were selected as the important ones in this reaction system. Among the rate constants of these reactions shown in Table 2. Those of Reactions 1, 3, 7, and 8 were well established. From the preliminary calculation, the dissociation reaction of NH_3 was eliminated from the scheme, because the rate constant of this reaction[3] was smaller than that of Reaction 1 by about 200 times at 2000 K, and the rate of NH_3 consumption was hardly affected by the former reaction.

In order to examine the contribution of other elementary reaction to the rate of NH_3 consumption, the sensitivity checks described previously[4] were applied as follows. The calculated reaction time required for 10% consumption of NH_3, τ in Fig. 1, was found to be very sensitive to the change in the rate constants of Reactions 1—4, but not sensitive to those of other elementary reactions. However, when the N_2O concentration was not smaller than that of NH_3 and the temperature was higher than 2000 K, the calculated reaction time τ was not sensitive to the rate constant of Reaction 4. The conditions were satisfied only by mixture II.

Therefore, only Reactions 1—3 were used in the simulation for mixture II and the rate constant of Reaction 2 was determined accurately by choosing the value to fit best the calculate τ value of NH_3 consumption to the experimental one. In this calculation, the heat of reaction and the correction for the nonideality of shocked flow caused by the boundary layer behind the incident shock front[5] were taken into account. The rate constants of Reaction 2 obtained are shown in Fig.

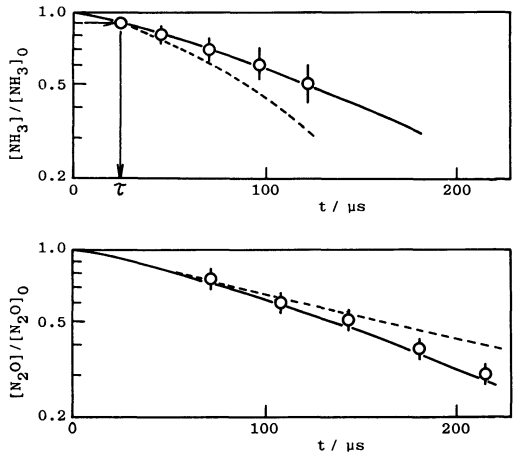

Fig. 1. Profiles of NH_3 and N_2O consumption for the mixture $NH_3 : N_2O : Ar = 1 : 1 : 98$ at $T=2000$ K and $p=2.04$ atm.
○: Experimentals, dotted lines: calculations by using Reactions 1—3, solid lines: calculations by using Reactions 1—8 and their reverse reactions.

TABLE 1. EXPERIMENTAL CONDITIONS

Mixture	NH_3	N_2O	Ar	T/K	p/atm[a]
I	1.0	0.3	98.7	1690—2310	1.78—2.04
II	1.0	1.0	98.0	2000—2260	2.04—2.14
III	2.0	0.4	97.6	1860—2290	0.91—1.05

a) 1 atm = 101 325 Pa.

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Table 2. Reaction scheme and rate parameters
$k = AT^B \exp(-E/RT)$ cm^3 mol^{-1} s^{-1}

Elementary reactions	log A	B	E/kJ	Ref.
1) $N_2O + M \longrightarrow N_2 + O + M$	15.21	0	257.7	8
2) $NH_3 + O \longrightarrow NH_2 + OH$	12.49	0	25.5	
3) $NH_3 + OH \longrightarrow NH_2 + H_2O$	12.50	0	8.4	9
4) $NH_3 + NH_2 \longrightarrow N_2H_3 + H_2$	11.90	0.5	90.4	7
5) $O + NH_2 \longrightarrow NH + OH$	11.96	0.5	0	10
6) $N_2H_3 + M \longrightarrow NH_2 + NH + M$	12.80	0	41.8	7
7) $N_2O + O \longrightarrow NO + NO$	14.00	0	117.2	1
8) $N_2O + O \longrightarrow N_2 + O_2$	14.00	0	117.2	1

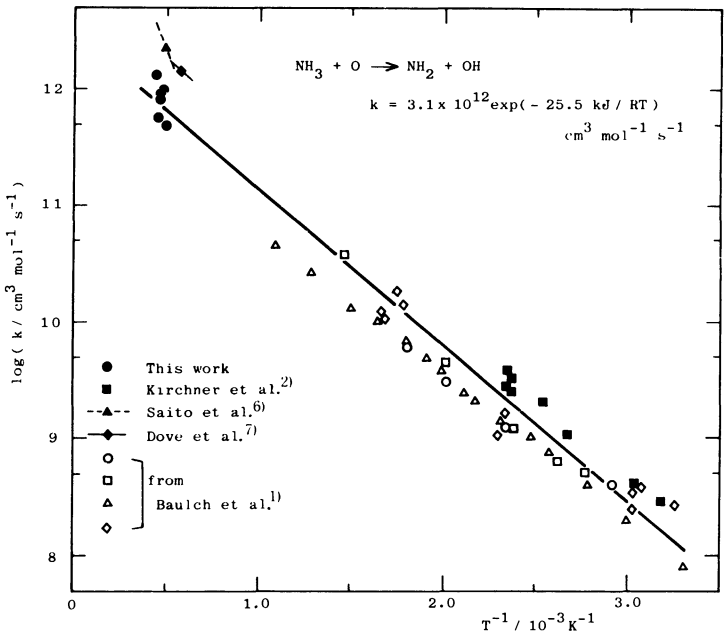

Fig. 2. Arrhenius plots of the rate constants for Reaction 2.

2. The values obtained recently by Satio and Bradley[6] and those obtained as the upper limit by Dove and Nip[7] are shown together in Fig. 2. Comparing the values obtained in the present work, both reported values are larger than the extrapolated value from those obtained in the lower temperature region.

A combination of our values with the mean values at low temperatures reported by Kirchner *et al.*[2] and by other researchers[1] yields the following Arrhenius expression for Reaction 2.

$$k_2 = 3.1 \times 10^{12} \exp(-25.5\ \text{kJ}/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}.$$

The NH_3 and N_2O consumption profiles calculated by using Reactions 1—3 are shown by the dotted lines in Fig. 1. The agreement between the calculated and experimental values at the initial stage of the reaction is good. In the figure, the deviations of the calculated curves from the experimental values after the reaction time τ were improved by adding subsequent Reactions 4—8 to the reaction scheme, as shown by the solid lines. The rate constants obtained for mixtures I and III, which did not satisfy the conditions, were also within the scattering of the above-obtained values.[8]

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