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LETTERS

No Barrier for the Gas-Phase $C_2H + NH_3$ Reaction

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The absolute rate constant of the reaction $C_2H + NH_3 \rightarrow$ products has been experimentally determined over the temperature range 295−765 K at a pressure of 10 Torr (He) and over the pressure range 5−30 Torr at 295 K. The concentration of C_2H radicals was monitored in real time using the CH chemiluminescence method following their production by pulsed laser photolysis of C_2H_2 at 193 nm in a slow-flow reaction vessel. The pressure-independent rate constant is large and exhibits a pronounced negative temperature dependence: $k_1(T) = (1.2 \pm 0.2) \times 10^{-11} \exp[(370 \pm 40)\ \mathrm{K}/T]\ \mathrm{cm^3\ s^{-1}}$, both unusual for reaction of a radical with a saturated molecule. This may be rationalized by strong dipole−dipole and dipole − quadrupole interactions, as have been put forward for the isoelectronic $CN + NH_3$ reaction. The $C_2H + NH_3$ reaction is somewhat faster than $CN + NH_3$, even though ab initio calculations predict the CCH dipole moment to be smaller than that for CN. However the opposite sign of the dipole moment of C_2H implies an initial HCC- - -HNH_2 alignment, favorable for subsequent H-abstraction. The (extrapolated) high rate constant both at combustion temperatures and at interstellar temperatures should make this reaction very important in those environments.

I. Introduction

Most gas-phase reactions of radicals with closed-shell molecules face sizable energy barriers, and thus have negligible rate constants at the very low temperatures (10 K ≤ T ≤ 100 K) found in interstellar clouds where the chemistry is dominated by barrier-less reactions governed by long-range attractive forces. Some radical-molecule reactions though do have large rate constants at low temperatures; a notable example being the reaction of the cyano radical with ammonia, $CN + NH_3$, with $k(100\ \mathrm{K}) \approx 1 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$.[1] This large rate constant and its unexpectedly sharp decrease with increasing temperature has been of recent interest to experimentalist and theoreticians.[1−4]

Capture theories[5] that assume the reaction dynamics are controlled by long-range forces and that reaction is guaranteed once over the centrifugal barrier have attempted to reproduce the rate constants of such reactions. For $CN + NH_3$ there has been limited success: capture theory roughly reproduces the magnitude of the rate constant at low temperatures but the predicted T dependence is much too weak. These deficiencies in relation to the $CN + NH_3$ reaction have been pointed out by Faure et al.[3,4] They have shown that inclusion of (NH_3−) quadrupole− (CN) dipole interaction significantly increases the attraction potential at large to midrange internuclear distances but that the temperature dependence is reproduced only by inclusion of rotational selection, in which the reaction is favorable when low-energy rotations are involved. Such theoretical treatments though are still in development.

The isoelectronic counterpart of CN, the ethynyl radical (C_2H), is also found in interstellar regions[6−9] and in planetary atmospheres.[10,11] Thus, its low-temperature kinetics too have received attention,[12−17] though the reaction

$$C_2H + NH_3 \rightarrow \text{products} \qquad (1)$$

has not previously been studied either theoretically or experimentally.

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At higher temperatures, C_2H is found as an intermediate in hydrocarbon combustion[18,19] where it is linked to acetylene oxidation and to the formation of polycyclic aromatic hydrocarbons, the precursors of soot.[20−24] C_2H is also known to be responsible for the intense CH(A→X) chemiluminescence in flames via $C_2H + O \rightarrow CH(A) + CO$ and $C_2H + O_2 \rightarrow CH(A) + CO_2$.[25,26] Finally, C_2H radicals may take part [27] in "NO_x reburning", in which small hydrocarbon radicals, generated from fuel injected above the main combustion zone, reduce NO_x emissions by rapid reactions with NO and NO_2 to yield HCN or NCO, thus initiating a series of reactions leading to N_2 via NH_2, NH, N, and other intermediates.[28−32] This "NO_x reburning" can be enhanced by injecting NH_3 ("advanced reburning")[33] into the combustion zone thus generating larger concentrations of NH_i intermediates. Besides, fuel-bound nitrogen will also give rise to NH_3 in combustion environments.

II. Experimental Section

The pulsed-laser photolysis/chemiluminescence experimental apparatus used in this study is described elsewhere.[34,35] The principal features are given here. C_2H radicals were generated by pulsed laser photolysis of C_2H_2 at 193 nm in a heatable, blackened, stainless steel reaction cell equipped with windows for passage of the photolysis beam and for chemiluminescence detection at right angles to it. A homogeneous mixture of the excess reactant (NH_3), carrier gas (He), and C_2H precursor (C_2H_2) was flowed through the cell at a sufficient rate to refresh the gas between successive photolysis pulses. The gas purities were as follows: He, 99.999%; C_2H_2 (acetone free), 99.6%; NH_3, 99.96%. NH_3 was diluted in high-purity He to a fraction of about 0.1 before use. For most experiments the total gas pressure was 10 Torr.

Any [C_2H(A)] formed with [C_2H(X)] by photolysis of C_2H_2 [36,37] will be quenched rapidly by (10 Torr) helium, at a rate of about 1.3×10^6 s^{-1},[37] such that only a fraction of less than 1.5×10^{-3} survives after 5 μs, at the inception of the C_2H decay measurements.

Contrary to some earlier suggestions,[38,40] it has been firmly established recently[41,42] that C_2H is the only primary photoproduct of the 193 nm C_2H_2 dissociation. The low 193 nm laser fluence of ca. 1.0×10^{16} photons cm^{-2} per pulse precludes possible two-photon products.[36]

The real-time decay of [C_2H] was monitored by measuring the intensity of the 431 nm CH(A→X) chemiluminescence resulting from the reaction of C_2H with O_2 added in large excess.[35] Thus, C_2H radicals undergo reactions with the coreactant NH_3, its precursor C_2H_2, and O_2, all in large excess

$$C_2H + NH_3 \rightarrow \text{products} \quad (1)$$

$$C_2H + O_2 \rightarrow \text{other products} \quad (2a)$$

$$\rightarrow CH(A) + CO \quad (2b)$$

$$CH(A) \rightarrow CH(X) + h\nu \quad (3)$$

$$C_2H + C_2H_2 \rightarrow \text{products} \quad (4)$$

As the CH(A) lifetime, of ≈ 0.5 μs,[39] is less than the chemical lifetime of C_2H in our experiments, the CH(A→X) emission intensity, $I_{obs}(t)$, is proportional to [C_2H], since [O_2] is constant, such that

$$I_{obs}(t) \propto [C_2H](t) \propto [C_2H]_0 \exp(-k't) \quad (i)$$

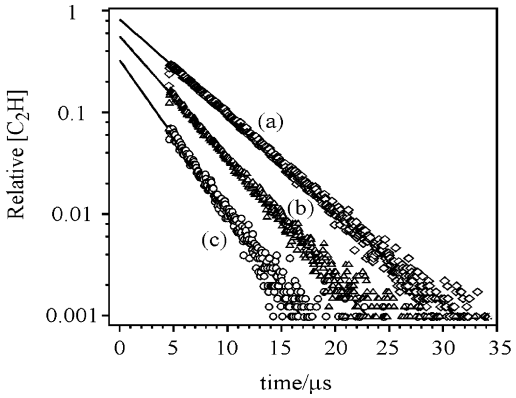

Figure 1. Typical time profiles of [C_2H] following its production by pulsed photodissociation of C_2H_2 at 193 nm in the presence of [C_2H_2] $= 1.7 \times 10^{15}$ cm^{-3}, [O_2] $= 1.5 \times 10^{15}$ cm^{-3}, temperature of 450 K, and a total pressure of 10 Torr (He): (a) [NH_3] $= 0.0$ cm^{-3}; (b) [NH_3] $= 1.1 \times 10^{15}$ cm^{-3}; (c) [NH_3] $= 3 \times 10^{15}$ cm^{-3}. Each decay is fitted by the expression $k' = A \exp(-k_{total}t)$.

with

$$k' = k_1[NH_3] + k_2[O_2] + k_4[C_2H_2]$$

The CH(A→X) chemiluminescence from the irradiated reaction volume chamber was imaged onto an optically filtered (430 ± 10 mn) photomultiplier tube (PMT). The transient signal was digitized and stored on computer. Typically 15 intensity-vs-time profiles were averaged for each k' measurement. At each single temperature, k' values were measured for seven to nine different [NH_3] ranging from 0 to ca. 7×10^{15}(295 K/T) cm^{-3}, but at a fixed [C_2H_2] of 2.5×10^{15} (295 K/T) cm^{-3} and fixed [O_2] of 2.3×10^{15} (295 K/T) cm^{-3}. On the basis of a 193 nm absorption cross-section for C_2H_2 of 1.4×10^{-19} cm^{-2} [40] and a quantum yield for C_2H production of unity,[41,42] $[C_2H]_0$ was calculated to be 3.5×10^{12} (295 K/T) cm^{-3}, sufficiently small to ensure a negligible influence (<1%) of any secondary or side (C_2H-radical) reactions. The absence of any effects from H atoms and NH_2 generated by NH_3 photolysis is discussed below.

The first-order decay rates, k', are determined by a weighted least-squares fit to $I_{obs}(t)$, each time after subtraction of an emission transient taken in the absence of O_2 to correct for scattered laser light and window fluorescence.

Since k_2' and k_4' are constants for a fixed [O_2] and [C_2H_2], respectively, the term $k_2[O_2] + k_3[C_2H_2]$ appears only as an ordinate intercept in a plot of k' vs [NH_3], whereas the slope of the resulting straight line equals the bimolecular rate constant k_1.

III. Results and Discussion

Figure 1 shows three $I_{obs}(t)$ C_2H-decay profiles at 450 K: (a) in the absence of NH_3, where C_2H is removed solely by O_2 and C_2H_2; (b and c) in the presence of (increasing amounts of) NH_3, resulting in an increase of the decay rate. All $I_{obs}(t)$ profiles exhibit single-exponential behavior over about 2 orders of magnitude. The smaller [C_2H] at $t \rightarrow 0$ for increasing [NH_3] is due to 193 nm absorption by NH_3. Figure 2 shows plots of k' as a function of [NH_3] for three temperatures T. Linear fits yield k_1 as slope and $k_2[O_2] + k_4[C_2H_2]$ as intercept.

At the 193 nm NH_3 absorption cross section of 5.4×10^{-18} cm^2,[43] and at our typical 193 nm laser fluences of 9−11 mJ cm^{-2} pulse^{-1} a fraction ca. 0.05 of the NH_3 should be photolyzed, generating H and NH_2 at near-unity quantum yield.[43] As the rate constants of the combinations of H and NH_2 with C_2H at 10 Torr of He may be estimated to be of the order 5 ×

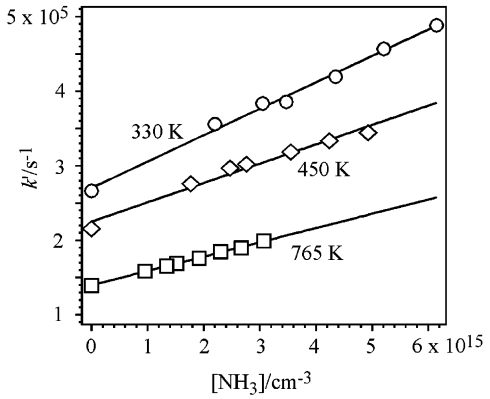

Figure 2. Second-order plots of k' vs $[NH_3]$ at three representative temperatures.

TABLE 1: Derived Experimental Rate Constants for the $C_2H + NH_3$ Reaction

T/K	P/Torr	k'/cm^3 s^{-1}
295	30	4.3 ± 0.6
295	5.0	4.2 ± 0.8
295	10.0	4.4 ± 0.8
333	10.0	3.5 ± 0.6
350	10.0	3.0 ± 0.5
450	10.0	2.6 ± 0.4
500	10.0	2.2 ± 0.4
650	10.0	2.2 ± 0.2
765	10.0	1.9 ± 0.1

10^{-11} cm^3 s^{-1}, i.e., close to $k_1(C_2H + NH_3)$, the k_1 values from the slopes of k' vs the *input*-$[NH_3]$ plots might be systematically 5−10% too high. To test this, k_1(295 K) was measured at laser fluences of 4.3 and 11.8 mJ cm^{-2} per pulse, under the same chemical conditions, yielding k_1 values differing less than 3%. Thus, the combined influence of NH_3 photolysis with H and NH_2 generation on the derived k_1 is small and lies within the uncertainty of our determinations. A rationalization is fast recombination of H and NH_2 at the higher $[NH_3]$; also, H and/or NH_2 may react slower than NH_3 with C_2H. Nonetheless, an additional systematic error of ±8% was imposed on the derived A factors on the fits to $k_1(T)$ vs T. All k_1 values with their 2σ statistical uncertainties are listed in Table 1. Measurements over the pressure range 5−30 Torr of He, also in Table 1, show k_1-(295 K) to be independent of pressure.

Our $k_1(T)$ results show that $C_2H + NH_3$ is unusually fast for a radical + closed-shell-molecule reaction, with $k_1(295\ K) = (4.2 \pm 0.6) \times 10^{-11}$ cm^3 s^{-1}, though it slows down markedly at higher T. The Arrhenius fit of Figure 3 yields $k_1(T) = (1.2 \pm 0.2) \times 10^{-11} \exp[(370 \pm 40)\ K/T]$ cm^3 s^{-1}. A more useful expression for extrapolation to lower T is $k_1(T) = (3.9 \pm 0.4) \times 10^{-11} (T/295\ K)^{-0.75\pm0.10}$. Both expressions include statistical (2σ) and likely systematic errors. Clearly, reaction 1 proceeds without a barrier, similar to $CN + NH_3$.[1,44] The plot of k vs T in Figure 4 shows the similar $k(T)$ behavior of the two isoelectronic reactions, though $C_2H + NH_3$ is faster at the lower end of the T-range of overlap. Most likely, dipole−dipole and dipole−quadrupole interactions, as invoked to reproduce the low-T behavior of $k(CN + NH_3)$,[4] are also involved in the fast capture of C_2H by NH_3. An important difference, however, is that the dipole moment $\mu(C-N) = +1.70$ D[4] whereas $\mu(C-CH) = -0.77$ D.[45] The lower $\mu(C-CH)$ is likely (over-)compensated by its opposite sign which results in an initial HCC- - -H_3N alignment favorable for an H-abstraction transition structure HCC- -H−NH_2 − contrary to the CN counterpart. Note that the low-T rate constant should be due

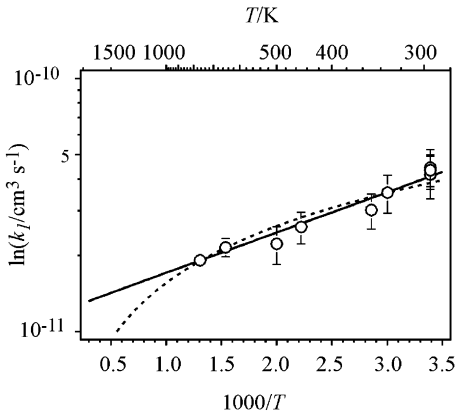

Figure 3. Arrhenius plot of the $C_2H + NH_3$ rate constants. The best fit Arrhenius expression (solid line) is $k_1(T) = (1.2 \pm 0.2) \times 10^{-11} \exp[(370 \pm 40)\ K/T]$. The dotted line is a fit to the data of the form $k_1(T) = A(T/295\ K)^n$, with $A = (3.9 \pm 0.4) \times 10^{-11}$ and $n = -0.75 \pm 0.10$.

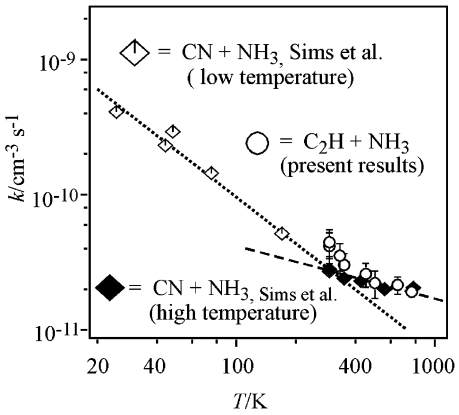

Figure 4. Plot of the experimental rate constants for $C_2H + NH_3$ (open circles) encompassing the low-temperature range over which data for the isoelectronic, $CN + NH_3$, reaction exists (also plotted). The dotted line shows a fit to the low-temperature experimental data of Sims et al.[1] for $CN + NH_3$ (open diamonds) and the dashed line shows the fit to the high-temperature experimental data of Sims et al.[44] for $CN + NH_3$ (filled triangles).

mostly to slowly rotating reactants as these are more sensitive to the anisotropy of the long-range potential.[4] The product channel in line with the above is $C_2H + NH_3 \rightarrow C_2H_2 + NH_2$, $\Delta_r H(298\ K) = -21.7$ kcal/mol.[44] However, more exothermal channels ($\rightarrow CN + CH_4$; $\rightarrow HCN + CH_3$; $\rightarrow CH_3CN + H$; $\rightarrow CH_2CN + H_2$; ...), although requiring more extensive rearrangements, cannot be excluded. The dominant influence of long-range dipole−dipole and dipole−quadrupole effects on $k_1(C_2H + NH_3)$ is underscored by the fact that k_1(295 K) is a factor ca. 450 higher than expected from an Evans−Polanyi correlation between the rate constant of H-abstraction from R−H by C_2H and the R−H bond energy for *nonpolar* R−H compounds, C_2H_6, CH_4, and H_2.[46]

The high rate constant of the title reaction should make it an important process in the interstellar medium, in planetary atmospheres, and in combustion environments. It therefore deserves further experimental and theoretical investigation, aimed, among others, at determining k_1 at lower temperatures, where capture theory is more applicable, and establishing the product distribution.

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(46) $k(C_2H + C_2H_6) = 7.8 \times 10^{-12}$ cm^3 s^{-1} per absractable H at 295 K (Ceusters, B.; Nguyen, H. M. Y.; Nguyen, M. T.; Peeters, J. Vereecken, L. *Phys. Chem. Chem. Phys.* **2000**, *3*, 3070), and the H_5CC-H bond strength is 422.8 ± 1.5 kJ mol^{-1}. $k(C_2H + CH_4) = 7.28 \times 10^{-13}$ cm^3 s^{-1} per abstractable H at 298 K (Ceursters, B.; Nguyen, H. M. T.; Peeters, J.; Nguyen, M. T. *Chem. Phys. Lett.* **2000**, *329*, 412); the H_3C-H bond strength is 438.5 ± 1.5 kJ mol^{-1}. $k(C_2H + H_2) = 3.5 \times 10^{-13}$ cm^3 s^{-1} per abstractable H at 295 K (Peeters, J.; Van Look, H.; Ceursters, B. *J. Phys. Chem.* **1996**, *37*, 15125); the H−H bond strength is 436 kJ mol^{-1}. The H_2N-H bond strength is 449.4 ± 4.6 kJ mol$^{-1.}$