KINETICS OF REACTIONS OF NH WITH NO AND NO_2

J.A. HARRISON, A.R. WHYTE and L.F. PHILLIPS

Chemistry Department, University of Canterbury, Christchurch, New Zealand

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Ground-state NH radicals were generated by 248 nm KrF laser photolysis of N_2H_4 and their concentration monitored by laser-induced fluorescence at 336 nm, at total pressures near 1 Torr and temperatures between 269 and 377 K. He, Ar, N_2 and N_2O were used as carrier gases. Rate constants obtained at 300 K are $(1.61 \pm 0.14) \times 10^{-11}$ for $NH + NO_2$ and $(5.78 \pm 0.64) \times 10^{-11}$ for NH + NO (units cm^3 $molecule^{-1}$ s^{-1}). For NH + NO the rate constant is independent of temperature over the range studied; for $NH + NO_2$ there is a small negative temperature dependence. Within experimental error, results at 300 K are independent of the choice of carrier gas. The results are discussed in terms of a mechanism involving an intermediate HNNO or $HNNO_2$ complex.

1. Introduction

The reactions of NH with NO and NO_2 are of interest as possible examples of fast, multicentre reactions involving an intermediate complex, similar to the corresponding reactions of NH_2 [1–3]. From an alternative viewpoint, they are also of interest as possible examples of reactions whose rate is largely controlled by the rate of crossing the centrifugal barrier in a long-range (r^{-3}) dipole–dipole potential [4]. To begin to understand these reactions we require a knowledge of their rate constants, of the dependence of the rate constants on temperature and pressure, and of the nature of the reaction products. The present study provides experimental information about all but the last of these.

Previous kinetic studies of ground-state NH reactions with H-, N- and O-containing species are summarized in table 1. The number of such studies is remarkably few, and four of the values in the table are

Table 1
Previous kinetic studies of ground-state NH ($X\,^3\Sigma^-$) reactions

Reactant	k (cm^3 $molecule^{-1}$ s^{-1})	T (K)	P (Torr)	Method [a]	Ref.
NO	$(4.7 \pm 1.2) \times 10^{-11}$	300	30–700 (He)	FP/RA	[5]
NO	$(4.8 \pm 0.2) \times 10^{-11}$	300	5 (He)	LP/LIF	[6]
NO	3.8×10^{-11}	420	250–1000 (NH_3)	PR/RA	[7]
$O_2(^3\Sigma_g^-)$	$(8.5 \pm 0.9) \times 10^{-15}$	296	0.4–900 (He)	FP/RA	[8]
$O_2(^3\Sigma_g^-)$	9.1×10^{-15}	268–543	0.9–8	DF/RA	[9]
$O_2(^3\Sigma_g^-)$	$< 3.3 \times 10^{-14}$	349	760	PR/RA/CS	[10]
$O_2(^1\Delta_g)$	$(1.0 \pm 0.16) \times 10^{-15}$	295	0.9–8	DF/RA	[9]
NH	1.2×10^{-10}	349	760	PR/RA/CS	[10]
HO_2	7.2×10^{-11}	349	760	PR/RA/CS	[10]
NH_2	7.2×10^{-11}	349	760	PR/RA/CS	[10]
NH_3	$< 8 \times 10^{-17}$	300	0.005–0.9	FP/RF	[11]
NH_3	$< 2 \times 10^{-15}$	300	1013	PR/RA	[12]
NH_3	$< 3 \times 10^{-16}$	300	760	PR/RA	[13]

[a] FP = flash photolysis, RA = resonance absorption, LP = laser flash photolysis, LIF = laser-induced fluorescence, PR = pulse radiolysis, DF = discharge-flow, CS = computer simulation, RF = resonance fluorescence.

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derived from computer simulation of a complicated mechanism. We omit the early, very high, flash-photolysis value for NH + NH_3 by Mantei and Bair [14], which appears to have been affected by initially-high rotational temperatures [13]. Rate data for reactions of NH with hydrocarbons are also very sparse; generally the reactions are found to be slower than those of the isoelectronic CH_2 and O-atom species [6].

2. Experimental

The experimental system was as previously described [15], except for the photolysis cell, which is drawn in fig. 1. Temperature was controlled by circulating a glycol–water mixture from a thermostat through the cell's water jacket, and measured to ±1°C with a copper–constantan thermocouple located in the gas stream just below the viewing region. Pressure was measured with a Texas Instruments quartz spiral gauge. The 248 nm KrF laser (Lumonics TE861-T) operated at a pulse repetition frequency of 40 Hz. A 450 ℓ/min rotary pump ensured that the contents of the cell were swept out between pulses. Experiments with ArF 193 nm photolysis, using both NH_3 and N_2H_4 as the NH precursor, gave rate constants for the NO + NH reaction which were too low by about a factor of ten, presumably as a result of unidentified secondary reactions which generate ground-state NH in this system. The KrF laser pulse energies were in the range 75 to 100 mJ (Scientech model 364 power/energy meter). Typical flow ratios in the cell were Ar : N_2H_4 : NO = 300 : 28 : 0–10, with total pressure 0.9–1.1 Torr. Measurements of transmitted power under these conditions gave an upper limit of 5×10^{-19} cm^2 for the N_2H_4 absorption cross section averaged over the laser emission band. This figure actually represents the noise in the power reading; no absorption by N_2H_4

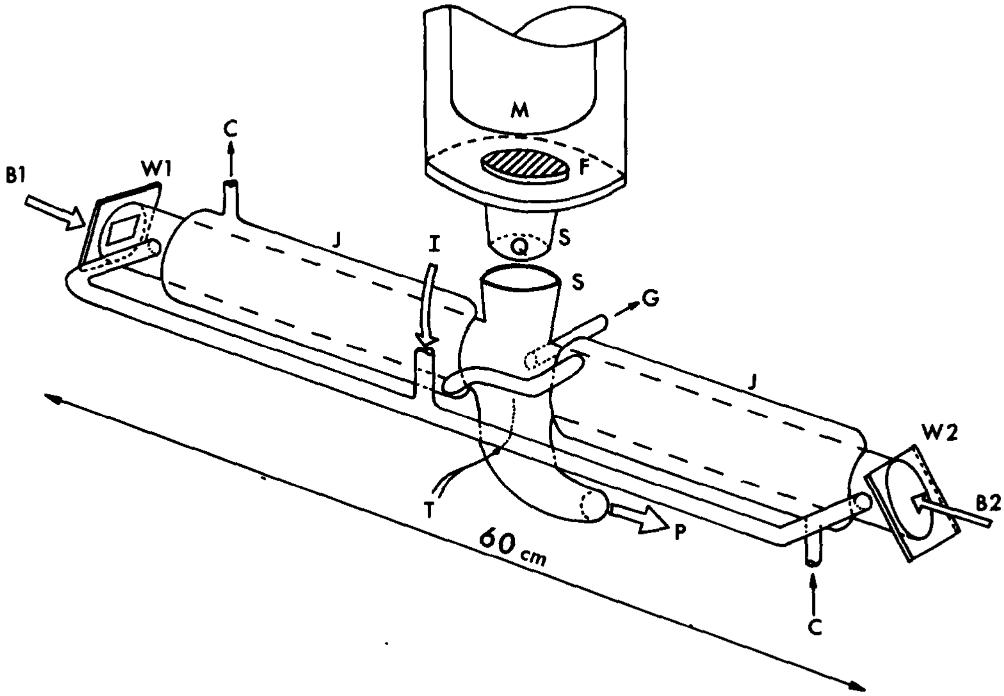

Fig. 1. Diagram of the Pyrex photolysis cell with insulating jacket and copper-foil wrapping removed. I = gas inlet; G = connection to pressure gauge; P = pumping lead; J = jacket for temperature control; C = coolant flow; M = photomultiplier tube in container; F = interference filter; S = standard taper joints; Q = quartz window; B1 = 248 nm beam; B2 = 336 nm beam; W1 = suprasil window with copper aperture to define photolysis beam; W2 = suprasil window; T = thermocouple leads.

was detected. The measured single-photon absorption cross section of N_2H_4 at 248 nm is 8.4×10^{-20} cm^2 [16], which is consistent with our upper limit for all processes.

NH fluorescence was excited by the frequency-doubled output (Inrad angle-tuned KDP) of the Avco nitrogen-pumped dye laser operating with a mixture of cresyl violet and rhodamine 590 dyes in ethanol. Initial tuning of the laser was facilitated by using a monochromator (McPherson model 218) and adjusting the doubled output to coincide with the Q(0,0) feature of the 336 nm NH A–X band from a flowing microwave discharge lamp, similar to that of Stuhl and coworkers [5], containing 0.8 Torr Ar plus a trace of N_2H_4. The fluorescence was observed through an interference filter (Corion Instrument Corp., fwhm = 18 nm at 328 nm) with an EMI 9813QA photomultiplier. Fluorescence signals were processed by a fast preamplifier located at the tube socket and a computer-controlled PAR model 160 boxcar integrator.

Carrier gases (Ar, He, N_2, N_2O) were passed through a column of reduced BASF BTS catalyst at 160°C (100°C, N_2O) followed by a silica gel trap at −78°C (−196°C, He). A portion of the carrier gas stream at roughly atmospheric pressure was bubbled through a saturator containing liquid hydrazine (Fluka AG) at room temperature, the final hydrazine concentration being calculated from the measured temperature and total pressure (0–1000 Torr MKS Baratron gauge) using the vapour pressure data of Scott et al. [17]. NO and NO_2 were as previously described [1].

3. Results

Representative pseudo-first-order decay plots for NH fluorescence in the presence of varying amounts of NO are given in fig. 2. The first 100 μs of the fluorescence decay was affected by emission arising from the excimer laser pulse and is excluded from the rate measurements. In figs. 3a and 3b the slopes of such first-order decay plots at $T \approx 300$ K are plotted against reactant pressure for NO and NO_2, respectively. Different symbols in these figures designate different carrier gases: within the limits of error of the measurements there is no dependence on the nature of the carrier, which implies that for both reactions there is no pressure dependence of the rate constant. For the reaction with NO the absence of a pressure effect is shown directly by the results of Hansen et al. [5] and indirectly by the satisfactory agreement at 300 K between their results for pressures from 30 to 700 Torr, our results at 1 Torr, and those of Cox et al. [6] at 5 Torr. Global linear fits of our data for all carrier gases, at 299 ± 1 K for NO_2 + NH (NO_2 = 0–0.027 Torr) and at 301 ± 2 K for NO + NH (NO = 0–0.0062 Torr), give rate constant values $(1.61 \pm 0.14) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(5.78 \pm 0.64) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively, where the limits shown are the sum of 95% confidence limits for the slopes of the lines and an estimated ±6% for systematic errors in pressure, temperature, gas flow and time measurements. From the observed very small effect of N_2H_4 concentration on the [NH] decay rate, we obtain values of $(3.6 \pm 2.2) \times 10^{-15}$ and $(3.0 \pm 2.5) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} for the rate constant for reaction of NH with N_2H_4, at 301 and 362 K, respectively.

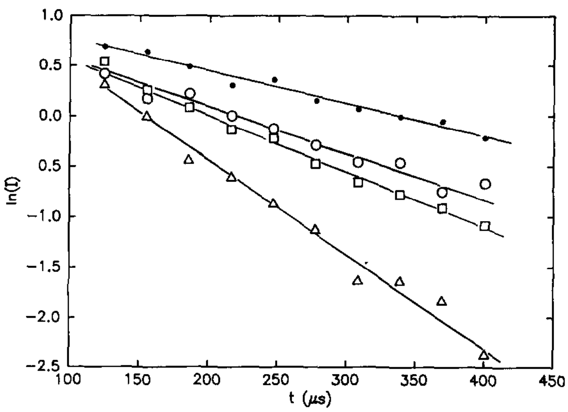

Fig. 2. Pseudo-first-order decay plots of NH fluorescence in the presence of NO at T = 300 K, P = 1 Torr (Ar), with [NO] (in 10^{13} cm^{-3}) = 0 (solid dots), 3.40 (circles), 6.31 (squares), 12.7 (triangles).

Rate constants for the NO and NO_2 reactions measured with an argon carrier at different temperatures are shown in fig. 4. The error bars shown here correspond to an uncertainty of ±15%, larger statistical errors arising from the smaller numbers of measurements at each temperature. Results for NH + NO are seen to be essentially independent of temperature while those for NH + NO_2 have a small, negative temperature coefficient. Arrhenius plots (which are not especially ap-

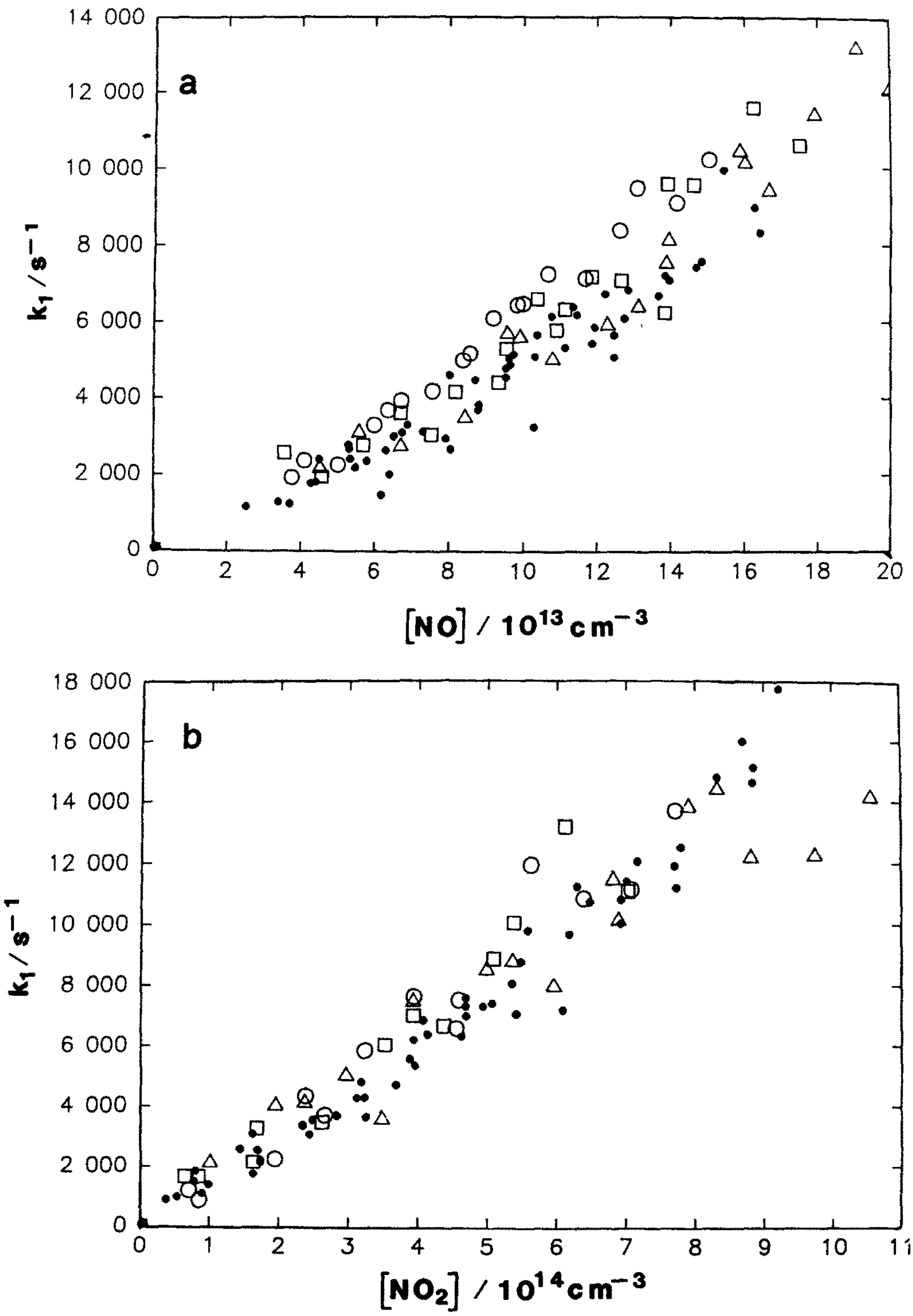

Fig. 3. (a) Slopes of first-order plots at 299 ± 1 K versus NO concentration. Solid dots, Ar carrier; circles, He; squares, N_2; triangles, N_2O. (b) As for (a), but reactant = NO_2, T = 301 ± 2 K.

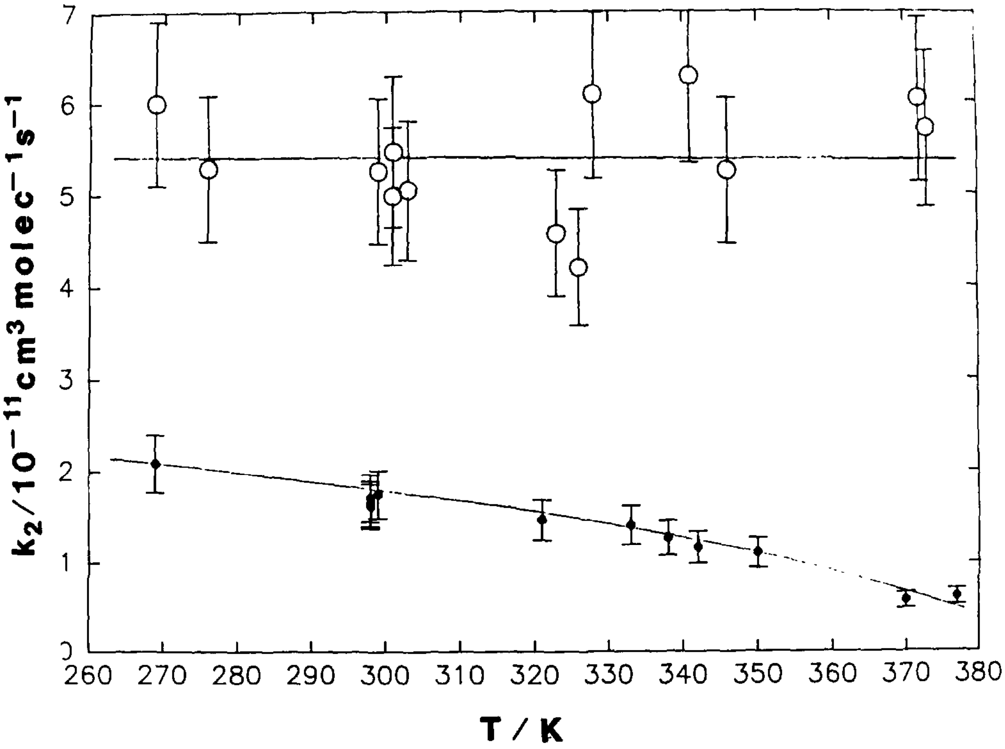

Fig. 4. Temperature dependence of rate constants measured with argon carrier. Open circles NH + NO; solid dots, NH + NO_2. Error bars ±15%.

propriate here) lead to activation energies of 0 ± 2 kJ for NH + NO and −9.5 ± 3.2 kJ for NH + NO_2.

4. Discussion

4.1. Nature of the reaction products

For the reaction of NH with NO there are two possible exothermic, spin-allowed, product channels, namely:

$$NH + NO \rightarrow N_2 + OH + 407\ kJ\ , \quad (1)$$

$$NH + NO \rightarrow N_2O + H + 146\ kJ \quad (2)$$

and for the reaction with NO_2 there are three:

$$NH + NO_2 \rightarrow N_2 + HO_2 + 387\ kJ\ , \quad (3)$$

$$NH + NO_2 \rightarrow N_2O + OH + 268\ kJ\ , \quad (4)$$

$$NH + NO_2 \rightarrow NO + NHO + 199\ kJ\ , \quad (5)$$

where we use the NH enthalpy of formation of Gibson et al. [18] together with data for 298 K from the compilation of Baulch et al. [19]. For reaction (2) there exists one negative result in the form of a failure to detect N_2O in a hydrogen flame containing NH_3 and NO [20], and another negative result in the form of a failure to detect H atoms formed by the reaction of NH_2 with NO, under conditions where NH would also have been present [21]. In the course of the present work we attempted unsuccessfully to detect OH radicals formed by reaction (1), using laser-induced fluorescence at 306.4 nm, but the excitation system was far from optimum for these experiments, which need to be repeated. Silver and Kolb [22] observed OH but not H in a system containing F, NH_3 and NO, a result which is readily explicable in terms of process (1). On balance, therefore, we consider that reaction (1) is probably the major channel, and may be the only channel, for the reaction of NH with NO. For the reaction of NH with NO_2 there is at present no experimental evidence as to the nature of the products. For this reaction also we failed to detect OH as a product but, for the reason mentioned above, this does not rule out reaction (4), which seems to us to be the most likely channel.

4.2. Reaction mechanisms

Processes (2) and (5) above can occur as direct reactions; the others are multicentre processes, requiring rapid H-atom migration to take place in an intermediate $HNNO^*$ or $HNNO_2^*$ complex, with the additional requirement of a major rearrangement of O–N–O bonds in the case of reaction (3). The example of the analogous NH_2 reactions shows that the lack of pressure dependence does not rule out a complex-forming mechanism and that rapid H-atom migration is quite an acceptable requirement, but there appears to be no precedent for a fast reaction of the type of reaction (3) and we therefore consider it unlikely to be a significant channel.

For reaction (1), the favoured NH + NO channel, the present results imply that the barrier to H-atom migration lies at or below the NH + NO dissociation limit of the HNNO complex, much as in the NH_2 + NO case [23]. Preliminary GAUSSIAN 82 calculations [24] indicate that HNNO is much less strongly bound than NH_2NO (which in turn is less strongly bound than NH_2NO_2), being essentially unbound at the Hartree–Fock limit. The value of the rate constant obtained from an approximate semi-classical calculation of the capture rate for the dipole–dipole potential is 7×10^{-11} cm^3 $molecule^{-1}$ s^{-1} [3], in fair agreement with the measured value, a result which emphasizes that H-atom migration must be extremely facile if (1) is to be the major channel.

In reaction (4) we have a process which leads to formation of N_2O, in a manner analogous to the known reactions of N and NH_2 with NO_2 [19,25]. Indeed, this analogy, which may prove deceptive, is one of our reasons for preferring the multicentre reaction (4) over the direct reaction (5). The negative temperature dependence of the rate constant also favours a complex-forming mechanism. It is noteworthy that the NH + NO_2 rate constant is lower than that for NH + NO by a factor of 3, despite the higher dipole moment of NO_2 (0.29 versus 0.16 D) which should lead to a greater dipole–dipole capture rate. Thus, if (4) is the major channel, H-atom migration in $HNNO_2^*$ must be considerably slower than in $HNNO^*$.

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