Association Reactions at Low Pressure. 2. The CH_3^+/CH_3CN System

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The reaction between CH₃⁺ and CH₃CN has been examined at pressures between 8×10^{-8} and 1×10^{-3} Torr in an ion cyclotron resonance mass spectrometer. At low pressures the reaction is bimolecular, having a rate coefficient of 1.8×10^{-9} cm³ s⁻¹. The major ion products are H_2CN^+ and $C_2H_5^+$, but a bimolecular association channel also competes with these two main binary exothermic channels. At pressures above $\sim 4 \times 10^{-5}$ Torr the termolecular association (CH₃CNCH₃⁺) reaction becomes the major reaction. The results are rationalized in terms of barriers on the potential energy surface of the binary exit channels. The rate coefficient observed for the termolecular association reaction $CH_3^+ + CH_3CN + M \rightarrow CH_3CNCH_3^+ + M$ was found to be $k = 1.90 \times 10^{-22}$ cm⁶ s⁻¹ when M = CH₃CN, and when M = N₂, Ne, and He, $k = 4.0 \times 10^{-23}$, 0.6×10^{-23} , and 1.0×10^{-23} cm⁶ s⁻¹, respectively. The lifetime of the collision complex was found to be $\geq 14 \ \mu s$.

Introduction

Association reactions in ion-molecule systems have been the object of several experimental and theoretical investigations in recent times. These studies have been concerned primarily with collisional stabilization of the intermediate (AB⁺)* and unimolecular dissociation with a rate coefficient k_{-1} back to reactants (reaction 1).¹⁻⁵ Under normal laboratory conditions most of the

$$A^{+} + B \xrightarrow[]{}_{k_{-1}} (AB^{+})^{*} \xrightarrow{M} AB^{+} + M$$
(1)

systems studied exhibit only dissociation back to reactants (A⁺ + B) or collisional stabilization (to AB⁺) as the major loss processes for (AB⁺)*. But under conditions of low temperature and low pressure, a competing stabilization process, radiative stabilization (reaction 2), has been suggested which may prove to be one of the important mechanisms for molecular synthesis in interstellar clouds.

$$(AB^+)^* \to AB^+ + h\nu \tag{2}$$

In our first study in this series⁶ we examined the efficiencies of collisional stabilization of $(A_2H^+)^{\ast}$ in the reaction AH^+ + Aover the pressure range 10^{-6} to 0.4 Torr where A₂H⁺ represents the proton-bound dimer of dimethyl ether and acetonitrile. Collisional stabilization of $(A_2H^+)^*$ was the only stabilizing process observed in these two systems, and termolecular rate coefficients were reported for several bath gases.⁶ It has become apparent from this and other studies,^{1,2,6,7} and also supported from statistical calculations,⁸ that the average lifetime of $(AB^+)^*$ with respect to unimolecular decomposition $(\tau_{(AB^+)^*})$ can be as large as several microseconds in a number of cases. For example, $(\tau_{(A_2H^+)^*})$ for A = $(CH_3)_2O$ was estimated as $\geq 13 \ \mu s.^6$ A consequence of long average lifetimes for $(AB^+)^*$ is large rate coefficients, k_3 , for ternary association (reaction 3). Values for $k_3 > 10^{-23}$ cm⁶ s⁻¹ have been observed.6,7

$$A^{+} + B + M \xrightarrow{k_{3}} AB^{+} + M$$
(3)

There are, however, a number of systems that exhibit association in which binary pathways occur that compete with association. Two such systems have received considerable attention from both an experimental and a theoretical point of view. Bass et al.9 examined proton-bound dimer formation of methyl alcohol in which association occurs in competition with H2O elimination from the complex.

$$CH_{3}OH_{2}^{+} + CH_{3}OH \xrightarrow{M} (CH_{3}OH)_{2}H^{+}$$
$$\rightarrow (CH_{3})_{2}OH^{+} + H_{2}O$$

The pressure dependence of proton-bound dimer formation was measured and adequately modeled by using a phase space form of statistical theory in which a barrier of 0.69 eV (relative to $(CH_3)_2OH^+ + H_2O$ at infinite separation) in the binary exit channel leading to water elimination was deduced. The barrier was required to account for the fact that this channel proceeds at only 5% of the collision rate and had a strong negative temperature dependence. Experimental evidence for a barrier was also found from measurements of the average kinetic energy release obtained from the (CH₃)₂OH⁺ peak shape produced by the decay of the $[(CH_3OH)_2H^+]^*$ metastable.⁶

Herbst¹⁰ has also undertaken phase space calculations of the association between CH3⁺ and NH3 which occurs in competition with two binary channels (reaction 4) and for which the measured

$$CH_3^+ + NH_3 \xrightarrow{M} CH_3 NH_3^+$$
(4a)

$$\rightarrow NH_4^+ + CH_2$$
 (4b)

$$\rightarrow CH_2NH_2^+ + H_2 \tag{4c}$$

rate coefficients at 300 K and 0.3 Torr are¹¹ $k_{4a} = 4.4 \times 10^{-10}$ cm³ s⁻¹, $k_{4b} = 2.2 \times 10^{-10}$ cm³ s⁻¹, and $k_{4c} = 1.5 \times 10^{-9}$ cm³ s⁻¹. According to simple RRKM theory, the existence of fast binary channels as are found in the CH_3^+/NH_3 system should prevent association via collisional stabilization from ever being competitive. Herbst¹⁰ reconciled the experimental observations with theory for the CH₃⁺/NH₃ system, by including a contribution from angular

- Academic Press: New York, 1979; Vol. 1, p 197. (2) Cates, R. D.; Bowers, M. T. J. Am. Chem. Soc. 1980, 102, 3994.
 - (3) Smith, D.; Adams, N. G. Chem. Phys. Lett. 1978, 54, 535.
 - (4) Bates, D. R. J. Phys. B 1979, 12, 4135
 - (5) Herbst, E. J. Chem. Phys. 1980, 72, 5284 (6) McEwan, M. J.; Denison, A. B.; Anicich, V. G.; Huntress, Jr., W. T.
- (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, R. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, R. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, R. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, R. M.; Bowers, M. T. J. Phys. Chem. 1985, 89, (7) Kemper, P. R.; Bass, R. M.; Bowers, M. T. J. Phys. Rev. 1985, 80, (7) Kemper, P. R.; Bass, R. M.; P. R.; P. R.;
- 1105. (8) Forst, W. Theory of Unimolecular Reactions; Academic Press: New York, 1973.
- (9) Bass, L. M.; Cates, R. D.; Jarrold, M. F.; Kirchner, N. J.; Bowers, M. T. J. Am. Chem. Soc. 1983, 105, 7024.
- (10) Herbst, E. J. Chem. Phys. 1985, 82, 4017.
- (11) Smith, D.; Adams, N. G. Astrophys. J. Lett. 1978, 220, L87.

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⁽¹⁾ Meot-Ner, M. In Gas Phase Ion Chemistry; Bowers, M. T., Ed.;

momentum on top of the potential barrier in the binary channels. Ab initio calculations predicted a height for a barrier of 9.6 eV above the $CH_2NH_2^+ + H_2$ exit channel.¹² Experimental support for a barrier in this reaction was provided by Smith and Adams¹³ and Bowers et al.¹⁴ When the effect of angular momentum was included,¹⁰ the height of the barrier in the binary exit channel is effectively increased, further preventing rapid dissociation of the complex and also reducing the amount of energy required to be removed in each collision by the stabilizing gas. Drift tube studies by Thomas et al.¹⁵ and Saxer et al.¹⁶ on the same system also obtained results consistent with the Herbst interpretation.

The association reaction presented in the present study is the association between CH_3^+ and CH_3CN (reaction 5). This re-

$$CH_3^+ + CH_3CN \rightarrow CH_3CNCH_3^+$$
 (5)

action was chosen for investigation in the present work because a selected ion flow tube (SIFT) study¹⁷ had earlier reported a rate coefficient for association ($k = 4.0 \times 10^{-9}$ cm³ s⁻¹) close to the collision rate of the collision complex in a helium carrier gas. It was also apparent from the SIFT study that reaction 5 was near the pressure saturation regime as the rate coefficient for association varied little in the pressure range 0.2–0.4 Torr. We report here the results of a low-pressure ion cyclotron resonance (ICR) investigation of the CH₃⁺/CH₃CN system.

Experimental Results

Rate Constants. All the results pertaining to branching ratios and rate coefficients for the CH_3^+/CH_3CN system were obtained on the JPL ICR mass spectrometer at a constant magnetic field of 1.5 T as described previously.^{6,18} Reaction rate coefficients were usually obtained by using the McMahon-Beauchamp trap-drift mode of operation.¹⁹ Branching ratios were determined by using the drift mode of operation in conjunction with double-resonance ejection. The CH_3^+ ion was generated by nearthreshold electron impact ionization of methane, a methane-argon mixture, or methyl bromide.

In the ICR cell, the CH₃⁺/CH₃CN system exhibited a very different behavior than that reported earlier in the SIFT study at ~ 0.3 Torr¹⁷ where the association product CH₃CNCH₃⁺ was the only major product ion observed. At pressures below $\sim 4 \times$ 10⁻⁵ Torr, two further exothermic bimolecular processes (reactions 5a and 5b) competed with association. The products of the two bimolecular channels subsequently reacted with the parent gas, and the following sequence of reactions was observed to occur:

$$CH_3^+ + CH_3CN \rightarrow H_2CN^+ + C_2H_4$$
 (5a)

$$\rightarrow C_2 H_5^+ + HCN \tag{5b}$$

$$\rightarrow$$
 CH₃CNCH₃⁺ (5c)

$$H_2CN^+ + CH_3CN \rightarrow CH_3CNH^+ + HCN$$
 (6)

$$C_2H_5^+ + CH_3CN \rightarrow CH_3CNH^+ + C_2H_4$$
(7)

$$CH_3CNH^+ + CH_3CN + M \rightarrow (CH_3CN)_2H^+ + M \quad (8)$$

The rate coefficients and branching ratios measured for these

- (12) Nobes, R. H.; Radom, L. Chem. Phys. 1983, 74, 163.
- (13) Smith, D.; Adams, N. G. Astrophys. J. 1977, 217, 714
- (14) Bowers, M. T.; Chesnavich, W. J.; Huntress, W. T., Jr., Int. J. Mass Spectrom. Ion Phys. 1973, 12, 357.
- (15) Thomas, R.; Barassini, J.; Barassini, A. Int. J. Mass Spectrom. Ion Phys. 1985, 33, 383.
- (16) Saxer, A.; Richter, R.; Villinger, H.; Futrell, J. H.; Lindinger, W. J. Chem. Phys. 1987, 87, 2105.
- (17) Knight, J. S.; Freeman, C. G.; McEwan, M. J. J. Am. Chem. Soc. 1986, 108, 1404.
- (18) Anicich, V. G.; Huntress, Jr., W. T.; McEwan, M. J. J. Phys. Chem. 1986, 90, 2446.
- (19) McMahon, T. B.; Beauchamp, J. L. Rev. Sci. Instrum. 1972, 43, 509.
 (20) Rosenstock, H.; Draxl, K.; Steiner, B. W.; Herron, J. T. J. Phys. Chem. Ref. Data 1977, 6.
- (21) Deakyne, C.; Meot-Ner, M. J. Am. Chem. Soc., in press.

TABLE I: Bimolecular Rate Coefficients (in Units of 10^{-9} cm³ s⁻¹) and Branching Ratios of Ion-Molecule Reactions of CH₃CN

reactant ion	products	branching ratio	rate coeff	$-\Delta H,^a$ kJ mol ⁻¹
CH ₃ ⁺	$H_2CN^+ + C_2H_4$	0.58		161
·	$C_2H_5^+$ + HCN	0.37	1.8 ^b	131
	CH ₃ CNCH ₃ ⁺	0.05		415 ^c
H ₂ CN ⁺	$CH_3CNH^+ + HCN$	1.0	3.8	69
$C_2H_5^+$	$CH_3CNH^+ + C_2H_4$	1.0	3.8	99
CH₃CNH ⁺	(CH ₃ CN) ₂ H ⁺	1.0	d	126 ^e

^a Exothermicities have been taken from ref 20 unless specified otherwise in text. ^b Results shown represent bimolecular processes that do not vary with pressure below 1×10^{-6} Torr. ^c Estimated from the alkyl affinity data of Deakyne and Meot-Ner in ref 21. ^d The rate coefficient for proton-bound dimer formation from ref 6 is expressed as a termolecular rate coefficient and has the value $k = 2.0 \times 10^{-24}$ cm⁶ s⁻¹ when M, the bath gas, is the parent molecule CH₃CN. ^e From ref 6.



Figure 1. Plot of reaction probability versus kinetic energy release of H_2CN^+ formed from the (CH₃CNCH₃⁺)* metastable.

individual reactions are summarized in Table I.

Kinetic Energy Distribution. The metastable species $(CH_3CNCH_3^+)^*$ was formed in the ion source of the VG analytical ZAB-2F mass spectrometer at Santa Barbara by the reaction of $CH_3^+ + CH_3CN$ in an $Ar/CH_4/CH_3CN$ mixture. After mass selection, the metastable underwent unimolecular decomposition in the second field-free region of the mass spectrometer to form the product ions $C_2H_5^+$ and H_2CN^+ (reactions 9 and 10)

$$(CH_3CNCH_3^+)^* \rightarrow H_2CN^+ + C_2H_4 \tag{9}$$

$$\rightarrow C_2 H_5^+ + HCN \tag{10}$$

for which the kinetic energy distribution was obtained from the peak shapes as previously described.²² The distribution measured is shown in Figure 1. An average kinetic energy release of 0.13 eV was obtained for $C_2H_5^+$ and 0.11 eV for H_2CN^+ . The relative branching ratio between the two channels was 70% for H_2CN^+ and 30% for $C_2H_5^+$.

Discussion

As noted above, the most obvious difference between the higher pressure SIFT study¹⁷ and the present low-pressure investigation was in the product distributions and the order of the reaction's dependence on the neutral pressure. In the ICR cell at pressures below $\sim 1 \times 10^{-4}$ Torr, the major source of removal of CH₃⁺ was in the two bimolecular channels leading to H₂CN⁺ and C₂H₅⁺ whereas these two channels were not observable in the SIFT study. This apparent discrepancy can readily be accounted for by considering the time between collisions. In the SIFT work, the time between collisions of the collision complex and the carrier gas is typically 0.1 μ s whereas the time between collisions of the collision

⁽²²⁾ Jarrold, M. F.; Illies, A. J.; Bowers, M. T. Chem. Phys. 1982, 65, 19.



Figure 2. Variation of the double-resonance signals H_2CN^+ , $C_2H_5^+$, CH_3CNH^+ , $CH_3CNCH_3^+$, and $(CH_3CN)_2H^+$ from CH_3^+ with CH_3CN pressure. The solid curves are the result of model calculations based on the reactions and rate coefficients of Table I and yield a best fit for the termolecular association of CH_3^+ and CH_3CN (M = CH_3CN) of 1.9 × 10^{-22} cm⁶ s⁻¹.

complex and the reactant neutral in the ICR cell at a pressure of 1×10^{-5} Torr is 0.8 ms. If a barrier exists in the potential energy surface in each of the exit channels, then the time taken to exit is considerably increased, thus extending the lifetime of the (CH₃CNCH₃⁺)* complex and thereby increasing the likelihood for stabilization by collision. The evidence for such a barrier is provided by the kinetic energy release spectrum shown in Figure 1 for the H₂CN⁺ channel in which the average kinetic energy release was 0.11 eV as determined from the peak shape. A barrier of ≥ 0.13 eV was similarly determined for the C₂H₅⁺ channel. Further evidence of a barrier in the C₂H₅⁺ + HCN exothermic binary channel is that CH₃CNCH₃⁺ is not a product of the C₂H₅⁺ + HCN reaction at thermal energies.²³

We conclude therefore that barriers greater than 0.11-0.13 eV exist between (H₂CN⁺ + C₂H₄) and (CH₃CNCH₃⁺)* and similarly between (C₂H₅⁺ + HCN) and (CH₃CNCH₃⁺)*. It is the existence of these barriers that enables the complex to live long enough for collisional stabilization and thus association to be the major outcome of the reaction between CH₃⁺ and CH₃CN at flow tube pressures. Furthermore, the large dipole moment in CH₃CN (3.92 D) ensures there is a significant contribution from angular momentum in this system which adds a centrifugal barrier to the existing barrier in the binary exit channel. The net effect of the combined barriers is to decrease further the dissociation rate of the complex and thus make collisional stabilization (or dissociation to reactants) more competitive.

In the pressure range of the present study (8×10^{-8} to 10^{-3} Torr) the time between collisions changes from ~75 ms to 8 μ s when CH₃CN is the parent gas. In this pressure range the reaction between CH₃⁺ and CH₃CN is observed to change from bimolecular to termolecular in keeping with the suggested mechanism. The reaction therefore exhibits bimolecular kinetics at pressures below 3×10^{-5} Torr and termolecular kinetics at pressures higher than this in the ICR but returns to first-order dependence on the neutral pressure in the SIFT flow tube because the termolecular kinetics are now in the saturation regime.

Stabilization in the CH_3^+/CH_3CN System. The variation in ion signals with pressure of the parent gas, CH_3CN , is shown in Figure 2. The data were obtained by monitoring the products of the m/e = 15 (CH_3^+) ion, by measuring the double-resonance peaks at m/e = 28 (H_2CN^+), 29 ($C_2H_5^+$), 42 (CH_3CNH^+), 56 ($CH_3CNCH_3^+$), and 83 (($CH_3CN)_2H^+$) at different pressures of CH_3CN . It was observed that the binary products of reaction 5, H_2CN^+ and $C_2H_5^+$, underwent subsequent proton transfer with CH₃CN to produce CH₃CNH⁺ at m/e = 42 (reactions 6 and 7). CH₃CNH⁺ in turn underwent association with CH₃CN to form the proton-bound dimer at m/e = 83. Because of the presence of sequential reactions, it was not possible to obtain the rate for association via collision stabilization (reaction 11) directly. Instead,

$$CH_3^+ + CH_3CN + M \rightarrow CH_3CNCH_3^+ + M \qquad (11)$$

the entire kinetic system was computer modeled by using the reactions and their measured rate coefficients shown in Table I with the addition of the association reaction (11). The model calculations are represented by the solid line in Figure 2 and the experimental observations by the points. The best fit to the data was found when the rate coefficient for reaction 11 was assigned a value of 1.9×10^{-22} cm⁶ s⁻¹ for M = CH₃CN.

The Limits of the Elementary Rate Constants. The bimolecular and termolecular association reactions occurring in the CH_3^+/CH_3CN system may be represented by the mechanism

complex formation: $CH_3^+ + CH_3CN \frac{k_f}{k_{-1}} (CH_3CNCH_3^+)^*$

dissociative rearrangement: $(CH_3CNCH_3^+)^* \xrightarrow{k_{-2}}$ $(H_2CN^+ \text{ and } C_2H_5^+)$ exothermic products

collisional stabilization:

$$(CH_3CNCH_3^+)^* + M \xrightarrow{\beta k_s} CH_3CNCH_3^+ + M$$

radiative stabilization:

$$(CH_3CNCH_3^+)^* \xrightarrow{\kappa_r} CH_3CNCH_3^+ + h\nu$$

where β represents the fraction of collisions effective in producing stabilization.

The following differential equations are thus defined:

$$d[A^+]/dt = -k_f[A^+][B] + k_{-1}[(AB^+)^*]$$

and

$$\frac{d[(AB^{+})^{*}]/dt}{k_{f}[A^{+}][B] - (k_{-1} + k_{-2} + k_{r} + \beta k_{s}[M])[(AB^{+})^{*}]}$$

where $A^+ = CH_3^+$, $B = CH_3CN$, and $AB^+ = CH_3CNCH_3^+$. In the steady-state approximation

 $d[(AB^+)^*]/dt = 0$

this reduces the equation for $d[(AB^+)^*]/dt$ to

$$[(AB^{+})^{*}] = k_{f}[A^{+}][B] / (k_{-1} + k_{-2} + k_{r} + \beta k_{s}[M])$$

The data are given in terms of the experimentally observed rate coefficients, either bimolecular, k_2^{obsd} , or termolecular, k_3^{obsd} . The bimolecular process defined in the reaction

$$A^+ + B \xrightarrow{k_2^{\text{obsd}}} \text{products}$$

is first order in [B] and has the partial differential equation

$$d[A^+]/dt = -k_2^{\text{obsd}}[A^+][B]$$

The two partials in $d[A^+]/dt$ can be equated and the value of $[(AB^+)^*]$ substituted to give the general equation

$$k_2^{\text{obsd}} = k_f(k_{-2} + k_r + \beta k_s[M]) / (k_{-1} + k_{-2} + k_r + \beta k_s[M])$$
(12)

In the limit where [M] = 0 this reduces to

$$k_2^{\text{obsd}} = k_f(k_{-2} + k_r) / (k_{-1} + k_{-2} + k_r)$$
 (13)

The termolecular rate coefficient, k_3^{obsd} , is defined in the reaction

$$A^+ + B + M \xrightarrow{k_3^{\text{obsd}}} \text{products}$$

so that k_3^{obsd} is defined as $d(k_2^{\text{obsd}})/d[M]$. Taking the derivative of eq 12 then gives an expression for k_3^{obsd} in the limit $[M] \rightarrow 0$ as

$$k_3^{\text{obsd}} = k_f k_{-1} \beta k_s / (k_{-1} + k_{-2} + k_r)^2$$
(14)

From eq 12-14 the results of the ICR and SIFT experiments can be analyzed.

In the ICR experiment, the termolecular rate is measured graphically by plotting k_2^{obsd} against [M]. Then the intercept at

⁽²³⁾ MacKay, G.; Vlachos, G.; Bohme, D. K.; Schiff, H. I. Int. J. Mass Spectrom. Ion Phys. 1980, 36, 259.



Pressure of CH₃CN, x10⁵ Torr

Figure 3. Fractional abundance of CH₃CNCH₃⁺, for association of CH_3^+ and CH_3CN measured in the drift mode at low pressures. Each data point represents the fractional abundance of CH₃CNCH₃⁺ to association. The solid line represents the contribution to association from the termolecular process when $k_3 = 1.9 \times 10^{-22} \text{ cm}^6 \text{ s}^{-1}$.

[M] = 0 is given by eq 13. In the SIFT experiment, when a reaction is near the saturation limit, i.e., $\beta k_s[M] \gg (k_{-1} + k_{-2})$ (k_r) , the rate coefficient experimentally observed is first order in the neutral pressure, and eq 12 in this case reduces to

$$k_2^{\text{obsd}} = k_f \tag{15}$$

and the k_2^{obsd} measured in the limit of "saturation" is then k_{f} . In most SIFT studies of association, the flow tube pressures are such that the "complete saturation" region is approached but never reached. Accordingly, values of k_2^{obsd} obtained will be less than the collision rate.²⁴ This is not the case for the reaction of this study. From eq 12 it can be shown that the SIFT result at 0.4 Torr is within 99% of the saturation limit, because the overall termolecular rate coefficient is very large for this system.

There are a variety of experimental data that can be used to evaluate the elementary rate coefficients. We will restrict ourselves in this analysis to data available from the SIFT and ICR experiments. The ICR experiments provide measurements of k_3^{obsd} for the parent gas and for other bath gases such as helium. The comparison of k_3^{obsd} for the different bath gases with the parent gas enables the collision efficiencies, β , to be evaluated relative to the parent gas. The parent gas is usually assumed to have β \leq 1.0; i.e., every collision of (AB⁺)* with B results in stabilization of less than or equal to one $(AB^+)^*$. We have found that β for the parent gas is typically the largest and is several times larger than the values of β observed for atomic bath gases. This is consistent with previous studies.24-26

Limits can be established from the experimental data available for the following elementary reaction rate coefficients: $k_{\rm f}, k_{-1}$, k_{-2} , k_s , k_r , and $\tau = 1/(k_{-1} + k_{-2} + k_r)$. To obtain this number of parameters, on equal number of independent experimental measurements are required. The following approximations were

1. $k_s = k_{coll}$, where k_{coll} is the calculated collision rate coefficient for $CH_3CNCH_3^+$ with the bath gas.

2. $\beta \leq 1.0$ for the parent gas. The upper limits to β values of the other bath gases are obtained directly from the measured k_3^{obsd} determined after normalizing against the collision rates such that

$$\beta(M) = (k_3^{\text{obsd},M} / k_{\text{coll},M}) / (k_3^{\text{obsd},B} / k_{\text{coll},B})$$

3. k_2^{obsd} ("saturated rate") in the SIFT $\leq k_{\text{f}}$.

4. $k_{\rm f} \leq k_{\rm coll}$. Variational transition state theory combined with classical trajectory calculations²⁷ provides a reasonable approximation to $k_{coll}(CH_3^+/CH_3CN)$ (5.5 × 10⁻⁹ cm³ s⁻¹) and k_{coll}^- $(CH_3CNCH_3^+/CH_3CN)$ (3.8 × 10⁻⁹ cm³ s⁻¹).

The following set of data were used:

1. The branching ratios for the bimolecular channels are those measured in the ICR at the lowest pressures.

2. k_2^{obsd} measured in the ICR in the limit [B] = 0. 3. k_3^{obsd} measured in the ICR, for the parent gas and for the other bath gases. This was measured as $d(k_2^{obsd})/d[M]$ in the limit $[M] \rightarrow 0$.

4. k_2^{obsd} ("saturated rate") measured in the SIFT.

A set of limits on the elementary rate coefficients can be uniquely determined, such that the values of k_2^{obsd} and k_3^{obsd} from the ICR experiment and the k_2^{obsd} from the SIFT experiments are reproduced from eq 13, 14, and 15, respectively.

Following this procedure for the CH_3^+/CH_3CN system, the following conclusions were made.

$$4.0 \times 10^{-9} \le k_{\rm f} \le 5.5 \times 10^{-9} \,{\rm cm}^3 \,{\rm s}^{-1}$$

For β (CH₃CN) = 1.0

 $2.5 \times 10^4 \le k_{-1} \le 5.0 \times 10^4 \,\mathrm{s}^{-1}$ $1.9 \times 10^4 \le k_{-2} \le 2.3 \times 10^4 \,\mathrm{s}^{-1}$ $1.0 \times 10^3 \le k_r \le 1.2 \times 10^3 \,\mathrm{s}^{-1}$ $14 \leq \tau \leq 23 \ \mu s$

For β (CH₃CN) = 0.5

 $1.2 \times 10^4 \le k_{-1} \le 2.5 \times 10^4 \,\mathrm{s}^{-1}$ $0.9 \times 10^3 \le k_{-2} \le 1.1 \times 10^3 \,\mathrm{s}^{-1}$ $4.9 \times 10^2 \le k_r \le 6.1 \times 10^2 \,\mathrm{s}^{-1}$ $27 \leq \tau \leq 46 \ \mu s$

We have thus learned the following information about this system. First, the overall lifetime of the collision complex at room temperature is $\geq 14 \ \mu s$. This long lifetime is to be expected for this type of complex and reflects the unusual stability of the complex and the large number of modes available for redistribution of energy. These times are consistent with the microsecond flight times of the metastable $(CH_3CNCH_3^+)^*$ in the VG analytical ZAB mass spectrometer. We also find at low pressures, when collisional stabilization is unimportant, that $\geq 67\%$ of the collision complexes revert to reactants and $\leq 33\%$ continue on to form new ions.

Finally, we point out that the association channel (m/e = 56)in Figure 2 has a nonzero intercept. The CH₃CNCH₃⁺ association peak was observed in both the drift and trap-drift modes of operation at pressures down to 8×10^{-8} Torr in the latter. The behavior of the rate coefficient for association at low pressures in the drift mode is shown in Figure 3. Each data point in the Figure represents a rate coefficient for association (reaction 11) which was obtained from the total rate coefficient after correction for the association branching ratio. Branching ratios were measured by double resonance at a drift time of 2.0 ms. We have superimposed on the data a solid line representing the contribution to association from both the radiative association reaction (16)

$$CH_3^+ + CH_3CN \rightarrow CH_3CNCH_3^+ + h\nu$$
(16)

and the termolecular association (reaction 11). The rate coefficient for the termolecular association reaction of 1.9×10^{-22} cm⁶ s⁻¹ was obtained from the model calculations shown in Figure 2. The agreement is satisfactory, but again a source of CH₃CNCH₃⁺ that is not via collision stabilization of the complex is evident at low pressures. We believe this process to be radiative stabilization, and our measured rate coefficient for the bimolecular association process is $9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

Conclusions

There are three regimes, based on kinetics, in the reaction between CH₃⁺ and CH₃CN. At pressures below 3×10^{-5} Torr the reaction is bimolecular and proceeds through exothermic channels with a rate coefficient of 1.8×10^{-9} cm³ s⁻¹. Competing

⁽²⁴⁾ Anicich, V. G.; Bowers, M. T. J. Am. Chem. Soc. 1974, 96, 1279. (25) McEwan, M. J.; Denison, A. B.; Anicich, V. G.; Huntress, W. T., Jr. Int. J. Mass Spectrom. Ion Phys. 1987, 81, 247. (26) Kemper, P. R.; Bass, L. M.; Bowers, M. T. J. Phys. Chem. 1985, 89,

¹¹⁰⁵

⁽²⁷⁾ Su, T.; Chesnavich, W. J. J. Chem. Phys. 1982, 76, 5183.

with the exothermic bimolecular process is bimolecular association which we suggest is the result of radiative stabilization of $(CH_3CNCH_3^+)^*$. At pressures above 3×10^{-5} Torr the reaction becomes termolecular with a rate coefficient of 1.9×10^{-22} cm⁶ s^{-1} when M = CH₃CN. The change to termolecular kinetics is due to an increasing fraction of the (CH₃CNCH₃⁺)* complexes being stabilized by collision. Barriers on the potential energy surface prevent rapid exiting from the complex to the binary exothermic channels that lead to H_2CN^+ and $C_2H_5^+$ as ion products. It is the existence of these barriers that allows termolecular association to become competitive with the bimolecular channels. At still higher pressures such as occur in flow tubes (>0.1 Torr), the reaction becomes bimolecular again corresponding to the onset of saturation when almost every complex is stabilized by collision. Under these conditions, association is the only product of the reaction and the rate coefficient for association (k = 4.0) $\times 10^{-9}$ cm³ s⁻¹) approaches the collision rate.

As a larger number of systems of this type are studied in the laboratory, more confidence can be gained in making assessments of the viability of association processes when in competition with binary exothermic processes at room temperature and under interstellar cloud conditions. At low temperatures and pressures the lifetime of the $(CH_3CNCH_3^+)^*$ to unimolecular dissociation of reaction may be sufficiently long that radiative association becomes the dominant outcome of reaction.

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Kinetic and Mechanistic Investigations of $F + H_2O/D_2O$ and $F + H_2/D_2$ over the Temperature Range 240–373 K

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The rate constants for the reactions of fluorine atoms with H_2O and D_2O have been determined over the temperature range 240-373 K by using a discharge flow system at 1-2 Torr of total pressure. F atoms were detected by chemical conversion with deuterium. The resulting D atoms were detected by atomic resonance scattering. The rate constants are $k_1 = (1.6$ ± 0.3) × 10⁻¹¹ exp[(-28 ± 42)/T] cm³ molecule⁻¹ s⁻¹ for F + H₂O \rightarrow HF + OH and $k_2 = (8.4 \pm 1.2) \times 10^{-12} \exp[(-260 \times 10^{-12} \text{ cm}^2)]$ $\pm 110/T$] cm³ molecule⁻¹ s⁻¹ for F + D₂O \rightarrow DF + OD. The reported error limits are at the 95% confidence level. The reactions F + H₂ \rightarrow HF + H ($k_3 = (1.2 \pm 0.1) \times 10^{-10} \exp[(-470 \pm 30)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and F + D₂ \rightarrow DF + D $(k_4 = (9.3 \pm 1.1) \times 10^{-11} \exp[(-680 \pm 50)/T]$ cm³ molecule⁻¹ s⁻¹) were also studied over the same temperature range. The rate constants for the latter reactions are in excellent agreement with previous studies. The low activation energy and A factor for the $F + H_2O/D_2O$ reactions, as well as the slightly enhanced kinetic isotope effect (3.9 at 298 K), suggest a tunneling mechanism for these reactions, and thus the mechanistic interpretation of this system requires some knowledge of the potential energy surface at the microscopic level. Ab initio calculations on this system predict a classical barrier height of approximately 10 kcal/mol, while a semiempirical BEBO calculation predicts a barrier height of <1 kcal/mol. Neither of these models is able to accurately reproduce the observed reaction rate parameters when used in transition-state theory and a one-dimensional tunneling model. With use of the theoretical implications in conjunction with the experimental evidence, a potential energy surface has been calculated for this reaction that leads to better agreement with the experimental results. The best-fit prediction of the observed activation energy and kinetic isotope effect suggest that the mechanism for this reaction involves tunneling through a classical barrier height of approximately 4 kcal/mol.

Introduction

The abstraction of hydrogen atoms by fluorine has received a substantial amount of attention in recent years, both experimentally,1 using the traditional methods of chemical kinetics and molecular beams, and theoretically.² The mechanistic interpretation of many of these reactions has usually been based on either the bulk-phase experimental implications or the results of highly involved ab initio and semiempirical calculations. The latter have been limited to simple systems that are accessible to detailed theoretical treatments. The interpretation of larger systems has often relied on the kinetic experimental evidence alone, which does not lend itself easily to a complete understanding of the mechanism on a microscopic level. Since larger systems are difficult to study on a high theoretical level, a balanced interplay between experiment and a moderate level of theory is necessary to understand the detailed mechanism of many of these reactions.

There are a number of reasons motivating the study of hydrogen abstractions by fluorine. Due to the strength of the HF bond, these reactions are highly exothermic and form the basis of the HF chemical laser.^{1b} In addition, reactions of fluorine atoms occur in the stratosphere after photolysis of chlorofluorocarbons.^{3,4} Although the fluorine atoms liberated in the stratosphere may react quickly to form a stable reservoir of HF, the reaction sequences have not been very well characterized. These reactions are also being used increasingly as primary sources of radicals (i.e., OH, HO₂) in experimental measurements as the high reactivity of fluorine allows for low concentrations of reacting species

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⁽¹⁾ For a review of fluorine reactions, see: (a) Jones, W. E.; Skolnik, E. G. Chem. Rev. 1979, 76, 563. (b) Foon, R.; Kaufman, M. Prog. React. Kinet. 1975, 8, 81.

⁽²⁾ See, for example: (a) Schaefer, H. F., III J. Phys. Chem. 1985, 89, 5336. (b) Truhlar, D. G.; Garrett, B. C.; Blais, N. C. J. Chem. Phys. 1984, 80, 232

⁽³⁾ Baulch, D. C.; Cox, R. A.; Crutzen, P. J.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J.; Watson, R. T. J. Phys. Chem. Ref. Data 1982, 11, 327.

⁽⁴⁾ World Meterological Organization. Atmospheric Ozone, 1985. Global Ozone Research and Monitoring Project, Report No. 16, 628, 1986.