Kinetic studies of the reaction $\text{NH}_2 + \text{H}_2\text{S}$

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ABSTRACT

Amidogen (NH_2) radicals were generated by pulsed laser photolysis of ammonia precursor at 193 nm, and monitored by laser-induced fluorescence excited at 570.3 nm. Experiments were conducted in argon bath gas with traces of hydrogen sulfide (H_2S) at pressures of 9–25 mbar and temperatures of 294–820 K. The $\text{NH}_2 + \text{H}_2\text{S}$ rate constant was found to be $(4.30 \pm 0.25) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of temperature. The rate constant for removal of vibrationally-excited NH_2 (0, 1, 0) by H_2S was estimated as $(1.5 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which includes both physical quenching and chemical reaction.

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1. Introduction

There have been no prior studies of the system:

Here we present results obtained over 295–820 K obtained via the laser pulsed photolysis/laser-induced fluorescence (LIF) technique, and briefly interpret them in the context of a computed potential energy diagram. One motivation for the present letter is that coupling between sulfur and nitrogen chemistry appears to influence formation of nitrogen oxides in sulfur-doped flames, but the mechanism is unclear [1,2]. Reaction (1) might couple S and N-species under reducing conditions. Another motivation arises from consideration of the reaction of isoelectronic OH with H_2S :

which exhibits an intriguing temperature dependence. Measurements of k_2 made at moderate temperatures yielded a zero or negative activation energy, which became significantly positive at higher temperatures. This behavior has been rationalized theoretically in terms of a reaction coordinate involving a bound intermediate [3]. An aim of the present letter is to see whether similar behavior is observed for reaction (1). As a surrogate for the encounter rate between NH_2 and H_2S , we measure the removal rate of vibrationally-excited NH_2 . Smith has proposed that, if an initially formed excited intermediate is sufficiently bound, it may have sufficient lifetime for excess vibrational energy in the reactants to be lost via intramolecular vibrational relaxation (IVR) [4]. Under these circumstances the rate of loss of NH_2 ($\nu = 1$) might be expected to be

similar to the initial capture rate of NH_2 by H_2S , even if the adduct is not collisionally stabilized.

2. Methodology

The reaction cell and general operating procedures have been detailed previously [5,6], while the LIF system is new. Following their generation by 193 nm pulsed laser photolysis of NH_3 , NH_2 radicals react with a large excess of H_2S diluted in Ar bath gas. The hydrogen sulfide (99.5% grade from MG Industries) was purified first by trapping at 77 K and degassing, which was repeated for several ‘freeze–pump–thaw’ cycles. The H_2S was then distilled repeatedly from 210 K (chloroform slush) and trapped at 77 K. Ammonia (MG Industries, 99.99%) was trapped and degassed at 77 K. Argon was used directly from the cylinder (99.995%, Air Liquide and Big Three). Gas mixtures were prepared manometrically in glass bulbs.

Under pseudo-first-order conditions we may write:

$$d[\text{NH}_2]/dt = -(k_1[\text{H}_2\text{S}] + k')[\text{NH}_2] = -k_{\text{ps1}}[\text{NH}_2] \quad (3)$$

where k' mainly accounts for diffusional loss of NH_2 out of the reaction zone, which is defined by the intersection of the photolysis and probe laser beams. Ground state X^2B_1 NH_2 radicals were electronically excited to the A^2A_1 state by a dye laser (Spectra-Physics, Quanta-Ray PDL-2E) pumped by a Nd:YAG laser (Spectra-Physics, Quanta-Ray INDI, with a repetition rate of 10 Hz) at 570.3 nm, which corresponds to absorption in the $2_{12}-2_{02}$ rotational transition of the $(0, 10, 0) \leftarrow (0, 0, 0)$ vibronic band [7]. In some experiments vibrationally-excited NH_2 was detected via LIF excitation at 531.8 nm which corresponds to the $2_1^6(0, 13, 0) \leftarrow (0, 1, 0)$ transition [8]. The fluorescence signal passed through a cut-off filter which transmitted wavelengths longer than 590 nm (OG590, Edmund Optics) and was detected by a photomultiplier tube

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(PMT, Electron Tubes, 9816B). The PMT output was amplified (Electron Tubes C632), and then recorded by a digital storage oscilloscope (BK Precision, model 2542). The time delay between the photolysis and probe laser pulses was controlled with a digital delay/pulse generator (Stanford Research Systems, model DG535). Above 650 K significant black body radiation interfered with detection and a bandpass filter (Oriel, model 53915, 10 nm fwhm centered at 590 nm) was used to block some of this radiation, allowing temperatures as high as 800 K to be reached.

The LIF signals captured in the digital storage oscilloscope were transferred to a computer for integration. This integrated signal is expected to be proportional to $[\text{NH}_2]$, and so is expected to vary as an exponential decay according to the form of Eq. (4), plus a constant background arising from scattered light. An example is shown in Figure 1. Initial radical concentrations were estimated from the UV absorption cross sections of H_2S and NH_3 , and the temperature in the reaction zone was monitored before and after experiments with a thermocouple and corrected for radiation errors [9]. Figure 2 is a plot of k_{ps1} vs. reactant concentration, whose slope equals the bimolecular rate constant k_1 . The intercept corresponds to k' and is small, so that the loss of NH_2 is dominated by reaction (1).

3. Results

Table 1 summarizes the experimental conditions for 12 determinations of k_1 for ground-state NH_2 over 294–820 K, and 5 measurements for NH_2 in the $\nu = 1$ state. τ_{res} is the average residence time of gas in the reactor before photolysis, F is the photolysis pulse energy (beam cross section 1.0 cm^2), and P is the total pressure, mainly Ar bath gas. For each determination typically 10 values of $[\text{H}_2\text{S}]$ were employed, and the highest value is listed. The corresponding maximum initial $[\text{SH}]$, arising from photolysis of H_2S , is also listed. Similarly, the fixed $[\text{NH}_3]$ and corresponding initial $[\text{NH}_2]$ are given. It may be seen that k_1 is independent, within its statistical variation (derived from the slopes of plots like Figure 2), from F and the initial radical concentrations, which suggests that reaction (1) has been successfully isolated from secondary chemistry. Also, $[\text{NH}_2] \ll [\text{H}_2\text{S}]$, confirming that pseudo-first-order conditions applied. k_1 shows no clear variation with temperature and we report the weighted mean over 294–820 K as $4.30 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with a purely statistical standard deviation of $0.06 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. With an allowance of 5% for systematic instrumental errors, we estimate 95% confidence limits of $\pm 0.25 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The removal rate constant for NH_2 (0, 1, 0) can be approximately represented

Figure 1. Example of the LIF signal for NH_2 X(0, 0, 0) in the presence of H_2S as a function of the delay time between the photolysis and probe lasers together with an exponential fit to the decay.

Figure 2. Variation of the pseudo-first-order rate coefficients for the removal of NH_2 X(0,0,0) with the concentration of H_2S at $T = 295 \text{ K}$, $P = 28 \text{ mbar}$, and a photolysis laser energy of 0.4 mJ . The error bars represent $\pm 1\sigma$ in concentration and decay rate and the filled point corresponds to the decay shown in Figure 1.

as $(1.5 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which includes both physical quenching and chemical reaction.

4. Discussion

There are no prior measurements of k_1 for comparison. According to a recent review, the isoelectronic process 2 is an order of magnitude faster at room temperature and exhibits a very small positive activation energy of 0.6 kJ mol^{-1} [10]. The temperature dependence is therefore similar to that for reaction (1). We have investigated the $\text{NH}_2 + \text{H}_2\text{S}$ potential energy surface using the W1Usc approach of Martin and coworkers [11] implemented in the GAUSSIAN09 program suite [12]. Geometries and frequencies (scaled by 0.985) of stationary points were derived at the B3LYP/cc-pVT(d)Z level of density functional theory, followed by several steps which combine to approximate the coupled cluster CCSD(T) energy at the infinite basis set limit, with all electrons correlated and corrected for scalar relativistic effects at the DKH level.

Because of the observed effectively zero activation energy for reaction (1), our focus is on product channels which are exothermic or only slightly endothermic. The obvious choice is:

for which the W1Usc reaction enthalpy at 0 K is $\Delta_r H_0 = -65.8 \text{ kJ mol}^{-1}$. Correction for the spin-orbit splitting in SH yields $\Delta_r H_0 = -68.1 \text{ kJ mol}^{-1}$, which compares well with the experimental value of $-67.3 \text{ kJ mol}^{-1}$ [13,14]. This is consistent with the root-mean-square deviation of 2.4 kJ mol^{-1} for application of W1Usc theory to a test set of diverse energies [11]. The only other NSH_4 combination lower in energy than the reactants is:

for which the computed $\Delta_r H_0$ is $-32.8 \text{ kJ mol}^{-1}$. The enthalpy of formation of H_2NS appears to be unknown; our result implies $\Delta_f H_0 = 138.5 \text{ kJ mol}^{-1}$. The isomers HNSH and NSH_2 are higher in enthalpy by 62 and 266 kJ mol^{-1} , respectively, and are not plausible candidates. Formation of $\text{H} + \text{trans-H}_2\text{NSH}$, the most stable NSH_3 isomer [15], is endothermic by 104 kJ mol^{-1} so these isomers are not considered further.

The corresponding reaction pathways are plotted in Figure 3. For reaction (1b) there is a direct transition state (TS) which is drawn in Figure 4. However, its energy is 187 kJ mol^{-1} above the reactants so this cannot be a significant channel under our conditions. Pathway 1a has a weakly bound complex in the entrance

Table 1Summary of measurements of the rate constant k_1 for $\text{H}_2\text{S} + \text{NH}_2$ ($v=0$ and $v=1$).

T (K)	τ_{res} (s)	F (mJ)	P (mbar)	$[\text{H}_2\text{S}]_{\text{max}}$ (10^{15} molecule cm^{-3})	$[\text{HS}]_{\text{max},0}$ (10^{12} molecule cm^{-3})	$[\text{NH}_3]$ (10^{14} molecule cm^{-3})	$[\text{NH}_2]_0$ (10^{12} molecule cm^{-3})	$k_1 \pm \sigma$ (10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$)
294	2.0	0.1	27	8.15 ± 0.33	5.0	11.80	0.6	4.28 ± 0.19^a
294	1.6	0.2	14	4.62 ± 0.18	5.7	5.30	0.5	4.05 ± 0.21^a
294	1.6	0.5	14	3.45 ± 0.14	10.6	5.40	1.3	4.11 ± 0.18^a
295	2.1	0.4	28	2.46 ± 0.10	6.1	7.90	1.5	4.21 ± 0.22^a
295	1.3	0.1	11	3.16 ± 0.13	2.0	5.10	0.3	4.39 ± 0.13^a
396	1.4	0.4	25	2.26 ± 0.09	5.6	7.26	1.4	4.15 ± 0.20^a
526	0.8	0.4	12	2.14 ± 0.09	5.3	11.10	2.2	4.42 ± 0.15^a
611	0.6	0.4	11	3.24 ± 0.13	8.0	7.21	1.4	4.55 ± 0.25^a
611	0.9	0.2	25	2.62 ± 0.10	3.2	10.80	1.1	4.20 ± 0.22^a
615	0.9	0.8	16	3.25 ± 0.13	16.0	5.10	2.0	4.32 ± 0.19^a
802	0.4	0.5	9	1.73 ± 0.07	5.4	4.40	1.1	4.41 ± 0.28^a
820	0.4	0.4	9	1.63 ± 0.07	4.0	4.30	0.8	4.48 ± 0.31^a
294	0.8	0.4	12	0.64 ± 0.03	1.6	4.59	0.9	137 ± 8^b
294	0.8	0.8	12	0.86 ± 0.03	4.3	4.65	1.8	130 ± 10^b
415	0.6	0.5	12	0.33 ± 0.01	1.0	5.71	1.4	153 ± 12^b
512	0.5	0.4	12	0.27 ± 0.01	0.7	6.52	1.3	166 ± 15^b
513	0.5	0.8	12	0.19 ± 0.01	1.0	5.55	2.2	159 ± 11^b

^a $v=0$.^b $v=1$. **Figure 3.** Potential energy diagram for $\text{NH}_2 + \text{H}_2\text{S}$ derived via W1Usc theory.

channel, where the reactants are hydrogen-bonded with an N–H distance of 2.29×10^{-10} m and are stabilized by 6 kJ mol^{-1} . This is followed by a TS for H-atom transfer from S to N where the N–H distance has shortened to 1.58×10^{-10} m (see Figure 4).

Initial density functional (B3LYP/cc-pV(T+d)Z) results indicated that this abstraction TS had an energy (including zero point energy) 1.6 kJ mol^{-1} below the reactants. This would be a scheme of type IV as classified by Golden [16], which is capable of yielding a small or negative temperature dependence. The removal rate constant of vibrationally-excited NH_2 of $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ provides a possible measure of the rate of formation of entrance complexes. To be consistent with the observations, around one in 30 of these reactive collisions must lead to dissociation of the bound complex to $\text{SH} + \text{NH}_3$, with the rest leading back to the reactants. The complex itself is insufficiently stable to be a significant sink for NH_2 . We recognize that because the complexes are weakly bound they may not all survive long enough for every vibrationally-excited NH_2 to lose energy via IVR, in which case the true capture rate constant would be higher than $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Because the transition state for dissociation of the complex to $\text{H}_2\text{S} + \text{NH}_2$ is loose, with a high entropy, it is feasible for this dissociation to be faster than reaction of the complex via the tight transition state leading to final products, even though it has a lower energy.

However, our more accurate wavefunction-based (coupled cluster at the infinite basis set limit) results show this abstraction TS to lie 10.8 kJ mol^{-1} above the reactants, which makes the scheme of type I [16] and we may view the mechanism as

Assuming [complex] is in steady state, the effective bimolecular rate constant for NH_2 removal is $k_a k_b / (k_{-a} + k_b)$. Using the 'Thermo' module of the Multiwell system [17,18] we have calculated the equilibrium constant $K_c = k_a / k_{-a}$ to be approximately constant over 298–800 K at $\sim 2.5 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1}$, and the high-pressure limit for k_b to have $A = 1.1 \times 10^{11} \text{ s}^{-1}$ (which illustrates the tightness of this TS) with $E_a = 10.7 \text{ kJ mol}^{-1}$. The Multiwell input file is provided in the Supplemental material, and it lists the rotational constants and frequencies in the complex and the TS as hindered rotors and simple Eckart tunneling for k_b . Initially we assumed the capture rate constant k_a to be equal to the NH_2 ($v=1$) quenching rate constant, $\sim 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The model of Eq. (4) yields k_1 in

Figure 4. Structures for transition states computed at the B3LYP/cc-pV(T+d)Z level of theory. TS1a is for $\text{NH}_2 + \text{H}_2\text{S} \rightarrow \text{NH}_3 + \text{SH}$ and TS1b is for $\text{NH}_2 + \text{H}_2\text{S} \rightarrow \text{H}_2\text{NS} + \text{H}_2$. Distances are in 10^{-10} m and angles are in degrees.

agreement with experiment at 298 K but k_1 is more than an order of magnitude too high at 800 K. Reducing the barrier for k_b lowers the temperature dependence of k_b and thus k_1 , but makes its magnitude greater at the same time, so a compensating reduction in k_a is also required. A tolerable fit can be obtained by forcing $k_a = 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a reduction by a factor of 30, along with lowering the barrier at TS1a by 5 kJ mol⁻¹. We regard these changes as large compared to the uncertainty in these quantities, and therefore consider this fit is unsatisfactory. We also comment that a more detailed RRKM analysis of the scheme in Eq. (4) which considers the energy dependence of k_{-a} and k_b yields similar results.

In the presence of a second molecule of H₂S the abstraction barrier is reduced by the requisite 5 kJ mol⁻¹ at the CBS-QB3 level of theory, relative to NH₂ + 2H₂S. This is equivalent to the reaction of NH₂ with H₂S dimer, which is bound by 4 kJ mol⁻¹ [19]. While giving an activation energy closer to that observed, this mechanism would yield a second-order dependence of the reaction rate on [H₂S] and therefore is rejected.

5. Conclusion

The first experiments on the NH₂ + H₂S system yield a rate constant that is both temperature-independent and small. While the exothermic products NH₃ + H₂S are plausible thermodynamically, we are not able to rationalize their formation quantitatively in terms of our existing potential energy diagram. We speculate that other pathways to these products, or possibly to NH₂S + H₂, remain to be elucidated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2014.01.016>.

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