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Competition between binary ion molecule reactions and ternary association reactions of CH_3^+ with NH_3 in He buffer gas in the pressure range 0.2–1.7 Torr

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The binary reaction of CH_3^+ with NH_3 as well as their ternary association have been investigated in the regime from 0.047 to 0.2 eV, KE_{cm}, using the Innsbruck selected ion drift tube (SIDT). In this energy regime the association rate coefficient declines from 4×10^{-26} to 6×10^{-27} cm^6 s^{-1} and the lifetimes of the collision complex $(CH_3^+ - NH_3)^*$ range from $\sim 10^{-7}$ to $\sim 10^{-8}$ s.
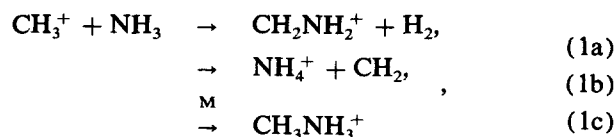
INTRODUCTION

A significant number of ion–molecule reactions have been investigated in which competition between binary and ternary reaction pathways have been demonstrated at near-thermal energies and at pressures at or below 1 Torr.[1,2] Many of them have involved the reactions of CH_3^+ with several small molecules,[1,3] clearly implying lifetimes for the ion–molecule association complex of the order of microseconds. Smith and Adams have shown that these lifetimes increase dramatically with decreasing temperature.[3] An RRK-based description[4] of lifetimes of these highly excited intermediates suggests that the three-body association reaction can be parameterized in the form $k_{3B} = k_{300} (300/T)^n$, where k_{300} is the measured rate coefficient at 300 K and n is related to the "effective number of oscillators" in the association complex. The lifetime of the complex is proportional to T^{-n}, with n values ranging from 2–5 for the systems reported to date. Thus lifetimes increase dramatically with declining temperatures of interstellar clouds. In this time regime radiative stabilization of the complex competes effectively with dissociation reactions, suggesting that these radiatively stabilized complexes may play a major role in interstellar molecular synthesis.

Although energetically-allowed binary reactions of CH_3^+ are typically very fast[1] ($k \sim 10^{-9}$ cm^3 s^{-1}) the remarkably long lifetimes of the association complex frequently results in competition between three-body association and binary reactions of CH_3^+ even at the low pressure where binary ion–molecule reactions are conventionally investigated in drift and flow tubes. Four examples where this occurs are the cluster reactions forming $CH_3^+ \cdot X$, with $X = NH_3$, $H_2 CO$, $CH_3 OH$, and $CH_3 NH_2$.[5] One of these, the reaction of CH_3^+ with NH_3, has been extensively investigated, both experimentally and theoretically.

When the normal operating pressure (10^{-6} to 10^{-5} Torr) was extended to 10^{-4} Torr in an ICR experiment, Huntress and Elleman[6] observed the association product $CH_3NH_3^+$ in addition to the fast binary reaction product CNH_4^+. In a selected ion flow tube (SIFT) experiment (performed at 300 K) Smith and Adams[5,7] reported two binary reaction channels [(1a), (1b)]:

$$CH_3^+ + NH_3 \rightarrow CH_2NH_2^+ + H_2, \quad (1a)$$
$$\rightarrow NH_4^+ + CH_2, \quad (1b)$$
$$\xrightarrow{M} CH_3NH_3^+ \quad (1c)$$

producing $CH_2NH_2^+$ and NH_4^+ competition with the association reaction (1c). Here we write the formula of the detected $m/z = 30$ product as $CH_2NH_2^+$ because, as depicted in Fig. 8, the lowest energy transition state for H_2 elimination involves vicinal elimination. The association product $CH_3NH_3^+$ accounted for about 20% of the total reaction and was nearly independent of the helium buffer gas pressure from ~ 0.2 to ~ 0.8 Torr. This was interpreted on the basis that the ternary association mechanism reaches saturation at about 0.2 Torr for a fraction of collision complexes, while another fraction reacted too quickly to be stabilized in the pressure range accessible to SIFT experiments.

In a drift tube experiment using helium as a buffer gas at pressures between 0.3 and 0.7 Torr Thomas *et al.*[8] investigated the product distribution of the reaction of CH_3^+ with NH_3 in the energy regime from 0.04 eV $\leqslant KE_{cm} < 0.8$ eV (KE_{cm} is the mean relative kinetic energy between the reactants). Both the abundances of the binary product ion $CH_2NH_2^+$ [reaction 1(a)] and the associative product ion $CH_3NH_3^+$ [reaction 1(c)] were observed to decline with increasing KE_{cm}, from 68% and 18%, respectively, at 0.04 eV to 17% and 0% at 0.8 eV. With increasing collision energy a fourth reaction channel

$$CH_3^+ + NH_3 \rightarrow NH_3^+ CH_3 \quad (1d)$$
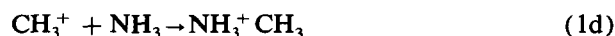
was also observed. The abundances of the products NH_4^+ and NH_3^+ were found to increase from 14% and $\sim 0\%$ to 48% and 35%, respectively, as the kinetic energy was increased from 0.04 to 0.8 eV. The total rate coefficient for all channels showed a decline from $\sim 2 \times 10^{-9}$ cm^3 s^{-1} at 0.04 eV to $\sim 6 \times 10^{-10}$ cm^3 s^{-1} at 0.8 eV.

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No significant pressure dependence was observed for the total rate coefficient or for the relative abundances of products, also suggesting that saturation for the three-body association channel was reached at the buffer gas pressures investigated. However, under the conditions of the previous SIFT[7] and drift tube experiments[8] only lower limits could be obtained for the values of the rate coefficient for the ternary association and for the corresponding lifetime of the complex $(CH_3NH_3^+)^*$. In order to deduce actual values for these parameters the title reaction was investigated using the Innsbruck SIDT[9,10] over the ranges of pressures 0.1 to 1.7 Torr and kinetic energies 0.047 to 0.2 eV. This range of experimental parameters was large enough to observe significant changes in both the total rate coefficient and the relative abundances of the $CH_3NH_3^+$ product channel.

A recent theoretical study of the same system by Herbst[11] discusses the serious difficulties in rationalizing on the basis of statistical theories the simultaneous existence of fast binary reaction channels and a saturated association channel for the same reactants. He proposed a detailed model for the competition between binary and ternary reaction channels and carried out detailed calculations for CH_3^+/NH_3 reactions based in part on an *ab initio* potential energy surface for $(CH_3NH_3)^+$ calculated by Nobes and Radom.[12]

The detailed calculations of Herbst for the actual system investigated here constitutes an ideal framework for discussing our experimental results. A similar model, involving a potential energy barrier in the exit channel, was advanced earlier for the CH_3OH^+/CH_3OH system by Bass *et al.*[13] This paper treats a case in which the stabilizing molecule (CH_3OH) has been demonstrated to have approximately unit efficiency in removing vibrational excitation; further, the decomposition channels are less exothermic than the present case. As will be shown in the present paper, the CH_3^+/NH_3 system exhibits distinctively different characteristics from CH_3OH^+/CH_3OH clustering reactions.

EXPERIMENTAL

The present experiments were carried out using the Innsbruck SIDT apparatus[9,10] shown schematically in Fig. 1. CH_3^+ ions are generated in a low pressure $(P < 10^{-2}$ Torr) electron impact ion source by dissociative ionization of CH_4. Ions extracted from the source enter an octupole field guided beam region. Here other reactant gases may be introduced to modify the internal energy distributions of the reactant ions. However, as no significant changes in both the overall reactivity and the product distribution of the reaction of CH_3^+ with NH_3 were observed, we removed the octupole system for most of the present measurements. Next the ions are mass selected by a quadrupole mass filter and injected via a Venturi jet into the drift tube section operated with helium buffer gas. Mean kinetic energies are controlled by means of a linear axial field. Binary or effective binary rate coefficients are obtained from the decline of the reactant ion signal as a function of the reactant gas flow into the drift section (added to the buffer gas) in the usual way.[10] Using the ion mobility data of Peska *et al.*,[14] the data are directly converted into rate constants as a function of center-of-mass relative kinetic energy, KE_{cm}, of the reacting pairs.

Because a ternary association channel occurs in addition to the binary reaction channels, an increase of the overall rate coefficient is observed with increasing buffer gas pressure. In order to check for contributions of artifacts as the buffer gas pressure is increased we have investigated the purely binary reaction of CH_3^+ with CH_4 at $KE_{cm} = 0.055$ eV over the buffer pressure regime from 0.2 to 1.25 Torr. Since we obtained a pressure-independent rate coefficient, $k = 2.9 \times 10^{-9}$ cm^3 s^{-1} ($\pm 5\%$), we conclude that our rate coefficient measurements for CH_3^+ with NH_3 as a function of buffer gas pressure are reliable. For an additional check we used the reaction of C^+ with NH_3, at $KE_{cm} = 0.061$ eV, obtaining again a pressure-independent value for the rate coefficient, $k = 2.3 \pm 0.1 \times 10^{-9}$ cm^3 s^{-1}.
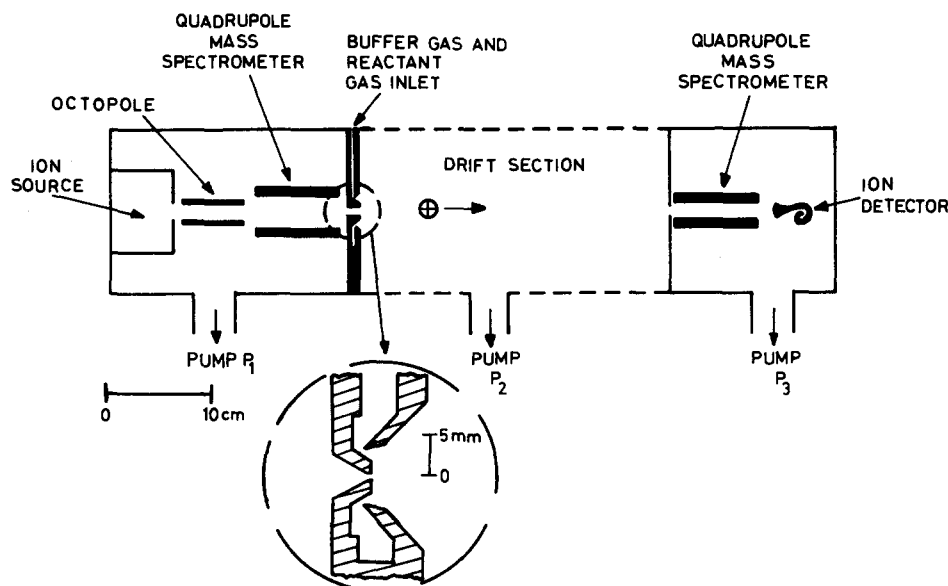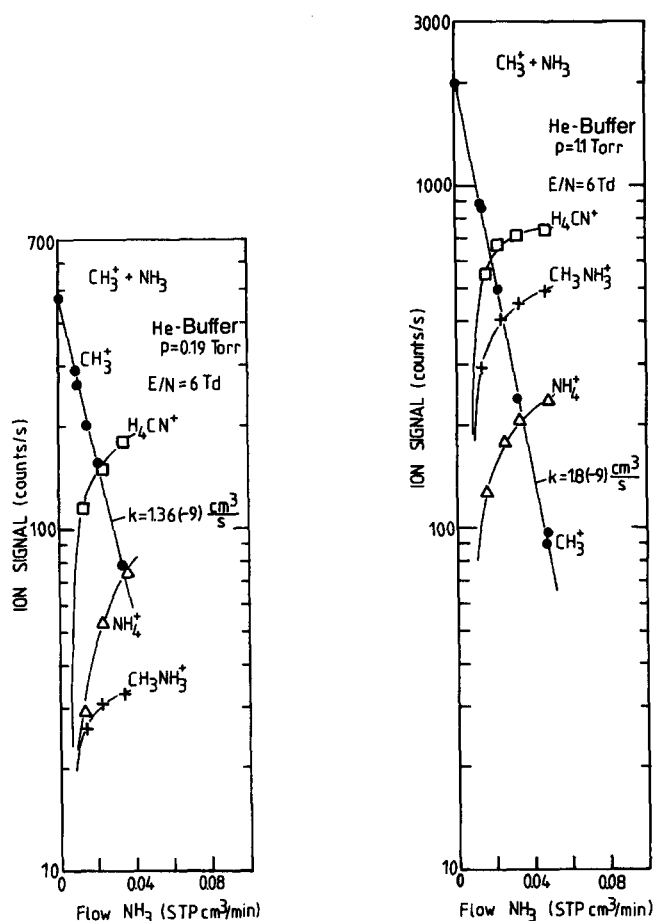

FIG. 1. Schematic representation of the Innsbruck SIDT.

FIG. 2. Semilogarithmic plots of the intensities of the reactant CH_3^+ and the binary product ions $CH_2NH_2^+$, NH_4^+, and the association reaction product $CH_3NH_3^+$, at $KE_{cm} = 0.047$ eV (~ 365 K) in a helium buffer (a) at a gas pressure of 0.19 Torr and (b) at a gas pressure of 1.1 Torr.

FIG. 3. Total partial rate coefficients as a function of the mean center-of-mass collision energy KE_{cm} and the comparison with data of Smith and Adams (Ref. 1) and Thomas *et al.* (Ref. 8) $P \gtrless 1$ Torr.

RESULTS AND DISCUSSION

Figure 2 shows semilogarithmic plots of the intensities of the reactant CH_3^+ and the binary product ions CNH_4^+ (1a), NH_4^+ (1b), and the association reaction product $CH_3NH_4^+$ (1c) as a function of added NH_3 at an average energy of 0.047 eV. Figure 2(a) presents these data at the lowest He buffer gas pressure of 0.19 Torr, while Fig. 2(b) shows the equivalent experiment after the buffer gas partial pressure is increased to the intermediate value of 1.1 Torr. The increase in the total rate coefficient for disappearance of CH_3^+ (deduced from the slope of the straight line showing the decline of CH_3^+ intensity) with increasing He pressure and the fractional increase in the association channel are both evident in the figure. The measured overall rate coefficients, $k_t = 1.8 \times 10^{-9}$ cm^3 s^{-1} at 1.1 Torr are in good agreement with the SIFT results of Adams and Smith ($k_t = 2.2 \times 10^{-9}$ cm^3 s$^{-1.7}$) and with the low energy drift tube result of Thomas *et al.*,[8] $k_t \sim 2.5 \times 10^{-9}$ cm^3 s^{-1}. Only trace quantities of NH_3^+ were detected in our experiments and reaction (1d) is not included in our discussion of reactions occurring below 0.2 eV collision energy.

The total rate coefficient is partitioned into the partial rate coefficients using the relative intensities deduced in the
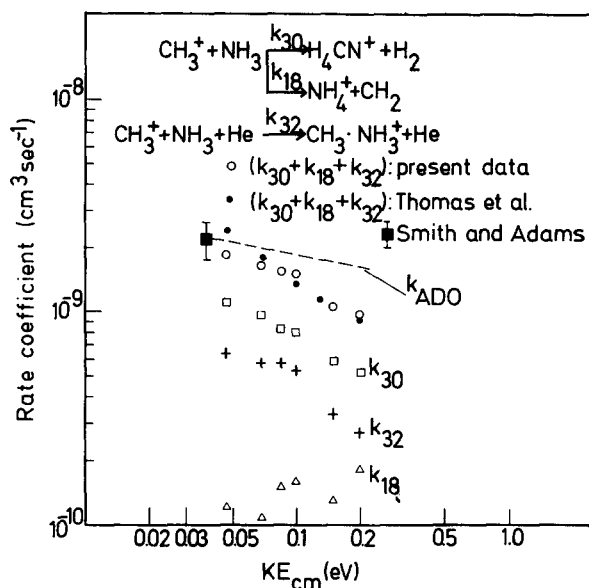
total series of experiments from semilogarithmic plots analogous to Fig. 2 at various ion kinetic energies and buffer gas pressures. Figure 3 summarizes the partial and total rate coefficient dependencies on collision energy and also defines (by product ion mass number) the product channel designation used in subsequent figures ($k_{1a} = k_{30}, k_{1b} = k_{18}$, and $k_{1c} = k_{32}$). Excellent agreement with previous experimental data are demonstrated. The coalescence of the low energy total rate coefficients with the collision frequency deduced from the average dipole orientation (ADO) theory[15] and its inadequate description of the KE dependence are also evident in this figure.

Figures 4 and 5 illustrate the dependence of the three rate coefficients on the pressure of the buffer gas at two different kinetic energies (0.047 and 0.068 eV, respectively). Within our experimental error no pressure dependence of
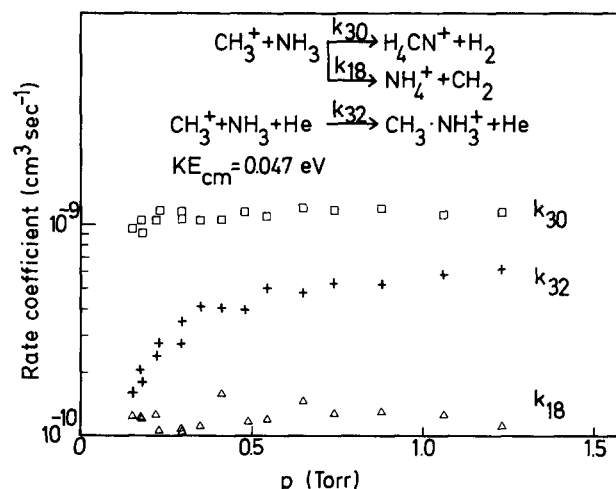

FIG. 4. Dependencies of k_{18}, k_{30}, and k_{32} (for definition see text) on the helium buffer gas pressure obtained at $KE_{cm} = 0.047$ eV.
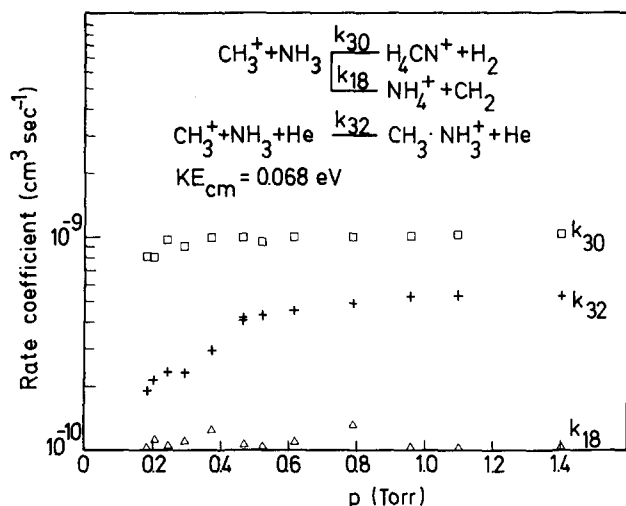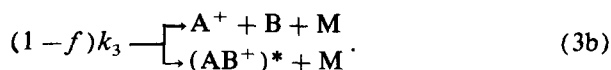
FIG. 5. Dependencies of k_{18}, k_{30}, and k_{32} on the helium buffer gas pressure obtained at $KE_{cm} = 0.068$ eV.

the binary reaction channels is noted; however, the association reaction k_{32}, exhibits the characteristic shape anticipated for the saturation of a three-body association mechanism. The transition from a ternary to an effective binary association rate is essentially complete at a buffer pressure in excess of 1 Torr.

A general kinetic analysis for describing the stabilization of ternary recombination reactions has been given by Adams *et al.*[16]:

$$A + B \underset{\tau_d}{\overset{k_2}{\rightleftharpoons}} (AB^+)^*,\tag{2}$$

$$(AB^+)^* + M \overset{fk_3}{\rightarrow} AB^+ + M,\tag{3a}$$

$$(1-f)k_3 \overset{\longrightarrow A^+ + B + M}{\underset{\longrightarrow (AB^+)^* + M}{\overbrace{\qquad}}}.\tag{3b}$$

The activated complex $(AB^+)^*$ is formed in reaction (2) with a rate coefficient k_2, and has a lifetime against unimolecular decomposition τ_d. Reaction (3) describes the collision of $(AB^+)^*$ with M; k_3 is the rate coefficient for this process, which is partitioned into a fraction f resulting in stable AB^+ and $(1-f)$ leading either to decomposition of $(AB^+)^*$ into reactants or to excited $(AB^+)^*$ surviving the collision. Competing binary reactions of A^+ with B are not included in this kinetic scheme but could easily be incorporated.

It may be shown using the steady state approximately for $(AB^+)^*$ that the overall rate for reaction (1) is given by

$$-\frac{d(A^+)}{dt} = k_c[A^+][B][M],\tag{4}$$

where

$$k_c = k_2 f \cdot k_3 \tau_d / (1 + k_3 \tau_d [M]).\tag{5}$$

The apparent or effective binary rate coefficient is given by

$$K_{2B}^{eff} = k_c[M].\tag{6}$$

At low pressures of M, k_{2B}^{eff} is proportional to [M] and at high pressures, k_{2B}^{eff} is independent of [M]. The pressure range at which this transition from ternary to binary kinetics

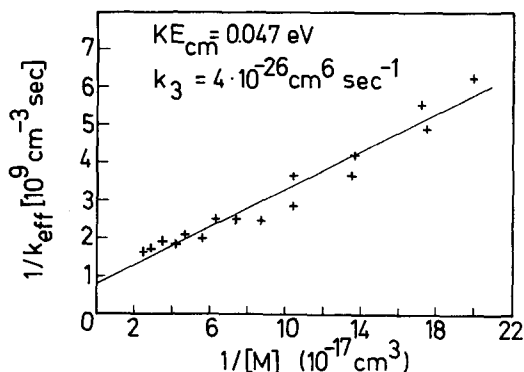FIG. 6. Plot of $1/k_{eff}$ vs $1/[M]$, where [M] equals the helium buffer gas density [He], obtained from the data for $KE_{cm} = 0.047$ eV. From the slope a rate coefficient for binary association $k_{3B} = 4 \times 10^{-26}$ cm^{-26} s^{-1} is obtained.

takes place is dependent on both temperature and pressure.

Equations (5) and (6) may be combined to give

$$1/k_{2B}^{eff} = 1/k_{3B}[M] + 1/fk_2,\tag{7}$$

where

$$k_{3B} = k_2 f k_3 \tau_d\tag{8}$$

is the ternary rate coefficient. Further, Eq. (7) shows how the data may be manipulated to obtain simultaneously k_{3B} and fk_2.

Figure 6 utilizes this kinetic scheme to deduce fk_2, and k_{3B} at our lowest energy of 0.047 eV KE_{cm}. Using the usual assumption of this treatment that k_2 and k_3 are well approximated by Langevin or ADO rate coefficients,[15] τ_d is deduced from Eq. (8). At 0.047 eV KE_{cm} the ion and neutral species are not very far removed from an internal energy of 300 K and these approximations provide a plausible general description of the reactions of CH_3^+ with NH_3. In particular, the intercept of Fig. 6 gives $f = 0.6$ and the slope gives the three-body association rate coefficients $k_{3B} = 4 \times 10^{-26}$ cm^6 s^{-1} at this collision energy. The corresponding lifetime of the collision complex $(AB^+)^*$ is estimated to be 1×10^{-7} s by setting k_2 equal to the ADO rate (see Fig. 3) and k_3 equal to the Langevin collision frequency.

A similar analysis of k_{3B} (and $f\tau_d$) as a function of collision energy is presented in Fig. 7. Nice agreement with the 300 K datum of Smith and Adams is demonstrated along with a sharp dependence on collision energy. A detailed analysis leading to parameterization of k_{3B} (or, equivalently τ_d) as a declining power function of temperature is precluded for ternary reactions by the fact that two successive ion-neutral collisions occur and it is impossible to equate the mean kinetic energy to an "effective temperature" at any point other than the low-energy thermal equilibrium limit.

This point is illustrated more explicitly by the two superposed temperature scales of Fig. 7. As discussed in the Experimental section, the Wannier expression is used to calculate KE_{cm} in drift tubes. Further, it has been shown in some cases[9,17] that binary reaction activation energies can be deduced adequately by defining an effective temperature
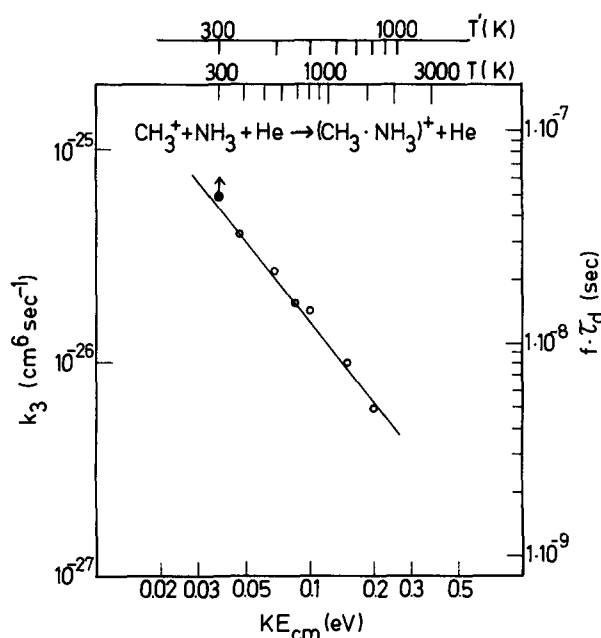
$$T_{eff} = \frac{2\langle KE_{cm}\rangle}{3k_B},\tag{9}$$

FIG. 7. k_{3B} and $f \cdot \tau_d$ as dependent on KE_{cm}. Open symbols represent present results, the solid dot represents data of Smith and Adams (Ref. 1).

FIG. 8. Schematic representation of the energy profile for dissociation reactions of $CH_3^+ NH_3$ according to Nobes and Radom (Ref. 12).

where k_B is the Boltzmann constant. The upper scale of Fig. 7 labeled T is deduced from this equation for CH_3^+ / NH_3 collisions, while the scale labeled T' refers to CH_3^+ / He collisions. Parameterization of the three-body rate in the form

$$k_{3B,T} = k_{300} \left(\frac{300}{T} \right)^n \tag{10}$$

would give $n \simeq 1.3$ for the T scale and $n \sim 2.1$ for the T' scale. Neither properly accounts for internal energy and we cannot predict the true temperature dependence of the association rate other than the qualitative result that it depends strongly on internal energy and rather strongly on collision energy as shown quantitatively in Fig. 7. This result, plus the comparison with Fig. 6, demonstrates that the simplified kinetic scheme with its parameterized temperature dependence is an inadequate description of this system.

The inadequacy of this kinetic analysis is apparent from the fact that we deduce that the fraction of stabilizing collisions is of the order of 0.6 at 0.047 eV KE_{cm} while the increase in the total rate, attributable entirely to the effect of stabilizing collisions, appears to saturate at only about 20% (as also found by Smith and Adams[1]). Moreover, as discussed by Herbst,[11] there are fundamental difficulties in rationalizing how a binary reaction channel which is 3.1 eV exothermic can be closed efficiently by collisional stabilization. Although the complex is bound by 4.6 eV, removal of 3.1 eV in a single collision by any quencher molecule is very difficult to rationalize for molecular colliders and impossible for He, which has only translational modes for absorbing energy. A specific mechanism for extraordinarily effective V–T energy transfer is required. Such a mechanism is given by the complex model suggested by Ferguson[18] for diatomic ions interacting with highly polarizable species. Unfortunately this mechanism cannot apply to the deexcitation scheme described here (as the binding energy between
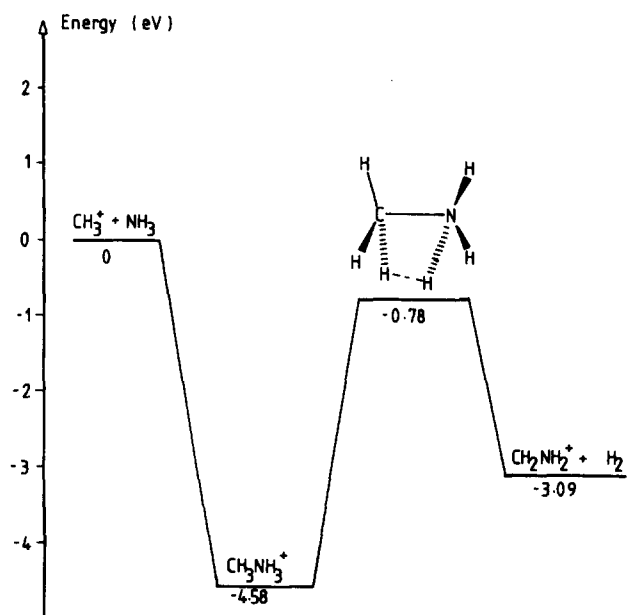
$CH_3^+ \cdot He$ is much too low) and no other plausible mechanism has been proposed.

A significant part of the puzzle is removed by Fig. 8 which depicts schematically the existence of a barrier in the exit channel leading to $CH_2NH_2^+$. The *ab initio* calculations of zero point energies of the stable species shown and the transition state are taken from the theoretical potential energy surface of Nobes and Radom[12] for this system. Vibrational frequencies and rotational constants also calculated by these workers were utilized by Herbst[11] in a model which satisfactorily accounts for further details of the somewhat anomalous behavior of the $CH_3^+ \cdot NH_3$ system.

As noted, the existence of a significant barrier in the binary reaction channel shown in Fig. 8 reduces the stabilization problem from that of removing 3.1 eV to the removal of only 0.8 eV. However, the removal of even this smaller amount of energy by an atomic collider in a single collision is still a difficult problem to rationalize on statistical grounds. Simple RRKM calculations would predict much shorter lifetimes than those observed experimentally.

The point which is missing in the simple RRKM model is the conservation of angular momentum which, because of the large cross sections and correspondingly large range of impact parameters for ion–molecule reactions of the type considered here, significantly alters the relevant barrier height. Those complexes formed with large amounts of energy stored in angular momentum will have significantly enhanced lifetimes because of the addition of this centrifugal barrier to the potential energy barrier height depicted in Fig. 8.

Herbst models the mechanism described by Eqs. (1a) and (1c) using the state-to-state statistical theory developed by Klots[19] and extended by Bowers *et al.*[20–22] In particular, the rotational energies associated with the reactants A and B, and the impact parameter and collision energy for each individual collision are summed to describe a collision com-

plex of total energy E and angular momentum J_{tot}. The forward and backward rate coefficients for the formation of the collision complex [Eq. 2] were computed by Herbst[11] using the semiclassical counting of vibrational states and integral approximately for rotational states as described by Chesnavich and Bowers.[22]

The existence of a barrier in the exit channel implies that the appropriate RRKM model is that of a "tight" dissociation complex.[23] Herbst[11] modified this approach to include explicitly the conservation of angular momentum. His equation for the dissociation rate coefficient of the collision complex to give the two-body reaction product is [see Eq. 3(a)]

$$k_{-2}(J,E_{tot})$$

$$= \left\{ \frac{\prod_{i=1}^{s} v_2^*}{\prod_{i=1}^{s-1} v_2^{\ddagger}} \right\}$$

$$\times \frac{\sigma^*(E_{total} + D_0 - \Delta E + a^{\ddagger}E_z^{\ddagger} - E_{rot}^{\ddagger})^{s-1}}{\sigma(E_{total} + D_0 + a^*E_z^* - E_{rot}^*)^{s-1}}. \quad (11)$$

The symbol * refers to the structure at the minimum of the potential energy profile in Fig. 8, while the symbol $\ddagger$ refers to the number of vibrational degrees of freedom of the complex (at the minimum of the PES) while $s - 1$ refers to the activated complex configuration. D_0 is the binding energy with respect to the initial reactants, $(D_0 - \Delta E)$ is the energy available to the transition state at 0 K, the v's are the various vibrational frequencies, E_z the zero point energies, a the Witten–Rabinowich factors,[23] and σ the symmetry factors.

Neglecting radiative stabilization (which was included in Herbst's treatment,[11] the three-body rate coefficient is

$$k_{3B} = \frac{k_2(J_A,J_B,E_{coll} \rightarrow J,E_{tot})k_{stab}}{k_{-1}(J,E_{tot}) + K_{3a}(J,E_{tot}) + k_{stab}[He]}, \quad (12)$$

with $k_{-1} = 1/\tau_d$. This equation displays explicitly the dependence on angular momentum, collision energy, and He pressure of the three-body association reaction. Completion of the calculation requires an expression of k_{stab}, which was expressed by Herbst[11] in the empirical equation

$$k_{stab} = 3 \times 10^{-10} \exp(-E_{vib}/k_B T), \quad (13)$$

where E_{vib} is the vibrational energy of the transition state given by

$$E_{vib} = E_{tot} + D_0 - \Delta E - E_{rot} \quad (14)$$

and is set to zero for all negative values. The preexponential factor is about one half the Langevin collision frequency. This is an approximation in the theoretical formulation[11] which nevertheless accounts in a simple way both for the efficient passage of many reaction complexes over the barrier (e.g., the observed difficulty in stabilizing a large fraction of collision complexes and the apparent "saturation" at binary rate less than k_2) and for maximizing of V–T transfer when $E_{trans} \approx E_{vib}$.

The effective two-body rate coefficient is obtained from Eq. (5) by multiplying by [He]. A plot of this effective rate coefficient is given in Fig. 9 as a function of He concentration and compared with both the present measurements of this quantity and the earlier 300 K measurements by Smith and
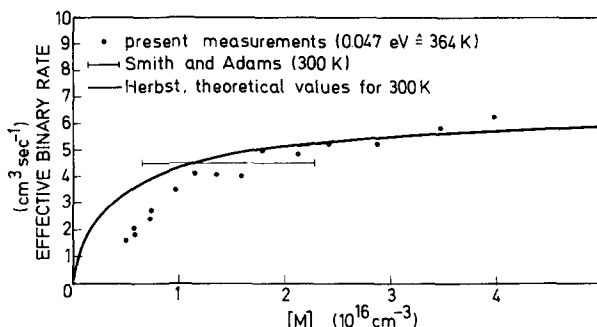

FIG. 9. Effective binary rate coefficients for the association of $CH_3NH_3^+$ as dependent on the helium buffer gas density [M].

Adams.[1] The qualitative agreement between our results (0.047 eV $\simeq$ 364 K) and the theoretical curve is excellent. In particular, the two difficulties noted by Herbst[11] in comparing his results with the only relevant experimental data (Smith and Adams[1]) that saturation was already achieved at 0.2 Torr and no increase in the effective binary rate was observed in the range 0.2–0.7 Torr are both removed by the present results. The low pressure falloff is clearly visible in our experimental curve and a gradual increase over the pressure range investigated is indicated. Both features are required by the Herbst theory.[11]

The detailed shape of the curve is affected most strongly by the form of the equation for k_{stab}, Eq. (13). A modification of this empirical equation along with the appropriate changes in Eqs. (11) and (12) for our 0.047 eV experiment would be expected to demonstrate essentially quantitative agreement between the state-to-state statistical model and our experimental results. In particular, the model accounts quite satisfactorily for the observation that the effective binary rate in Fig. 9 appears to saturate at a value which is about 25% of the k_2 collision rate coefficient. It is required, of course, that the curve rises eventually to k_2, but does so at a He pressure which is unachievably high experimentally. Accordingly, it is unnecessary to include a privileged reaction path to binary products in the overall kinetic scheme which does not proceed via stabilizable reaction complexes.

Although this satisfactory comparison of theory and experiment cannot rule out the existence of such privileged pathways there appears to be no reason to invoke such a reaction mechanism for the CH_3^+/NH_3 system. This supports Herbst's suggestion that radiative stabilization of all $(CH_3NH_3^+)^*$ complexes should be considered as a plausible mechanism for interstellar molecular synthesis.[4,11] By inference, this also applies to other reactions which exhibit analogous competitive behavior between fast two-body ion–atom exchange and three-body association reactions.

It may be inferred from our results that a large fraction (> 0.25)—and possibly all—CH_3^+/NH_3 collisions will result in radiatively stabilized adducts at the low temperatures (10 to 100 K) of interstellar clouds. The relatively abundant interstellar molecules CH_3NH_2 and CH_2NH are plausible products from dissociative recombination of $CH_3NH_3^+$ and $CH_2NH_2^+$ with electrons and this should be considered as one of the important reactions for their formation.

ACKNOWLEDGMENTS

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