An Experimental and Theoretical Study of the Reaction Between $\text{NH}(\text{X}^3\Sigma^-) + \text{SO}(\text{X}^3\Sigma^-)$

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Dedicated to Prof. Dr. Reinhard Zellner on the occasion of his 65th birthday

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$\text{NH}(\text{X}^3\Sigma^-) / \text{SO}(\text{X}^3\Sigma^-) / \text{Reaction}$

The kinetics of the reaction between $\text{NH}(\text{X}^3\Sigma^-) + \text{SO}(\text{X}^3\Sigma^-)$ have been studied over the range 295–703 K using pulsed laser photolysis / laser induced fluorescence in 100 Torr He. The rate coefficient is $(5.0 \pm 2.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and is independent of temperature within experimental scatter. Electronic structure calculations show that reaction proceeds *via* bound intermediates to form $\text{NS} + \text{OH}$ and $\text{NO} + \text{SH}$ as the major bimolecular products. An RRKM / master equation analysis shows that stabilization of the intermediates is negligible at the pressures investigated ($< 10^4$ Torr), so that the overall rate coefficient is independent of pressure. The calculations show that the main product channel under combustion conditions is $\text{NS} + \text{OH}$. Attempts to observe NS under the experimental conditions were unsuccessful. The experimental decay data are consistent with the occurrence of the reaction $\text{NH}_2 + \text{Cl} \rightarrow \text{NH} + \text{HCl}$ at temperatures above 500 K; approximate Arrhenius parameters are provided.

1. Introduction

An understanding of combustion emissions of both nitrogen and sulphur oxides is important because of their impact on both air quality and climate change. There have been significant reductions in the emissions of SO_2 in Europe, where nitrogen oxides now have a greater impact on air quality than SO_2 , through the effects of NO_2 on human health and of NO on ozone formation. Both sulphur and nitrogen oxides are involved in the formation of secondary aerosols, which are of importance in both air quality and climate change.

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There is a comparatively poor understanding of the interaction between nitrogen oxides and sulphur species in combustion systems. Experimental and modelling studies indicate that sulphur species can lead to both enhancement and suppression of NO emissions, depending on combustion conditions. Hughes *et al.* [1] reviewed this field in their study of nitrogen sulphur interactions in a low pressure flame. They discussed a number of reactions, including that between $\text{NH}(\text{X}^3\Sigma^-) + \text{SO}(\text{X}^3\Sigma^-)$; they found that the concentrations of both NS and NO showed high sensitivity to this reaction, which was first tentatively suggested by Pfefferle and Churchill [2], who estimated a rate coefficient of $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. There have been no previous direct measurements of the rate coefficient or determinations of the products.

$\text{NH}(\text{X}^3\Sigma^-)$ reacts quite slowly with O_2 to form $\text{NO} + \text{OH}$ with a rate coefficient of $1.5 \times 10^{-13} \exp(-770/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [3] corresponding to an activation energy of $\sim 6 \text{ kJ mol}^{-1}$. At high temperatures, formation of $\text{O} + \text{HNO}$ also becomes important. NH is isoelectronic with CH_2 , and both singlet and triplet CH_2 react rapidly with O_2 , with a number of reaction channels.

In this paper we explore the reaction:

Experiments were carried out where a known amount of $\text{SO}(\text{X}^3\Sigma^-)$ was generated in the presence of a small amount of $\text{NH}(\text{X}^3\Sigma^-)$ (both triplet species are abbreviated to SO and NH for the rest of this paper). By monitoring the removal of NH in the presence of SO the rate coefficients for this reaction were determined over the temperature range 295–703 K. To explore the products of this reaction electronic structure calculations were performed to determine the potential energy surface for reaction and this was then coupled to a master equation analysis to investigate further the effects of pressure on the rate coefficient and to identify the likely products of the reaction.

2. Experimental

The experiments were conducted in a conventional slow flow, laser flash photolysis-laser induced fluorescence (LIF) apparatus, similar to that used in previous studies [4]. The reaction mixtures were photolysed using a pulsed excimer laser (Lambda Physik LPX 100) operating at 193 nm (ArF) and 2 Hz, with a photolysis energy of 20–60 mJ/cm^2 . The probe radiation was generated from a Nd:YAG (Spectron SL803, doubled output at 532 nm) pumped dye laser (Spectron 4000 G), where output from the dye pyridine 1 was doubled (KDP) to generate the light that was used to probe $\text{NH}(\text{X}^3\Sigma^-)$ via LIF at $\sim 336 \text{ nm}$ using the A-X

transition [5,6]. The reaction cell was a stainless steel six-way-cross equipped with cartridge heaters, which allowed the temperature to be varied between 295–703 K. The temperature was measured using a type K thermocouple and was known to better than ± 5 K. The photolysis laser beam was masked such that the cross-sectional area as it entered the cell was 1.0 cm^2 ; its energy was measured using a power meter (Gentec, Model ED-200L) situated beyond the cell. The fluorescence induced by the probe laser passed through an interference filter, if required, and then onto a photomultiplier (EMI 9813 QKB). The signal from the photomultiplier was integrated by a boxcar averager (SRS250), digitized and stored on a personal computer. The time profiles of the radicals in the system were recorded by scanning the delay between the photolysis and probe lasers; each kinetic trace consisted of 100 points where each point was an average of between 6–10 laser samples.

The reagents were diluted with helium and stored in bulbs. Gas mixtures were flowed, together with helium buffer gas, *via* calibrated mass flow controllers into a mixing manifold, before entering the reaction cell. Typically, the total flow was ~ 2500 sscm and the total pressure was 100 Torr, measured using a capacitance manometer. This flow rate ensured a fresh gas mixture for each laser sample. SOCl_2 (Aldrich) and hydrazine (solution 90% in H_2O) were degassed and distilled before being diluted in helium (CP grade, 99.999%, BOC).

2.1 Determination of [SO] and its relaxation

Photolysis of thionyl chloride, SOCl_2 , at 193 nm was used as the SO precursor for the kinetic measurements and typically its pressure in the cell was varied between 2–20 mTorr, and the photolysis energies used led to between 20–60 % photolysis. Previous studies on thionyl chloride photolysis at 193 nm [7,8] have shown that SO is formed vibrationally hot in the major product channel (P1a):

In our previous study on $\text{OH} + \text{SO}$ [9] we showed that vibrationally excited SO is relaxed in less than $20 \mu\text{s}$ at a total helium pressure of 100 Torr, which is in agreement with Wang *et al.* [8] who reported that SO is effectively relaxed after ca. 10^4 collisions with helium. All experiments were carried out at a pressure of 100 Torr He and all the kinetic traces were analysed after the first $20 \mu\text{s}$.

The absolute [SO] was determined by titrating it with NO_2 to form NO using the calibration reaction [9]:

which is well characterised [8] and converts the transient SO radical to the stable NO radical. The NO formed from reaction R2 was detected by LIF and its absolute concentration was determined by comparing the LIF signal to that from

introducing a known amount of NO to the reaction cell. From the measured [NO], the quantum yield for SO from 193 nm SOCl₂ photolysis, $\Phi_{\text{SO},193\text{nm}}$, was determined from

$$\Phi_{\text{SO},193\text{nm}} = \frac{[\text{SO}]}{[\text{SOCl}_2] \times F \times \sigma_{\text{SOCl}_2,193\text{nm}}} \quad (\text{E1})$$

where F is the laser fluence in photon cm⁻², as measured by the energy meter, and $\sigma_{\text{SOCl}_2,193\text{nm}}$ is the SOCl₂ absorption cross-section, which is equal to 1.30×10^{-17} cm². $\Phi_{\text{SO},193\text{nm}} \sim 0.8$ was obtained, over the temperature range 295–503 K [9], which is consistent with the room temperature studies of Baum *et al.* [7] (> 0.80) and Wang *et al.* [8] (0.73 ± 0.10). For the present study, the SO concentration was determined using equation E1 and assuming that the quantum yield for SO production is 0.8 at all temperatures. The measurement of [SO] was precise, but its accuracy was limited by the problems in comparing the NO LIF signal deriving from reaction of the photolytically generated SO with that from the NO introduced into the cell. A reasonable estimate of this accuracy is $\pm 30\%$; it is a major contributor to the overall uncertainty in the final rate coefficient.

Previous studies have shown that photolysis of hydrazine, N₂H₄, produces NH in both the excited singlet state, NH($a^1\Delta$), and in the ground triplet state, NH($X^3\Sigma^-$).⁶ The mechanism for NH formation is uncertain but it must be a multi-photon process. In preliminary tests at 248 nm with a laser energy of ~ 100 mJ / pulse both triplet and singlet NH were observed *via* LIF using the $A^3\Pi - X^3\Sigma^-$ transition at ~ 336 nm [10] and the $c^1\Pi - a^1\Delta$ transition at ~ 326 nm, respectively [11]. It was noted that the singlet NH LIF signal was significantly weaker than that for the triplet. At 193 nm hydrazine was observed to yield significantly greater amounts of both singlet and triplet NH, with approximately equal signals observed. With just hydrazine present, the triplet NH signal was observed to grow at early times, which is consistent with loss of the singlet by relaxation to ground state triplet NH; the magnitude of the initial and delayed signals were consistent with the production of equal amounts of singlet and triplet NH in the 193 nm photolysis of N₂H₄. However, when hydrazine was photolysed in the presence of SOCl₂ no significant growth in the NH($X^3\Sigma^-$) signal was observed, presumably because of rapid reaction of NH($a^1\Delta$).

It is difficult to estimate [NH] accurately, given the multi-photon nature of its formation. The absorption cross-section for hydrazine at 193 nm is 4.6×10^{-18} cm², so that, with a photon flux of $\sim 5 \times 10^{16}$ cm⁻² and 5 mTorr of N₂H₄, $\sim 10^{12}$ molecule cm⁻³ of the triplet were generated for a two photon dissociation with a similar cross-section for the second absorption. However, the strength of the signal, and our experience with OH, suggests that the initial concentration is $< 10^{11}$ molecule cm⁻³ since Hack *et al.* [10] reported that NH could be detected with a factor 40 higher sensitivity than OH. On this basis, the detection limit for NH is $< 10^9$ molecule cm⁻³. These considerations, coupled with the quality of the fit to an exponential decay for the NH signal, demonstrate

Fig. 1. Typical time profile for NH in the presence of an excess of SO. The line represents a single exponential fit to the data with a small long time, background offset. The residual plot is shown below the fit.

that $[\text{NH}] \ll [\text{SO}]$; the concentration range employed for SO was $(2\text{--}20) \times 10^{13} \text{ molecule cm}^{-3}$.

3. Results

3.1 Rate coefficient for $\text{NH} + \text{SO}$

The kinetics of reaction R1 were determined by monitoring NH as the concentration of SO was varied. A typical NH LIF time profile at 295 K is shown in Figure 1. The data exhibit single-exponential behaviour, consistent with NH being removed under pseudo-first-order conditions; the profile is described by the equation:

$$[\text{NH}] = [\text{NH}]_0 \exp(-k_1' t) + B \quad (\text{E2})$$

where $[\text{NH}]_0$ is the initial concentration formed from the multi-photon dissociation of N_2H_4 , k_1' is the pseudo-first-order removal rate coefficient and B is a small background offset, which is due to a long-lived fluorescence signal resulting from photolysis of either N_2H_4 or SOCl_2 . Figure 1 shows the residuals and demonstrates the quality of the fit to equation E2. Plots of k_1' , obtained from these fits, versus $[\text{SO}]$ results in a straight-line whose slope is equal to the bimolecular rate coefficient for reaction R1, k_1 . Figure 2 shows such a plot for 295 K which gives $k_1(295 \text{ K}) = 4.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The intercept is zero, within error. Other losses of the radicals, both NH and SO, result from diffusion from the reaction zone defined by the overlap of the photolysis and probe lasers. In our previous study on $\text{OH} + \text{SO}$ [9], radical loss via either diffusion or self-

Fig. 2. Plot of the observed pseudo-first-order rate coefficient, k_1' , versus SO concentration at 295 K. The straight-line fit to the data yields a bimolecular rate coefficient of 4.7×10^{-11} molecule $^{-1}$ cm 3 s $^{-1}$ for the NH + SO reaction, R1. The intercept is $-(230 \pm 280)$ s $^{-1}$.

reaction was observed to be only a minor loss channel. In the present case, removal of NH by reaction other than with SO was negligible at room temperature and a minor contributor at higher temperatures (See Figures 2 and 4).

Equation E2 is an accurate description of the data at temperatures below 500 K. However, at temperatures ≥ 500 K the decays showed biexponential behaviour, as shown in Figure 3. The fast component of this biexponential decay correlates with the lower temperature measurements of k_1 while the slow component is consistent with a reaction that forms NH on a longer timescale:

Figure 4 shows that the NH growth rate coefficient is proportional to [SO], and hence to [Cl], formed with SO in the initial photolysis. It is known that fluorine atoms in the presence of NH_3 lead to formation of NH via consecutive H atom abstraction [12]. By analogy we propose that reaction R4 forms NH:

Abstraction of H from NH_2 by SO, which would conform to the experimentally observed behaviour, is endothermic. In reactions R1 and R4 the SO and Cl concentrations are respectively in excess and therefore the reactions may be treated as coupled first-order reactions, which leads to the following biexponential expression for the NH time dependence:

$$[\text{NH}] = (k_4' / (k_1' - k_4')) [\text{NH}_2]_0 \{ \exp(-k_4' t) - \exp(-k_1' t) \} + [\text{NH}]_0 \exp(-k_1' t) \quad (\text{E3})$$

where k_1' and k_4' are the pseudo-first order rate coefficients for the reactions R1 and R4, respectively, and $[\text{NH}_2]_0$ and $[\text{NH}]_0$ are the initial concentrations from

Fig. 3. NH time profile in the presence of SO at 553 K, where biexponential behaviour was observed. This behaviour implies that NH is formed in the system and is consistent with the reaction: $\text{NH}_2 + \text{Cl} \rightarrow \text{NH} + \text{HCl}$. The line is a biexponential fit to the data and the residual plot is shown below the fit.

Fig. 4. Plots of the two pseudo-first-order rate coefficients, k_1' (squares) and k_4' (circles) versus $[\text{SO}]$ at 603 K, where k_1' and k_4' were obtained from fitting equation E3 to the biexponential decays. The larger bimolecular rate coefficient is equal to $4.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and is consistent with the $\text{NH} + \text{SO}$ reaction, R1, and the smaller bimolecular rate coefficient is equal to $3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and is assigned to the abstraction reaction $\text{NH}_2 + \text{Cl} \rightarrow \text{NH} + \text{HCl}$, based on $[\text{Cl}] = 2.25 \times [\text{SO}]$.

hydrazine photolysis. Equation E3 was fitted to all the data at temperatures $\geq 500 \text{ K}$ and Figure 3 shows an example of the quality of the fit. The pseudo-first order rate coefficients were plotted versus $[\text{SO}]$ (and hence $[\text{Cl}]$) to obtain k_1 and k_4 , via the slopes of the plots. $[\text{SO}]$ was determined from equation E1, where $\Phi_{\text{SO},193\text{nm}}$ equals 0.8, and $[\text{Cl}]$ was assumed to be 2.25 times the SO

Table 1. Bimolecular rate coefficient, k_1 , for the NH + SO reaction in 100 Torr He. Errors represent 1σ .

Temperature / K	$k_1/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
295	4.71±0.34
403	5.57±0.91
453	3.77±0.22
503	4.73±0.55
553	4.25±0.25
603	4.29±0.49
653	6.86±1.53
703	6.00±0.50

Table 2. Bimolecular rate coefficient, k_4 , for the $\text{NH}_2 + \text{Cl}$ reaction and the $[\text{NH}_2]_0 / [\text{NH}]_0$ ratio obtained from fitting equation E3 to the experimental data. Errors represent 1σ .

Temperature / K	$k_{R4} / 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$[\text{NH}_2]_0 / [\text{NH}]_0$
503	1.50±0.43	0.77±0.15
553	1.25±0.17	1.16±0.16
603	3.68±0.34	1.26±0.34
653	4.24±0.91	1.22±0.26
703	9.03±0.71	0.71±0.32

concentration, based on quantum yields of 0.8 for P1a and 0.2 for P1b. Figure 4 shows an example of the good linearity of these bimolecular plots. The assumption that $[\text{Cl}] = 2.25 \times [\text{SO}]$ may be an overestimate since Cl may react with hydrazine, for which there are no kinetic data. Such a reaction would give a decrease in $[\text{Cl}]$ during the NH decay, so that the later stages would not conform strictly to a biexponential profile. The contribution of the term in k_4' to the NH decay is quite small and the scatter in the data does not allow an assessment of any deviations from equation E4; our determination of k_4 should be viewed as a lower limit. The k_1 data are summarised in Table 1 and the k_4 data together with the $[\text{NH}_2]_0 / [\text{NH}]_0$ ratios are summarized in Table 2.

3.2 Potential energy surface and master equation calculations

The potential energy surface (PES) for NH + SO interactions was initially explored using density functional theory (B3LYP/6-311G(2d,d,p)) to locate minima and transition states. The Gaussian 03 program [13] was used to obtain geometries and vibrational frequencies (scaled by a standard factor of 0.99 [14]), which were used to verify the nature of the stationary points on the PES. Next, relative enthalpies were assessed via the CBS-QB3 approach [14]. Two main reaction paths, leading to SH + NO and OH + NS, were identified and selected for more detailed analysis. Geometries and frequencies (scaled by a factor of 0.954 [15]) were obtained via QCISD/6-311G(2d,d,p) theory, followed by eval-

Table 3. Computed data for stationary points on the $\text{NH} + \text{SO}$ potential energy surface.

Species	Rotational constants / cm^{-1}	Frequencies / cm^{-1}	Relative enthalpy at 0 K / kJ mol^{-1}
NH	16.495, 16.495	3121	0.0
SO	0.711, 0.711	1084	
NS	0.766, 0.766	1103	−42.7
OH	18.921, 18.921	3616	
NO	1.682, 1.628	1767	−127.3
SH	9.588, 9.588	2588	
HNSO <i>cis</i>	1.604, 0.330, 0.274	433, 769, 947, 1066, 1212, 3342	−388.0
TS1	1.007, 0.415, 0.294	2005 i, 594, 891, 1115, 1143, 1845	−186.5
HOSN	1.517, 0.290, 0.244	275, 366, 590, 1003, 1273, 3655	−301.1
HN(O)S	2.964, 0.219, 0.204	503, 835, 881, 1420, 1470, 3198	−222.0
TS2	2.865, 0.208, 0.195	2151 i, 296, 405, 775, 1562, 1927	−31.1
HSNO	2.328, 0.200, 0.184	292, 344, 530, 873, 1650, 2636	−241.1

uations of the energy at the UCCSD(T)/aug-cc-pV(n+d)Z level of theory with $n = 4$ and $n = 5$, made with the Molpro program [16]. The latter results were extrapolated to the infinite basis set limit via the relation of Halkier *et al.* [17]. These data are summarized in Table 3 and Figure 6.

The reaction system was investigated using the stationary point data given in Table 3 in a master equation (ME) analysis. Briefly, an energy grained master equation was set up using methods discussed previously [18] and the populations of the energy grains and the chemically significant eigenvalues were determined based on an eigenpair analysis of the reaction / energy transfer matrix. The microcanonical rate constants for the isomerisation reactions were calculated from the data in Table 3, using RRKM theory. An exponential down energy transfer model was used, with $\langle \Delta E \rangle_{\text{down}} = 200 \text{ cm}^{-1}$. The initial association reaction to form HNSO is barrierless. It is less clear whether that forming HN(O)S, by addition across the SO bond, is also barrierless. These associations were not studied in detail. If they are barrierless, then an approach such as flexible transition state theory is needed to calculate the microcanonical rate constants for association and dissociation. Instead, we used inverse Laplace transformation [19] of the limiting high pressure association rate coefficient, $k_{1,\infty}(T)$. In the absence of any modelled (see below) pressure dependence the experimental rate coefficients can be equated to $k_{1,\infty}(T)$. This procedure does not allow the overall rate coefficient to be split between the rate coefficients for association into HNSO and HN(O)S; the fraction of association occurring into HNSO was set to a temperature independent parameter α in the following analy-

Fig. 5. Arrhenius plots of the temperature dependence of k_1 and k_4 .

sis. This procedure allows both the microcanonical rates of association into the two wells, and of thermal dissociation from them to regenerate the reactants, to be calculated based on the experimental rate coefficients. A similar approach was used to calculate the thermal dissociation rate coefficients to form the products in reactions R1a and b, OH + NS and SH + NO respectively. No rate data are available for OH + NS association and a high pressure limiting rate coefficient equal to that measured here for NH + SO was assumed. A high pressure limiting rate coefficient of $2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for SH + NO association was taken from the IUPAC evaluation [20].

4. Discussion

4.1 NH + SO

The experimental k_1 values are plotted as a function of temperature in Figure 5; there is no systematic dependence on T and $k_1 = (5 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the whole experimental temperature range, where the uncertainty derives from the statistical error in averaging the data, and from the uncertainty in [SO]. This is the first time this reaction has been studied, but it has been included in modelling of sulphur and nitrogen doped flames [1].

The study of radical + radical reactions presents significant practical problems, deriving, for example, from the reliability of the photolytic generation of the majority reactant, SO in the present case, over the experimental temperature range. For example, dissociation of thionyl chloride on the experimental time-scale could invalidate the higher temperature measurements. In our previous study on the reaction OH + SO [9], we used the same method to generate the SO radical and again operated under pseudo-first-order conditions, with [OH]

Fig. 6. Stationary points on the potential energy surface for $\text{NH} + \text{SO}$.

$\ll [\text{SO}]$. The rate coefficient exhibited a large negative temperature dependence, falling by a factor of 5 over the same temperature range. This large difference between the temperature dependences of the two reactions using a similar technique, coupled with the absence of any abnormal behaviour at higher temperatures adds support to the reliability of our method of generating SO and studying its kinetics as an excess reagent.

While reaction R1 has not previously been studied the iso-electronic reaction:

has been studied both experimentally [10,21,22] and theoretically [23] and has been evaluated by Baulch *et al.* [3]. The room temperature rate coefficient for reaction R5 is equal to $\sim 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [10,21] and increases significantly with temperature [10,21,22], rising to $8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 2000 K. This temperature dependence is consistent with a barrier to reaction of $\sim 6 \text{ kJ mol}^{-1}$, which is in accord with the calculations of Talipov *et al.* [23], who found that the main product channel is $\text{NO} + \text{OH}$.

In previous work we have observed the NS radical using laser induced fluorescence at around 324 nm [24], which could readily be generated using the dye used to probe the NH radical. Attempts were made to observe NS as a product of reaction R1 but no signal could be found. While the master equation analysis indicates that NS is formed in the major product channel (see below), the reason for our failure to detect it is most likely related to the LIF detection efficiency of NS compared to NH. It is noteworthy that, in the study of NH by Hack *et al.* [10], it was determined that the detection limit for NH ($6 \times 10^5 \text{ molecule cm}^{-3}$) was 40 times lower than resonant OH detection. No transition probability data are available for the NS radical but based on its small rotational constant com-

pared to either NH or OH it is likely that its detection sensitivity is relatively low.

The proposed reaction R4 has not previously been studied. It is exothermic by 50 kJ mol^{-1} but, as can be seen from the values of k_4 in Table 2 and Figure 5, the rate coefficient increases significantly with temperature, and clearly there is a barrier to reaction. An Arrhenius analysis of the data in Table 2 gives an activation energy of 28 kJ mol^{-1} , and $k_4(T) = 8.2 \times 10^{-10} \exp(-3320\text{K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 500–700 K; the high A factor suggests that extraction of accurate Arrhenius parameters from a scattered dataset over a limited range of temperatures may have introduced significant error in these parameters. A barrier to reaction is consistent with the behaviour of the more reactive F atom with NH_2 , which has a rate coefficient less than gas-kinetic ($k(298) = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [10]).

Table 2 shows that the ratios of $[\text{NH}_2]_0 / [\text{NH}]_0$ are consistent with NH_2 and NH being formed in equal amounts in hydrazine photolysis at 193 nm. This result allows speculation on the nature of the multiphoton dissociation of hydrazine. Vaghjiani [25] showed that photolysis of hydrazine at 193 nm produced exclusively hydrogen atoms:

which suggests that cleavage of the N-N bond is a minor channel. Thus the present experimental results imply that NH and NH_2 are formed in equal amounts by further light absorption by NHNH_2 :

Overall, P2 + P3 is endothermic by 706 kJ mol^{-1} and therefore requires at least two 193 nm photons. While the absorption cross-section for P2 is known [25], ($4.6 \times 10^{-18} \text{ cm}^2$) that for P3 is not, and it may not be the only channel to occur on absorption of the second photon. This mechanism is however consistent with the observation of approximately equal amounts of NH and NH_2 .

The observations of Vaghjiani [25], indicate that quite high concentrations of H ($\sim 10^{13} \text{ molecule cm}^{-3}$) are generated in the single photon photolysis of hydrazine. The very slow decay of NH with $[\text{SO}] = 0$ (intercept, Figure 2), even at 603 K (intercept, Figure 4) demonstrates that reaction of H with NH is not significant. The only measurement of the rate coefficient of this reaction is restricted to high temperatures in flames [3]. Reaction of H with N_2H_4 , which would generate N_2H_3 , occurs on a timescale of $\sim 0.1 \text{ s}$ under the conditions studied [25].

Fig. 7. Microcanonical rate constants as a function of energy above the zero point energy of the reactants: — (black), k_{a1} ; — (grey), k_1 ; - · - · (black), k_{-1} ; - - - (grey), k_{d1} ; - - (grey), k_{a2} ; - · - (grey), k_2 ; - - (black), k_{-2} ; - · · - (black), k_{d2} .

4.2 Master equation calculations

The main aim of the master equation calculations was to investigate the pressure dependence of k_1 and to estimate the relative rates of channels a, b and c in reaction R1. The following mechanism can be set up:

where the bold letters are used to label the intermediates in the following analysis. g_1 and g_2 are the rates into **A** and **B**; together with the rate coefficients, they are used to represent both overall and microcanonical processes. Figure 7 shows a plot of the microcanonical rate constants for the component reactions based on an energy zero corresponding to the zero point energy of the reactants $\text{NH} + \text{SO}$. The master equation analysis showed effectively zero formation of stabilized adducts at all the pressures investigated ($\leq 10^4$ Torr). The calculated overall rate coefficient was independent of pressure over this range. The fractional yields of channels 1a and 1b also showed little pressure dependence; that for channel 1a was 0.65 and at 298 K and 0.81 at 1000 K over the pressure range $10\text{--}10^4$ Torr, for equal rates of association into HNSO and HN(O)S, i.e. for $\alpha = 0.5$. Given the more constrained nature of the variational transition state in the association to form HN(O)S, α is likely to be significantly more than 0.5, so that the major product channel, at all temperatures above 300 K, is likely to be $\text{OH} + \text{NS}$.

At all energies greater than the zero point energy of the reactants, the sums of the rate constants for loss from each of the intermediates **A–D** are significantly greater than the collision frequency under the experimental conditions, so that the reaction system can be treated as collision-free. This allows the results of the master equation analysis to be probed in greater detail, because the microcanonical rate equations for the energy grain populations can be set up independently at each energy, since there is no communication between grains at different energies, only between isoenergetic grains by isomerisation. Applying the steady state approximation gives the following expression for the microcanonical rate of forming OH + NS at energy E ,

$$v_{\text{NS}}(E) = g_1(E)k_1(E)F_c(E)/(k_{a1}(E)+k_1(E))F_C(E),$$

where F_c is the fractional loss of the grain at energy E in isomer **C** to form the products OH + NS:

$$F_c = k_{d1}(E)/(k_{-1}(E)+k_{d1}(E))$$

An equivalent expression is readily obtained for $v_{\text{NO}}(E)$, with $g_2(E) = g_1(E)(1-\alpha)/\alpha$. The ILT gives rates of association into the energy grains of HNSO and HN(O)S that are approximately equal for $\alpha = 0.5$. Figure 7 shows that $k_1 \gg k_2$, k_{a1} at all energies, so that HNSO isomerises much more rapidly than HN(O)S, and also undergoes negligible dissociation to regenerate the reactants. The barrier to dissociation from HOSN is high, however, and there is competition between isomerisation back to HNSO, so that F_c is less than unity. For the route involving association via HN(O)S, k_2 and k_{a2} are comparable; the latter is larger at higher energies and the former at lower energies. $k_{d2} \gg k_{-2}$, so that dissociation is assured once the system crosses TS2, and F_d is unity. As a result, at energies close to the threshold, $v_{\text{NS}}(E)/v_{\text{NO}}(E)$ is ~ 1 for $\alpha = 0.5$, but increases at higher energies. As discussed above, α is likely to be larger than 0.5.

5. Summary and conclusions

1. The rate coefficient for NH + SO is, within experimental error, independent of temperature over the range 295–703 K, with a mean value of $(5.0 \pm 2.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

2. Master equation calculations, based on calculated potential energy surface parameters and experimental and estimated association rate data, show that the reaction rate and product distribution are independent of pressure below 10^4 Torr. The calculations indicate that the major product channel gives OH + NS, via the adducts HNSO and HOSN. The quantitative nature of this conclusion was limited by a lack of knowledge of the relative rates of association into HNSO and HN(O)S.

3. At $T > 500$ K, the NH kinetics show biexponential behaviour that is consistent with NH formation from $\text{NH}_2 + \text{Cl}$, with a rate coefficient $k_4(T) =$

$8.2 \times 10^{-10} \exp(-3320\text{K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The accuracy of this expression is limited, because it is primarily determined over a limited temperature range (500–700 K), from quite scattered long time data, where NH has decayed to small values.

4. LIF observations and the analysis of the $\text{NH}_2 + \text{Cl}$ reaction provide information on the relative yields of NH_2 and NH in the two photon photolysis of hydrazine at 193 nm. Based on the comparable yields of NH_2 and NH and the observations of Vaghjiani [25] on the high yield of H from the 1-photon photolysis, we speculate that the major channel in the two photon process is photolysis of NHNH_2 .

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