RATE CONSTANT FOR THE REACTION $NH_3 + OH \rightarrow NH_2 + H_2O$ OVER A WIDE TEMPERATURE RANGE

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The rate constant for the reaction of $NH_3 + OH \rightarrow NH_2 + H_2O$ has been measured in a high temperature fast flow reactor over the range 294–1075 K $k = (5.41 \pm 0.86) \times 10^{-12} \exp[-(2120 \pm 143)\ \text{cal mole}^{-1}/RT]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. This result is compared with literature values and discussed.

1. Introduction

The role of the reaction

$$NH_3 + OH \rightarrow NH_2 + H_2O,$$

$$\Delta H^0_{298} = -10.7 \pm 1.5\ \text{kcal mol}^{-1} \qquad (1)$$

is of importance in understanding atmospheric [1,2] and combustion [3,4] chemistry. Although well studied near room temperature [5–10], this reaction is also important at the elevated temperatures of combustors and combustor exhaust flows. It has been proposed as the key initiation step in the removal of NO_x by ammonia addition to combustor exhaust flows [3,11].

This work represents the first direct high temperature measurement of the $NH_3 + OH$ reaction rate constant, and shows that over a large range of temperatures, it can be well represented by an Arrhenius expression.

2. Experimental

The experiments are carried out in a high temperature fast flow reactor, illustrated in fig. 1. The apparatus is described in detail elsewhere [12,13], but in brief, a 7.26 cm diameter, 120 cm long alumina tube is used. Kanthal heater elements radiatively control the temperature from 294–1500 K. Four perpendicular alumina side arms at the tube end permit resonance lamp fluorescence detection. Provisions also exist for IR White cell absorption of IR active species, and for laser induced fluorescence detection techniques. Flow gases can be monitored by a molecular beam sampling mass spectrometer to facilitate in the identification of reaction products. Gas temperatures are obtained with shielded W–5%Re/W–26%Re thermocouples using a technique [14,15] which removes the contribution of wall radiation to the measurement.

Radicals are made with discharge flow techniques, utilizing a 2450 MHz microwave discharge source, and introduced through the inner of two coaxial alumina inlet tubes. By adding a second gas through the outer tube, new reactant species can be produced. Hydrogen atoms made in the microwave source react with NO_2, resulting in a clean source of OH. The concentration of OH is always kept low enough to prevent secondary reactions. An alternate source of H atoms is the use of heated tungsten coil to dissociate H_2 at the inserted end of the inner tube. Both production methods gave comparable results.

A second reactant, in this case ammonia, is added through a moveable quartz injector. Helium buffer gas is added at the entrance of the flow tube through mullite multichannel arrays which preheat and laminarize the flow. The purities of gases used are: He(99.995%), H_2 (99.999%), NH_3 (99.99%), and

Table 1
Experimental rate data

T (K)	P (Torr)	v (cm/s)	k_w (s^{-1})	[NH_3] (cm^{-3})	k^I_{corr} (s^{-1})	k_{NH_3+OH} (cm^3 molecule^{-1} s^{-1})
294	1.20	895	54.8	1.42(14)	40.4	
294	1.20	895	54.8	2.32(14)	61.9	
294	1.20	895	54.8	3.94(14)	78.9	$(1.42 \pm 0.28) \times 10^{-13}$
294	1.38	916	54.8	1.45(14)	58.6	
294	1.38	916	54.8	2.73(14)	94.2	
294	1.42	873	54.8	3.50(13)	26.6	
294	1.42	873	54.8	1.09(14)	41.?	
294	1.42	873	54.8	1.86(14)	48.5	$(1.45 \pm 0.29) \times 10^{-13}$
294	1.42	873	54.8	2.90(14)	72.8	
294	1.42	87?	54.8	4.20(14)	80.5	
575	1.38	1790	45.9	5.08(13)	64.7	
575	1.38	1790	45.9	9.25(13)	99.7	
575	1.38	1790	45.9	1.65(14)	169.4	$(8.67 \pm 1.73) \times 10^{-13}$
575	1.38	1790	45.9	2.48(14)	233.9	
575	1.38	1790	45.9	1.26(14)	130.0	
775	1.43	2390	63.4	2.18(13)	53.5	
775	1.43	2390	63.4	4.62(13)	85.4	
775	1.43	2390	63.4	9.52(13)	157.2	$(1.43 \pm 0.28) \times 10^{-12}$
775	1.43	2390	63.4	1.52(14)	239.7	
775	1.43	2390	63.4	6.94(13)	120.6	
875	1.45	2590	75.7	1.50(13)	33.9	
875	1.45	2590	75.7	3.51(13)	60.4	
875	1.45	2590	75.7	6.27(13)	119.0	$(1.37 \pm 0.27) \times 10^{-12}$
875	1.45	2590	75.7	9.53(13)	154.7	
875	1.45	2590	75.7	1.34(14)	193.7	
975	1.39	3340	80.5	1.36(13)	43.2	
975	1.39	3340	80.5	2.73(13)	66.2	
975	1.39	3340	80.5	4.28(13)	99.6	$(2.39 \pm 0.47) \times 10^{-12}$
975	1.39	3340	80.5	7.05(13)	158.9	
975	1.39	3340	80.5	1.10(14)	273.0	
1075	1.62	3450	121.5	2.41(13)	59.3	
1075	1.62	3450	121.5	4.30(13)	104.5	
1075	1.62	3450	121.5	6.60(13)	162.3	$(1.93 \pm 0.36) \times 10^{-12}$
1075	1.62	3450	121.5	9.05(13)	192 0	
1075	1.62	3450	121.5	1.16(14)	240.2	

Table 2
Comparison of experimental rate determinations for NH_3 + OH with selected literature values

Room temperature rate constant (cm^3 molecule^{-1} s^{-1})	A (cm^3 molecule^{-1} s^{-1})	E (cal/mole)	Temperature range (K)	Method	Ref.
2.42×10^{-13}	$(5.3 \pm 0.8) \times 10^{-12}$	1830	298–669	flow reactor	[9]
$(2.7 \pm 0.3) \times 10^{-13}$	1.1×10^{-12}	870 ± 80	298–365	pulsed radiolysis	[10]
$(1.5 \pm 0.4) \times 10^{-13}$	—	—	298	flash photolysis	[6]
1.58×10^{-13}	2.3×10^{-12}	1600	228–472	flash photolysis	[7,8]
$(1.64 \pm 0.16) \times 10^{-13}$	2.93×10^{-12}	1710 ± 300	297–427	flash photolysis	[5]
$(1.44 \pm 0.29) \times 10^{-13}$	$(5.41 \pm 0.86) \times 10^{-12}$	2120 ± 143	294–1075	flow reactor	present work

3. Results

Hydroxyl decay is measured as a function of the injector position for a fixed NH_3 concentration with $[NH_3] \gg [OH]$ to ensure pseudo-first order kinetics. Some representative data are shown in fig. 2 for 875 K. Rate constants (k^I) for each measurement are obtained by a least squares fit to the slope of –ln(signal) versus reaction time.

Removal rates of OH by the uncoated alumina tube wall are measured by varying the OH residence time at fixed pressure. This is done during each run and the observed k_w are shown in fig. 3. These values, along with estimated diffusion coefficients [16] ‡ for OH in He, are used to correct for the effects of wall removal and axial and radial diffusion on the observed rates. This is most accurately accomplished using the procedure outlined by Brown [17]. The corrections are small, ranging from 15–36%. The corrected first order rate coefficients, k^I_{corr}, are listed along with the measured k_w in table 1. A least squares fit to k^I_{corr} versus $[NH_3]$ results in $k_{NH_3+OH}(T)$. A few of these curves are illustrated in fig. 4. The overall accuracy of the rate constants is estimated ($\pm 1\sigma$) at 20%.

‡ The diffusion coefficient of OH in He is assumed to be equivalent to that of O in He.

4. Discussion

The temperature dependence of the measured rate constants can be represented by the Arrhenius expression, $k(cm^3\ molecule^{-1}\ s^{-1}) = A\ exp(-E/RT)$, as shown in fig. 5. Also included are the data of Perry et al. [5] and Smith and Zellner [7,8], which are the most recent measurements over a range of temperatures.

A non-linear least squares fit to our present data results in values ($\pm 1\sigma$) for the pre-exponential factor $A = (5.41 \pm 0.86) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ and an activation energy of $E = 2120 \pm 143$ cal mol^{-1}. This is indicated by the solid line in fig. 5.

A comparison of the present results with selected literature values is shown in table 2. Our room temperature value is in excellent agreement with recent work. In general, they tend to exhibit a slightly lower A factor than our high temperature results. The implication is that the temperature dependence has a slight upward curvature, as would be expected from transition state theory for this simple hydrogen atom extraction, and as recently observed for a series of reactions of OH with substituted alkanes [19]. Due to the nature of our apparatus it is difficult to accurately maintain a temperature below ≈500 K (other than room temperature), thus in the present work measurements to determine the curvature directly

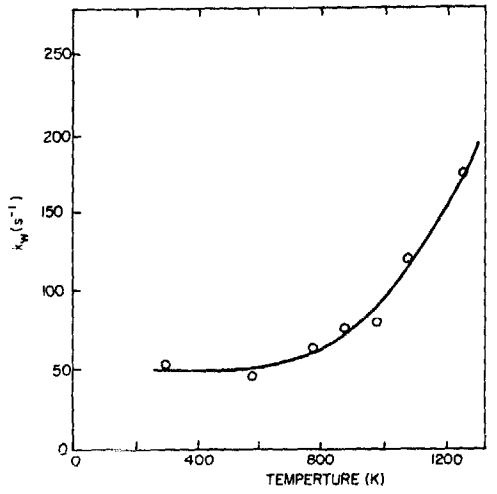

Fig. 3. Temperature dependence of the measured OH wall removal rate.

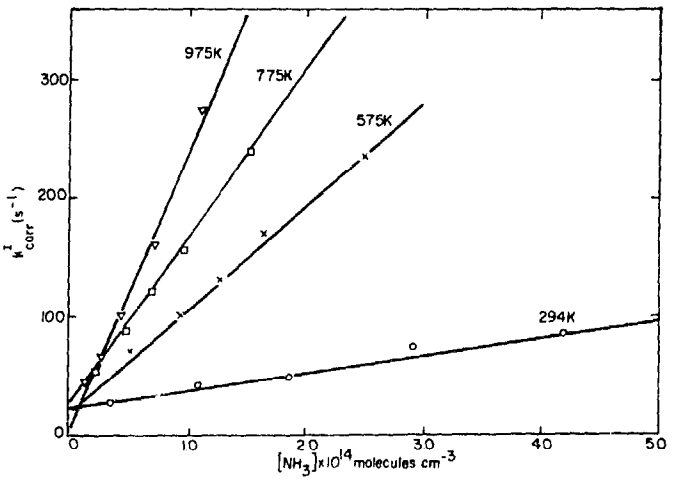

Fig. 4. Dependence of pseudo-first order rate constant on NH_3 concentration at various temperatures.

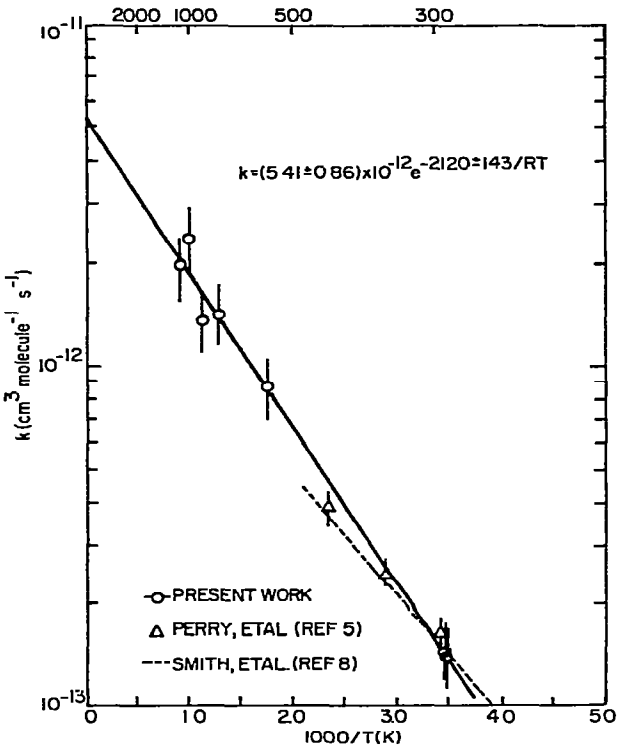

Fig. 5. Temperature dependence of measured rate constants for NH_3 + OH reaction.

could not be performed. Fitting all the points in fig. 5 to $k = AT^n \exp(-E/RT)$ was statistically unwarranted, thus any deviation from Arrhenius behavior is small. The conclusion can be drawn that the Arrhenius parameters extracted from the experiments below 500 K are indeed valid to temperatures above 1000 K, in the region of interest to many combustion and exhaust cleanup studies.

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