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Ion-molecule association in acrylonitrile

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Abstract

The association reactions of the acrylonitrile ion, CH_2CHCN^+, and the protonated ion derived from acrylonitrile, CH_2CHCNH^+ with acrylonitrile (CH_2CHCN) have been examined using ion cyclotron resonance (ICR) and flowing afterglow selected ion flow drift tube (FA/SIFDT) techniques at room temperature. These techniques yield different results for these two systems that can be rationalized by considerations of the lifetime of the collision complex. In the CH_2CHCN^+/CH_2CHCN system, the measured reaction rate coefficients are: $k_{ICR} = 2.5 \times 10^{-9}$ cm^3 s^{-1} with a single product channel ($CH_2CHCNH^+ + C_3H_2N$) and $k_{SIFT} = 3.1 \times 10^{-9}$ cm^3 s^{-1} (with a 30% product channel to the adduct $C_6H_6N_6^+$) The rate coefficient and product distributions in the FA/SIFDT instrument are invariant with pressure in the range 0.25–0.75 Torr. In the CH_2CHCNH^+/CH_2CHCN system, the measured rate coefficients are: $k_{ICR} = 9.2 \times 10^{-11}$ cm^3 s^{-1} at a CH_2CHCN pressure of 3.0×10^{-4} Torr and $k_{SIFT} = 1.6 \times 10^{-9}$ cm^3 s^{-1}, where association is the only product channel observed by each technique. The termolecular process corresponding to this latter association has a measured reaction rate coefficient of $k_3 = 1.2 \times 10^{-23}$ cm^6 s^{-1} (for M = CH_2CHCN) and $k_3 = 8.1 \times 10^{-25}$ cm^6 s^{-1} (for M = He). Both systems were modelled: A double well potential model involving the formation of loosely bound and tightly bound complexes was required to account for the kinetic behaviour of the CH_2CHCN^+/CH_2CHCN system whereas a single-well potential model satisfactorily accounted for the behaviour of the CH_2CHCNH^+/CH_2CHCN system. (Int J Mass Spectrom 185/186/187 (1999) 663–672) © 1999 Elsevier Science B.V.

Keywords: Acrylonitrile; ICR; SIFT; Ion-association reactions; Double-well potential model

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1. Introduction

Acrylonitrile (propenenitrile or vinyl cyanide) polymerizes readily via a radical mechanism in solution at room temperature. The propensity to polymerize is sufficiently strong that it is usual to add a radical scavenger to the solution to prevent polymerization when oxygen (an inhibitor) is removed. Polymerization of acrylonitrile is also known to occur via nucleophilic addition of an anion by a Michael-type reaction [1].

Some negative and positive gas phase ion chemistry of acrylonitrile has also been studied. The negative ions formed by electron attachment to acrylonitrile have been examined [2,3] and the ensuing intracluster anionic polymerization in acrylonitrile clusters formed in a sonic nozzle have also been investigated [4]. Several studies of the gas-phase ion chemistry of positive ions with acrylonitrile have been undertaken using the selected ion flow tube (SIFT) technique. The

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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reaction chemistry of $C_3H_2N^+$, CH_2CHCN^+ and CH_2CHCNH^+ with a number of simple neutrals was reported by Petrie et al. [5]. The ion-molecule chemistry of CH_2CHCN with C_n^+ ($n = 10 - 18, 20$) was reported by Sun et al. [6] and with the fullerine mono-, di- and trications by Javahery et al. [7].

Acrylonitrile is one of the molecules observed using radioastronomy techniques in interstellar clouds [8,9]. Several reactions of positive ions derived from CH_2CHCN with molecules of relevance to interstellar conditions were reported by Petrie et al. [10] using the SIFT technique. It was apparent in these earlier ion-molecule studies that just as acrylonitrile will polymerize in solution, so too, the gas phase ions CH_2CHCN^+ and CH_2CHCNH^+ readily associate with the parent gas to form adducts in the SIFT experiments. The product adduct ions formed by association were formed efficiently at close to the collision rate at flow tube pressures of 0.3 Torr of helium [5]. Efficient association signifies relatively long-lived collision complexes which may be stabilized by collision with the bath gas in the flow tube or the planetary ionospheric environment (e.g. in Titan's nitrogen atmosphere). In the interstellar cloud environment, stabilization by photon emission is a more likely outcome. It is of interest therefore, to examine further the nature of the association process in these systems.

We have previously conducted low pressure-high pressure investigations of several associating systems using the combined techniques of ion cyclotron resonance (ICR) and SIFT [11–14]. In this study, we extend these investigations to include association reactions of CH_2CHCN^+ and CH_2CHCNH^+ with CH_2CHCN over the wide pressure range of 10^{-7}–0.8 Torr.

2. Experimental

The flow tube experiments were made using a selected ion flow drift tube equipped with a flowing afterglow source (FA/SIFDT) operating at room temperature (300 ± 5 K), located at the University of Canterbury. The selected ion flow tube has been described previously [15]. The instrument has been extended by the addition of a drift tube [16] and flowing afterglow ion source. This new ion source is similar to that described by Van Doren et al. [17]. Other details of the modified FA/SIFDT will be described elsewhere [18]. The ICR experiments were made using an ICR, which has not been described before, located at Canterbury University. This ICR is similar in principle and design to the ICR at the Jet Propulsion Laboratory (JPL) which has been described elsewhere [12,19]. The instrument utilizes a McMahon-Beauchamp type cell design [20] with separate trapping plates in the source and resonance regions. The only significant difference between the ICR at Canterbury and the instrument at JPL is that the Canterbury instrument has a nine inch electromagnet with a two inch gap between the pole faces. The cell was operated in both trapped and drift modes of operation and all measurements were made with a magnetic field of 1.3 T.

3. Results and discussion

In principle, the techniques of ICR and SIFT should yield similar data from kinetic studies on identical systems. Although this situation holds generally for exothermic binary systems, it is not true for ion-molecule reactions that undergo association reactions: Particularly when the system undergoing association has a tertiary reaction rate coefficient $k > 1 \times 10^{-26}$ cm^6/s. The ion molecule reactions of CH_2CHCN^+ and CH_2CHCNH^+ with CH_2CHCN fall into this category. In these cases, the complementary information provided by the two techniques provides valuable insights into the nature of the association complex.

3.1. $CH_2CHCN^+ + CH_2CHCN$

At low pressure, the ICR investigation showed the bimolecular reaction (1)

$$CH_2CHCN^+ + CH_2CHCN \rightarrow CH_2CHCNH^+ + C_3H_2N \qquad (1)$$

occurs with a rate coefficient $k = 2.5 \times 10^{-9}$ cm^3 s^{-1} ± 10% and self protonation, CH_2CHCNH^+, was the only ion product found. The reaction was studied in both trapped and drift mode of operation of the ICR cell over the pressure range from 8×10^{-7} to 3×10^{-5} Torr of CH_2CHCN. The same behaviour was observed in each mode of operation. The reaction rate coefficient measured at these low pressures is 70% of the capture rate coefficient for the reaction, $k_{\mathrm{coll}} = 3.6 \times 10^{-9}$ cm^3 s^{-1} [21].

An earlier study using a SIFT reported the association adduct ion, $C_6H_6N_2^+$, as the only product of the reaction. The measured rate coefficient was similar to, but less than the ICR result above, viz. $k_{\mathrm{SIFT}} = 2.0 \times 10^{-9}$ cm^3 s^{-1} (in 0.30 Torr of He) [5]. A reexamination of this reaction in the FA/SIFDT as part of the present work identified *two products* of this reaction: CH_2CHCNH^+ and $C_6H_6N_2^+$ with a reaction rate coefficient of $k = 3.1 \times 10^{-9}$ cm^3 s^{-1} ± 15%.

$$CH_2CHCN^+ + CH_2CHCN \xrightarrow{0.70} CH_2CHCNH^+ + C_3H_2N \quad (2a)$$

$$\xrightarrow{0.30} C_6H_6N_2^+ \quad (2b)$$

In the earlier measurement, the product channel $CH_2CHCNH^+ + C_3H_2N$ was observed but was discounted from being a product because of CH_2CHCNH^+ also being present in the flow tube as an impurity ion which was formed in the ion source and injected along with CH_2CHCN^+. Using the FA/SIFDT it was possible to inject CH_2CHCN^+ cleanly without any interference from CH_2CHCNH^+. The branching ratio observed was 70% for reaction (2a) and 30% for reaction (2b) at a reaction tube pressure of 0.48 Torr using helium as the bath gas. In addition, the rate coefficient for reaction (2) was invariant ($k = 3.1 \times 10^{-9}$ cm^3 s^{-1} ± 15%) over the pressure range 0.25–0.75 Torr of helium. The branching ratio for the two channels was also invariant over this flow tube pressure range.

To assist our understanding of the nature of the $(CH_2CHCN)_2^+$ complex formed in the reaction, we examined the reaction using the drift tube capability of the FA/SIFDT. The mean center-of-mass energy for the reactant ion/reactant neutral encounter, E_r, is given by [22]

$$E_r = \frac{3}{2} k_B T + [m_r/(m_i + m_r)]\left(\mathrm{KE}_{\mathrm{ion}} - \frac{3}{2} k_B T\right) \quad (3)$$

where m_i, m_r are the masses of the ion and reactant gas, respectively. $\mathrm{KE}_{\mathrm{ion}}$ is the mean kinetic energy of the drifting ions from the Wannier formula and T is the carrier gas temperature. The mobilities of CH_2CHCN^+ were measured at each E/N value from their arrival times determined by pulsing rings within the drift tube as discussed in Fairley et al. [16].

As the center-of-mass energy increased, there was a noticeable decrease in the observed rate coefficient (Fig. 1) with the fall off being most marked in the association channel (2b) which eventually vanished at E_r energies ~ 0.1 eV.

What do these observations tell us about the lifetime of the $(CH_2CHCN^+)_2^*$ collision complex? The lifetime of the complex or complexes that are precursors to both products are clearly being shortened by increasing their internal energy. Further, the lifetime of the complex that leads to collision stabilization and, hence, association is shortened to such an extent at $E_r = 0.1$ eV, that it does not survive long enough for collision stabilization to be observed at flow tube pressures. As no collision-stabilized product is observed in the ICR, the mean lifetime of the complex, $\tau(CH_2CHCN^+)_2^*$, is much less than the time between collisions in the ICR at 3×10^{-5} Torr of CH_2CHCN: i.e. $\tau \ll 430$ μs. Furthermore, in the ICR, approximately 30% of all collisions undergo unimolecular dissociation back to reactants, because the measured reaction rate coefficient of $k = 2.5 \times 10^{-9}$ cm^3 s^{-1} is about 70% of the collision rate.

The potential surface often assumed in these reactions in the vicinity of the reaction coordinate is shown schematically in Fig. 2(a). $(AB^+)^*$ represents the association complex retaining the energy brought in by the two reactants. All forms of stabilization of $(AB^+)^*$ leads to (AB^+),‡ which retains sufficient energy to cross over the barrier and to form products $(C^+ + D)$. Energies of (AB^+) below E_B lead only to formation of the adduct and even though the complex

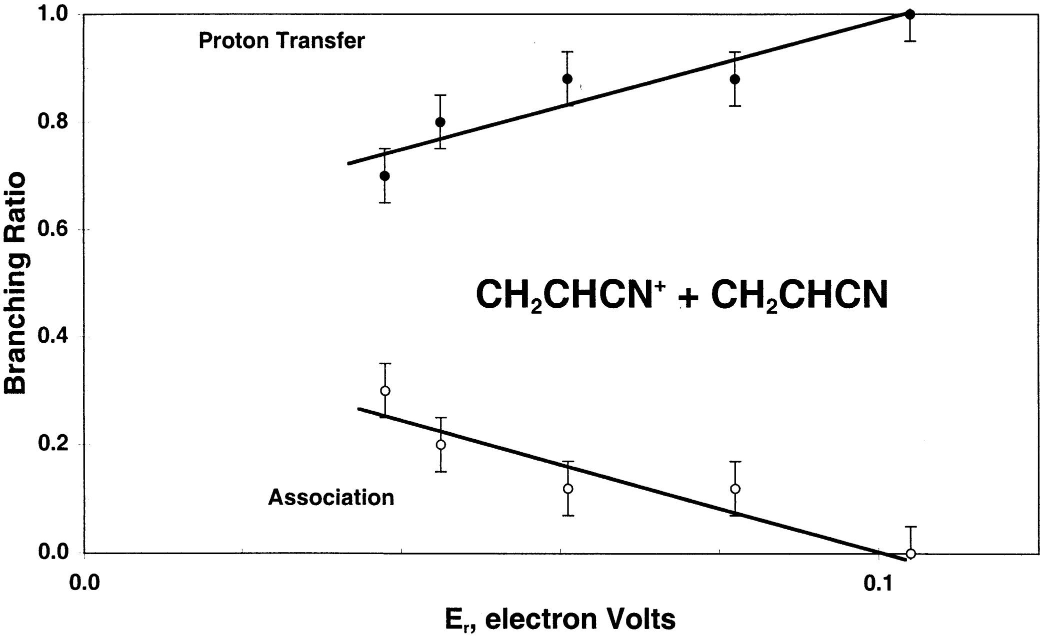

Fig. 1. The variation in the branching ratio with increasing E_R for the reaction $CH_2CHCN^+ + CH_2CHCN$.

possesses some internal energy, we represent it as AB^+. The sequence of reactions that occur may then be represented as follows:

$$A^+ + B \underset{k'_1}{\overset{k_f}{\rightleftharpoons}} (AB^+)^* \tag{4}$$

$$(AB^+)^* \xrightarrow{k'_2} C^+ + D \tag{5}$$

$$(AB^+)^* \xrightarrow{k'_r} (AB^+)\ddagger + h\nu \tag{6}$$

$$(AB^+)^* + \mathrm{M} \xrightarrow{\beta' k_{\mathrm{coll}}} (AB^+)^\ddagger + \mathrm{M} \tag{7}$$

$$(AB^+)^\ddagger \xrightarrow{k_2} C^+ + D \tag{8}$$

$$(AB^+)^\ddagger \xrightarrow{k_r} AB^+ + h\nu \tag{9}$$

$$(AB^+)^\ddagger + \mathrm{M} \xrightarrow{\beta k_{\mathrm{coll}}} AB^+ + \mathrm{M} \tag{10}$$

In this scheme, k'_{-2} (reaction (5)) and k_{-2} (reaction (8)) are energy dependent. k_{-2} decreases to zero when the available energy of $(AB^+)^\ddagger$ equals the barrier height energy E_B of Fig. 2(a). The lack of any pressure independent rate coefficient from the ICR trapped mode experiments, allows us to conclude that reactions (6) and (9) (radiative stabilization) are too slow to compete with the other channels.

The model represented in Eqs. (4)–(10), is the simplest representation of a bimolecular reaction in competition with association, and is the model that we have used to account for association in most of the systems we have studied previously [11–14]. This model however cannot fit the data observed in the present study under any circumstances, as the measured association channel [reactions (7) and (10)] fails to increase to the capture rate at high pressures. Instead, both channels remain invariant with pressure throughout the pressure regime of the FA/SIFDT study (0.25–0.75 Torr of helium). Models proposed to account for this behaviour must of necessity be more elaborate. One of the simplest models that can describe the qualitative behaviour that we have observed in this work is a double well model [23,24] [Fig. 2(b)]. In this model a loosely bound $(A^+ \ldots B)^*$ complex is in equilibrium with reactants and also with a more tightly bound $(AB^+)^*$ complex.

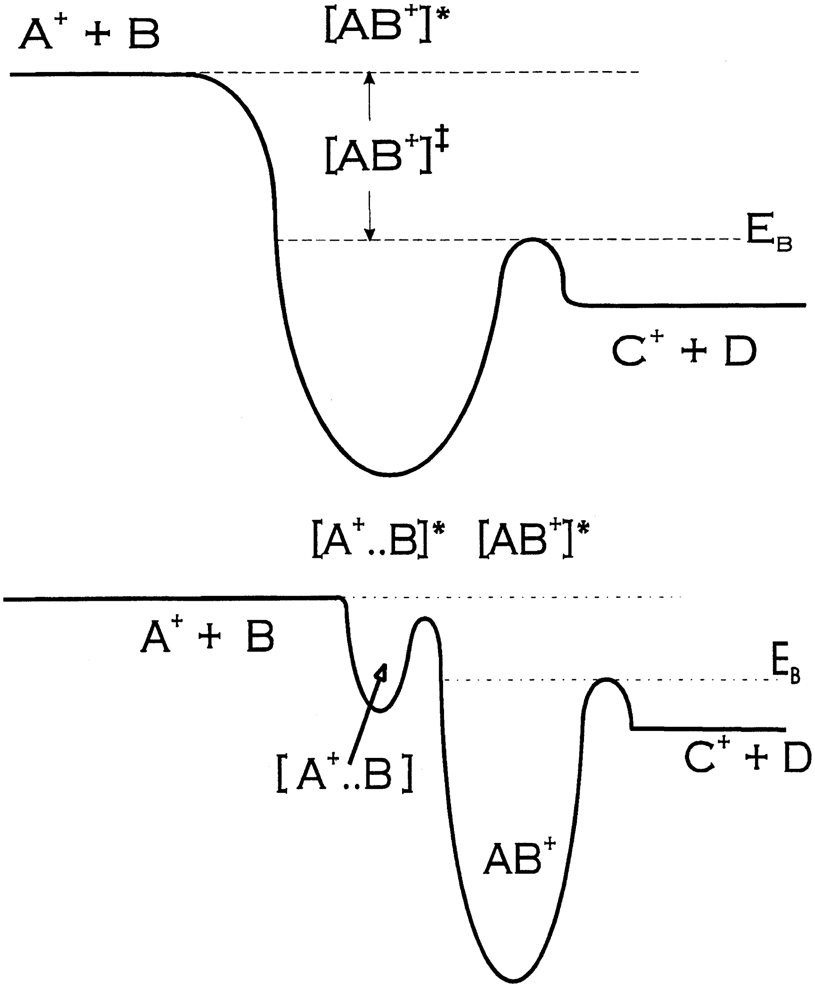

Fig. 2. (a) A schematic diagram of the potential energy surface along the reaction coordinate for the $A^+ + B$ reaction relative to the separated reactants having zero energy. (b) A schematic diagram of the potential energy surface along the reaction coordinate showing the formation of two different complexes. $(A^+ \ldots B)$ is a loosely bound complex and $(AB^+)^*$ a tightly bound complex having a greater binding energy.

$$A^+ + B \underset{k_{-1}}{\overset{k_f}{\rightleftharpoons}} (A^+ \ldots B)^* \xrightarrow{k_p} C^+ + D \tag{11}$$

$$(A^+ \ldots B)^* \underset{k'_{-1}}{\overset{k_t}{\rightleftharpoons}} (AB^+)^* \xrightarrow{k'_p} C^+ + D \tag{12}$$

$$(AB^+)^* + \mathrm{M} \xrightarrow{\beta k_s} AB^+ + \mathrm{M} \tag{13}$$

As in the simpler model discussed previously, all of the unimolecular reaction rate coefficients are energy dependent. Eqs. (11)–(13) have two important outcomes that are distinct from the previous model. First, the model allows total high pressure limiting rate coefficients that are less than the collision rate, k_f [25]. Second, it allows limiting rate coefficients that are pressure invariant in multiple channels. Both of these features were observed in the present work. In this model the two complexes $(A^+ \ldots B)^*$ and $(AB^+)^*$ have different "pressure regimes" of influence. The more tightly bound complex $(AB^+)^*$ is "saturated" (i.e. all $(AB^+)^*$ complexes that can be stabilized, are stabilized) in the 0.25–0.75 Torr helium pressure range in the FA/SIFDT measurement. In contrast, the

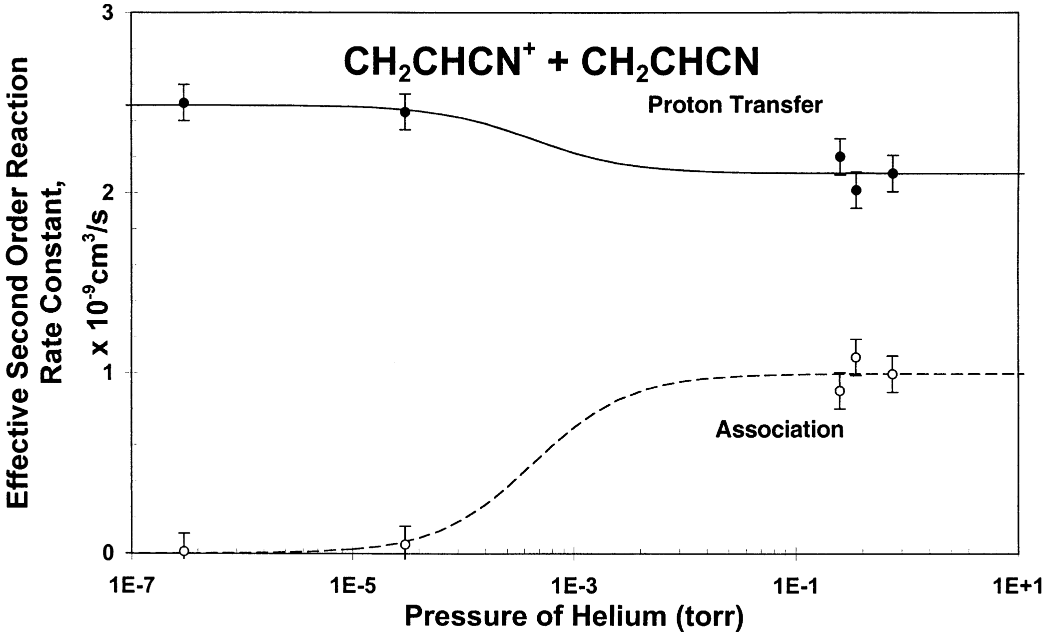

Fig. 3. The fit of the model expressed in Eqs. (14) and (15) to the ICR and SIFT data for the CH_2CHCN^+/CH_2CHCN system is shown. The effective bimolecular reaction rate coefficient is plotted against $\log(P_{CH_2CHCN})$ or $\log P_{He}$. The production of bimolecular products via Eq. (12) ICR and SIFT experimental, solid symbols) and the onset of association via Eq. (13) (SIFT experiment, open symbols) are shown by separate curves. The curves represent the modelled fits for the overall process.

loosely bound $(A^+ \ldots B)^*$ complex does not live long enough for stabilization to occur and generates bimolecular products continuously at flow tube pressures. It is the combination of both loose and tight complexes that give rise to the bimolecular channels observed in the flow tube whereas it is largely the loose complex that is responsible for the behaviour of the CH_2CHCN^+/CH_2CHCN system in the ICR.

Data points for the CH_2CHCN^+/CH_2CHCN system shown in reactions (1) and (2) were fitted to the model, represented by Eqs. (11)–(13). The fit achieved by the model is shown in Fig. 3. In achieving this fit the following assumption were made. The steady state approximation was applied to both complexes, $(A^+ \ldots B)^*$ and $(AB^+)^*$, from which it can be deduced that the observed bimolecular reaction rate coefficient for the formation of C^+, e.g. CH_2CHCN^+, is

$$k_{\mathrm{obs}}^{C+} = \frac{k_f(k_pZ + k'_pk_t)}{(YZ - k'_{-1}k_t)} \tag{14}$$

and

$$k_{\mathrm{obs}}^{AB+} = \frac{k_fk_t\beta k_s[\mathrm{M}]}{(YZ - k'_{-1}k_t)} \tag{15}$$

where $Y = (k_{-1} + k_p + k_t)$ and $Z = (k'_{-1} + k'_p + \beta k_s\ [\mathrm{M}])$. It was assumed in the model that $k_f = 3.6 \times 10^{-9}$ cm³/s (the capture rate for CH_2CHCN^+ and CH_2CHCN), $k_s = 1.68 \times 10^{-10}$ cm³/s (the capture rate for $(CH_2CHCN)_2^+$ and He); the remaining unimolecular dissociation reaction rate coefficients were allowed to vary. The model determined that $\tau(AB^+)^*$, the lifetime of the tight complex equals $75/\beta_{He}\mu s$ and that approximately >85% of the tight complex dissociates to $CH_2CHCNH^+ + C_3H_2N$. With regard to the loose complex, $(CH_2CHCN^+ \ldots CH_2CHCN)$, the model found that approximately 26% of the transitions lead to the tight complex, $((CH_2CHCN)_2^+)^*$, approximately 60% form $CH_2CHCNH^+ + C_3H_2N$ and the balance returns to reactants.

A similar model was discussed by Meot-Ner [25] in some detail except that we have made minor modifications to accommodate the observed proton transfer or hydrogen abstraction products ($CH_2CHCNH^+ + C_3H_2N$).

3.2. $CH_2CHCNH^+ + CH_2CHCN$

Association between CH_2CHCNH^+ and CH_2CHCN to give the proton bound dimer was the only channel observed in both instruments

$$CH_2CHCNH^+ + CH_2CHCN + M \rightarrow (CH_2CHCN)_2H^+ + M \quad (16)$$

In the SIFT instrument, the pseudobimolecular reaction rate coefficients ranging from 1.43×10^{-9} $cm^3\ s^{-1} \pm 15\%$ at 0.25 Torr of helium to 2.10×10^{-9} cm^3/s at 0.75 Torr of helium. In the ICR instrument operating in the drift-mode, the pseudobimolecular rate coefficient varied from 9×10^{-12} cm^3 s^{-1} at 2.5×10^{-5} Torr of CH_2CHCN to 1.0×10^{-10} $cm^3\ s^{-1}$ at 3.0×10^{-4} Torr of CH_2CHCN.

In contrast to the preceeding case, the simplest model that maybe applied to fit the data is the single potential well model outlined in Eqs. (4)–(10) except that all channels leading to bimolecular channels are too slow to be observed experimentally.

The equations arising from this model have been discussed previously [12]. In brief, for the process

$$A^+ + B \xrightarrow{k_2^{obs}} AB^+ \quad (17)$$

it has been shown that [12]

$$k_2^{obs} = k_f \beta_{rel} k_{coll}[M]/(k_{-1} + \beta_{rel} k_{coll}[M]) \quad (18)$$

where the coefficient β_{rel} is a number between 0 and 1 and gives a measure of the efficiency of stabilization of $(AB^+)^*$, by the bath gas relative to the parent gas.

Eq. (18), represents the total rate coefficient for disappearance of A^+ and is of course pressure dependent. The pressure variation of k_2 in the ICR data for this process enables the termolecular reaction rate coefficient to be found directly: viz.: $k_3 = 1.2 \times 10^{-23}$ $cm^6\ s^{-1} \pm 20\%$ ($M = CH_2CHCN$) and $k_3 = 8.1 \times 10^{-25}$ $cm^6\ s^{-1} \pm 20\%$ ($M = He$). This model expresses the basis for iteratively fitting the experimental ICR and SIFT data using k_{-1}, and β_{rel} as the only adjustable parameters. The minimized least squares line of best fit of the model to the experimental data is shown in Fig. 4. In achieving this fit, k_f was set at the reaction capture rate coefficient ($k_f = 3.6 \times 10^{-9}$ $cm^3\ s^{-1}$) and k_s to the capture rate of the collision complex with helium, ($k_s = 1.68 \times 10^{-10}$ $cm^3\ s^{-1}$).

The measurement of the rate coefficient for termolecular association in the ICR allows us to place constraints on the lifetime τ of the collision complex $((CH_2CHCN)_2H^+)^*$ with respect to unimolecular dissociation. The results summarized in Table 1 represent the best fit of the model to the experimental data. The minimum lifetime of the proton bound dimer is approximately 0.90 μs. Actually, the product $\beta^* \tau_{[(CH_2CHCN)_2H^+]^*}$ has a value of 0.90 μs, but β is less than one and therefore the lifetime is greater that 0.90 μs.

A summary of the experimental results is given in Table 2.

3.3. Collision efficiency β and lifetime τ

The values of k_3 measured in the ICR for $M = He$ and $M = CH_2CHCN$ enable the relative efficiencies for collisional stabilization of $((CH_2CHCN)_2H^+)^*$ by a helium bath gas compared to CH_2CHCN, to be found such that $\beta_{rel} = \beta_{He}/\beta_{CH_2CHCN} = 0.15$. This value is in the range previously determined for collisional stabilization by He [12–14,26–28] but is at the lower end of this range.

The *absolute* value for β, as opposed to the *relative* β value ($\beta_{He}/\beta_{CH_2CHCN}$) deduced here, is significantly less than unity because only weak collisions with the bath gas occur [29]. Values of $\beta_{PG} \sim 0.1$ (PG = parent gas) have been found for collisions of $(AB^+)^*$ with parent gas molecules in systems where bimolecular channels compete with collisional stabilization [29]. Similar competition occurs with the CH_2CHCN^+/CH_2CHCN system, but not with CH_2CHCNH^+/CH_2CHCN.

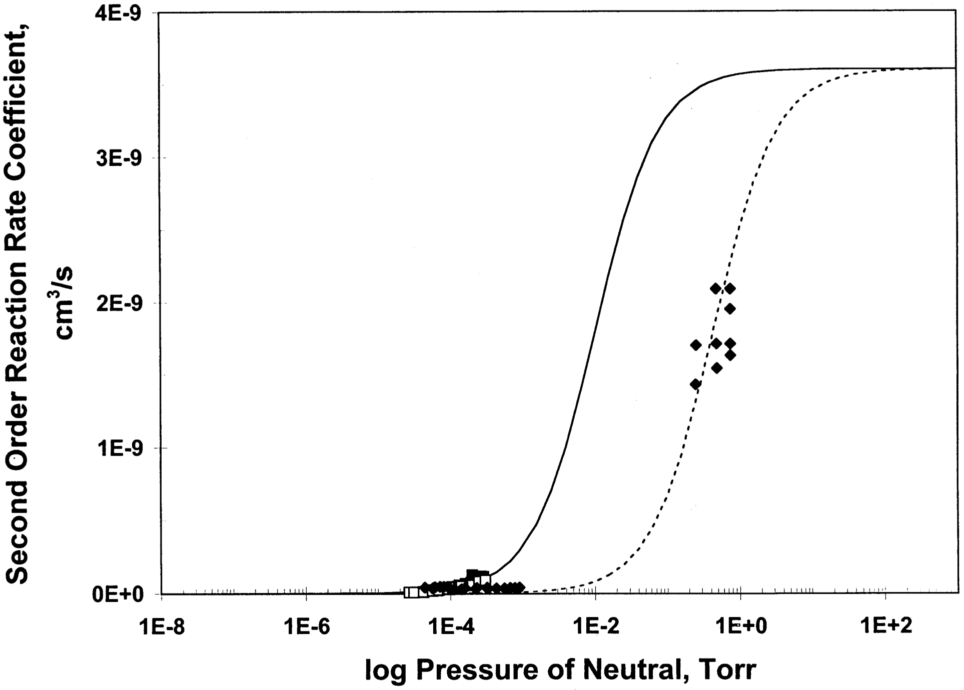

Fig. 4. The variation in the apparent bimolecular rate coefficient for the CH_2CHCNH^+/CH_2CHCN system shown as a function of log P for the two bath gases M = CH_2CHCN (solid curve) and M = He (dashed curve) from the model represented in Eq. (13). The ICR data is represented by circles, the SIFT data by a square.

4. Conclusions

In the two ion-neutral systems of acrylonitrile discussed in this work, a long-lived association complex $(AB^+)^*$ is formed. In each system there is competition for the $(AB^+)^*$ population between dissociation back to reactants and stabilization. The onset of association as observed by the appearance of AB^+ in the two systems, is however quite different even though the estimated complex lifetimes $\tau(AB^+)^*$ are in the microsecond range.

The simple model most commonly used to account for association expressed in reactions (4)–(10) satisfactorily accounts for the behaviour of the CH_2CHCNH^+/CH_2CHCN system but not the CH_2CHCN^+/CH_2CHCN system. The simplest model describing the kinetic behaviour of the latter system was a double potential well model in which loosely bonded and more tightly bonded complexes are formed. A consequence of this model is the so-called "pressure saturation" region does not lead to a collision rate association reaction. Instead, competing termolecular association and bimolecular reactions occur that become pressure invariant having a combined rate coefficient that may be less than the collision rate.

Stabilization of the $(AB^+)^*$ complex, although occurring predominantly by collision with the bath gas in this work, may also occur by radiation of a photon. The crucial parameter in both types of stabi-

Table 1
Evaluation of rate coefficients in the CH_2CHCNH^+/CH_2CHCN reactions based on the model represented in reactions (3)–(9)

Rate coefficient	Units	CH_2CHCNH^+/CH_2CHCN
k_f	$cm^3\ s^{-1}$	3.6×10^{-9}
k_{-1}/β	s^{-1}	1.11×10^6
k_{-2}/β	s^{-1}	0
$\beta^*\tau$	μs	0.90
$k_3(M = He)$	$cm^6\ s^{-1}$	8.1×10^{-25}
$k_3(M = CH_2CHCN)$	$cm^6\ s^{-1}$	1.2×10^{-23}
β_{rel}		0.15

Table 2
A comparison of the reactions of CH_2CHCN^+ and CH_2CHCNH^+ with CH_2CHCN using ICR and SIFT techniques

	ICR			SIFT		
Reactant ion	Branching ratio	Products	k_{ICR} (10^{-9} cm^3 s^{-1})	Branching ratio	Products	k_{SIFT}[a] (10^{-9} cm^3 s^{-1})
CH_2CHCN^+	1.0	$CH_2CHCNH^+ + C_3H_2N$	2.5[b]	0.70	$CH_2CHCNH^+ + C_3H_2N$	3.1
				0.30	$C_6H_6N_2^+$	
CH_2CHCNH^+	1.0	$(CH_2CHCN)_2H^+$	0.092[c]	1.0	$(CH_2CHCN)_2H^+$	1.43–2.10[d]

[a] Flow tube pressure = 0.30 Torr of helium.

[b] At a pressure of CH_2CHCN of less than 3×10^{-4} Torr.

[c] At a pressure of CH_2CHCN of 3.0×10^{-4} Torr. The rate coefficient is pressure dependent, $k_3 = 1.2 \times 10^{-23}$ cm^6 s^{-1} (M = CH_2CHCN) Torr.

[d] The rate coefficient varies from 1.43×10^{-9} cm^3 s^{-1} at 0.25 Torr of helium to 2.10×10^{-9} cm^3 s^{-1} at 0.75 Torr of helium.

lization process is the lifetime τ of $(AB^+)^*$. Factors that influence τ strongly are the chemical complexity and binding energy of the complex as predicted by statistical theories [29,30].

Our estimates of the $(AB^+)^*$ lifetimes for the CH_2CHCNH^+/CH_2CHCN system (Table 1), are consistent with our nonobservaton of radiative emission. The lifetime observed for the tight complex ($\beta\tau = 0.75$ μs) is at the lower end of the range of lifetimes that we have found in several similar association systems where the $\beta \times \tau$ values vary from 0.5 μs $(CH_3CN)_2H^+$ [11] to 180 μs $(HC_2N)_2^+$ [31]. A comparison of the present systems with those studied earlier suggests the binding energy of the association complex is a major factor in controlling the complex lifetime. Binding energies of a range of metal ion-ligand complexes have in fact been estimated from their radiative lifetimes [32].

What is not widely appreciated is that the collision efficiency parameters β are generally $\ll 1$. *Relative* collision efficiencies have been measured for a number of bath gases in several systems and are typically between 0.1 and 0.6 for most atomic or diatomic bath gases, relative to the polyatomic parent gas [19]. To determine β uniquely, we must also measure $\tau(AB^+)^*$. In the one ion-molecule system in which we have been able to obtain an *absolute* instead of a *relative* value for β, we find $\beta = 0.14$ for the parent gas (CH_3CN) and only 0.05 for a helium bath gas [30]. Assuming values of $\beta \sim 0.15$, the lifetimes of the proton bound dimer in this study is around 1 μs.

Association reactions of ions with neutrals can at times be very efficient leading to direct synthesis of new and larger molecular ions. The propensity of acrylonitrile to polymerise in solution is mimiced in its gas phase ion chemistry by efficient association processes leading to the formations of new covalently bound ions which survive long enough to be stabilized by collisions with the bath gas.

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References

[1] J. McMurry, Organic Chemistry, 2nd ed., Brooks/Cole, CA, 1988, p. 1117.
[2] S. Tsuda, A. Yokohata, T. Umaba, Bull. Chem. Soc. Jpn. 46 (1973) 2273.
[3] M. Heni, E. Illenberger, Int. J. Mass Spectrom. Ion Processes 73 (1986) 127.
[4] T. Tsukuda, T. Kondow, J. Am. Chem. Soc. 116 (1994) 9555.
[5] S. Petrie, T.J. Chirnside, C.G. Freeman, M.J. McEwan, Int. J. Mass Spectrom. Ion Processes 107 (1991) 319.
[6] J. Sun, H-F. Grützmacher, C. Lifshitz, J. Am. Chem. Soc. 115 (1993) 8382.
[7] G. Javahery, S. Petrie, J. Wang, H. Wincel, D.K. Bohme, J. Am. Chem. Soc. 115 (1993) 9701.

[8] F.F. Gardner, G. Winnewisser, Astrophys. J. Lett. 195 (1975) L127.

[9] H.E. Matthews, T.J. Sears, Astrophys. J. 272 (1983) 149.

[10] S. Petrie, C.G. Freeman, M.J. McEwan, Mon. Not. R. Astron. Soc. 257 (1992) 438.

[11] M.J. McEwan, A.B. Denison, V.G. Anicich, W.T. Huntress, Int. J. Mass Spectrom. Ion Processes 81 (1987) 247.

[12] M.J. McEwan, A.B. Denison, W.T. Huntress, V.G. Anicich, J. Snodgrass, M.T. Bowers, J. Phys. Chem. 93 (1989) 4064.

[13] A.D. Sen, W.T. Huntress, V.G. Anicich, A.B. Denison, M.J. McEwan, J. Chem. Phys. 94 (1991) 5462.

[14] M.J. McEwan, V.G. Anicich, J. Phys. Chem. 99 (1995) 12 204.

[15] M.J. McEwan, in Advances in Gas Phase Ion Chemistry, N.G. Adams, L.M. Babcock (eds.), J.A.I., Greenwich, CT, 1992, Vol. 1, p. 1.

[16] D.A. Fairley, G.B.I. Scott, D.B. Milligan, R.G.A.R. Maclagan, M.J. McEwan, Int. J. Mass Spectrom. Ion Processes 172 (1998) 79.

[17] J.M. Van Doren, S.E. Barlow, C.H. DePuy, V.M. Bierbaum, Int. J. Mass Spectrom. Ion Processes 81 (1987) 85.

[18] D.B. Milligan, D.A. Fairley, C.G. Freeman, M.J. McEwan (to be published).

[19] V.G. Anicich, W.T. Huntress Jr., M.J. McEwan, J. Phys. Chem. 90 (1986) 2446.

[20] T.B. McMahon, J.L. Beauchamp, Rev. Sci. Instrum., 43 (1972) 509.

[21] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.

[22] M. McFarland, D.L. Albritton, F.E. Fehsenfeld, E.E. Ferguson, A.L. Schmeltekopf, J. Chem. Phys. 59 (1973) 6620.

[23] M. Meot-Ner, J. Amer. Chem. Soc. 101 (1979) 2389.

[24] P.V. Neilson, M.T. Bowers, M. Chau, W.R. Davidson, D.H. Aue, J. Amer. Chem. Soc. 100 (1978) 3649.

[25] M. Meot-Ner, Gas Phase Ion Chemistry, M.T. Bowers (Ed.), Academic, New York, 1979, p. 198.

[26] M.J. McEwan, D.A. Fairley, G.B.I. Scott, V.G. Anicich, J. Phys. Chem. 100 (1996) 4032.

[27] P.R. Kemper, L.M. Bass, M.T. Bowers, J. Phys. Chem. 89 (1985) 1105.

[28] R.D. Cates, M.T. Bowers, J. Am. Chem. Soc. 102 (1980) 3994.

[29] S.C. Smith, P.F. Wilson, P. Bowers, P. Sudkeaw, R.G.A.R. Maclagan, M.J. McEwan, V.G. Anicich, W.T. Huntress, J. Chem. Phys. 98 (1993) 1944.

[30] R. Marx, P. Rosmus, in Unimolecular and Biomolecular Ion-molecule Reaction Dynamics C.-Y. Ng, T. Baer, I. Powis (Eds.), Wiley, New York 1994, p. 253.

[31] V.G. Anicich, A.D. Sen, W.T. Huntress, M.J. McEwan, J. Chem. Phys. 94 (1991) 4189.

[32] R.C. Dunbar, S.J. Klippenstein, J. Hrusak, D. Stöckigt, H. Schwarz, J. Am. Chem. Soc. 118 (1996) 5277.