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# Ion-Molecule Association in Acrylonitrile

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## Abstract

The association reactions of the acrylonitrile ion,  $\text{CH}_2\text{CHCN}^+$ , and the protonated acrylonitrile ion,  $\text{CH}_2\text{CHCNH}^+$ , derived from acrylonitrile with acrylonitrile ( $\text{CH}_2\text{CHCN}$ ) have been examined using ion cyclotron resonance (ICR) and selected ion flow tube (SIFT) 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  $\text{CH}_2\text{CHCN}^+/\text{CH}_2\text{CHCN}$  system, the measured reaction rate coefficients are:  $k_{\text{ICR}} = 2.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  with a single product channel ( $\text{CH}_2\text{CHCNH}^+ + \text{C}_3\text{H}_2\text{N}$ ) and  $k_{\text{SIFT}} = 2.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (with a 75% product channel to the adduct  $\text{C}_6\text{H}_6\text{N}_2^+$ ). In the  $\text{CH}_2\text{CHCNH}^+/\text{CH}_2\text{CHCN}$  system, the measured rate coefficients are:  $k_{\text{ICR}} = 9.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and  $k_{\text{SIFT}} = 1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , 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  $k_3 = 1.2 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  (for  $\text{M} = \text{CH}_2\text{CHCN}$ ).

## 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.<sup>1</sup>

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<sup>2,3</sup> and the ensuing intracluster anionic polymerization in acrylonitrile clusters formed in a sonic nozzle have also been investigated.<sup>4</sup> 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 reaction chemistry of  $C_3H_2N^+$ ,  $CH_2CHCN^+$  and  $CH_2CHCNH^+$  with a number of simple neutrals was reported by Petrie *et al.*<sup>5</sup> The ion-molecule chemistry of  $CH_2CHCN$  with  $C_n^+$  ( $n = 10-18, 20$ ) was reported by Sun *et al.*<sup>6</sup> and with the fullerene mono-, di- and tri-cations by Javahery *et al.*<sup>7</sup>

Acrylonitrile is one of the molecules observed using radioastronomy techniques in interstellar clouds.<sup>8,9</sup> Several reactions of positive ions derived from  $CH_2CHCN$  with molecules of relevance to interstellar conditions were reported by Petrie *et al.*<sup>10</sup> using the selected ion flow tube 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.<sup>5</sup> 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 selected ion flow tube (SIFT).<sup>1</sup> 1-14 In this study, we extend these investigations to include association reactions of  $\text{CH}_2\text{CHCN}^+$  and  $\text{CH}_2\text{CHCNH}^+$  with  $\text{CH}_2\text{CHCN}$  over the wide pressure range of  $10^{-7}$  Torr to 0.3 Torr.

## Experimental

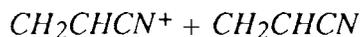
The flow tube experiments were made using a SIFT operating at room temperature ( $300 \pm 5$  K), located at the University of Canterbury and which has been described previously.<sup>15</sup> The ICR experiments were made using an ICR, which has not been described before, located at Canterbury University. This ICR is similar in principle and design to the ICR at the Jet Propulsion Laboratory (JPL) which has been described elsewhere.<sup>12,16</sup> The instrument utilizes a McMahan-Beauchamp type cell design<sup>17</sup> 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.

A trace of the radical inhibitor 4-methoxyphenol was added to the acrylonitrile to prevent its polymerization in the absence of oxygen.

## 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  $k > 1 \times 10^{-26} \text{ cm}^6/\text{sec}$ . The ion molecule reactions of  $\text{CH}_2\text{CHCN}^+$  and  $\text{CH}_2\text{CHCNH}^+$  with  $\text{CH}_2\text{CHCN}$  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.



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



occurs with a rate coefficient  $k = 2.5 \times 10^{-9} \text{ cm}^3 \text{ S}^{-1} \times 1070$  and  $CH_2CHCNH^+$  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  $8 \times 10^{-7}$  Torr to  $3 \times 10^{-5}$  Torr of  $CH_2CHCN$ . The same behaviour was observed in each mode of operation. The reaction rate coefficient measured at these low pressures is slightly less than the capture rate coefficient for the reaction of  $k_{\text{coll}} = 3.6 \times 10^{-9} \text{ cm}^3 \text{ S}^{-1}$ .<sup>18</sup>

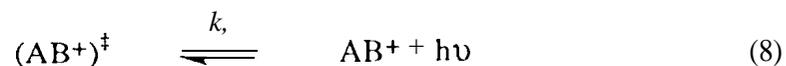
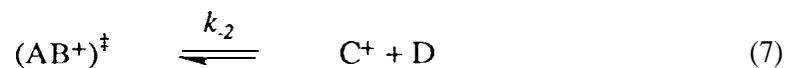
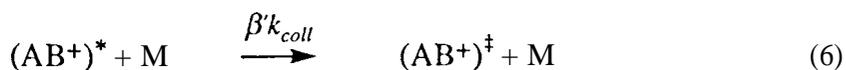
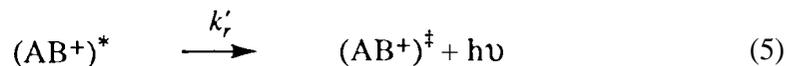
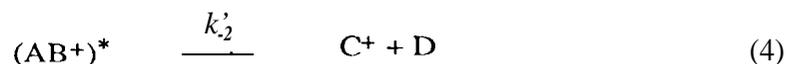
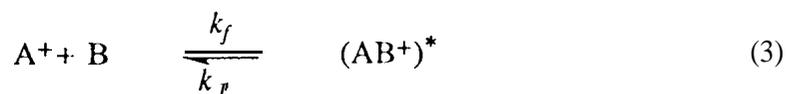
An earlier study using a SIFT reported the association adduct  $C_6H_6N_2^+$  as the only product of the reaction and the measured rate coefficient was similar to the ICR result above, viz.  $k_{\text{SIFT}} = 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .<sup>5</sup> A re-examination of this reaction in the SIFT 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  $k = 2.8 \times 10^{-9} \text{ cm}^3 \text{ S}^{-1} \pm 15\%$ .



In the earlier measurement, the product channel  $CH_2CHCNH^+ + C_3H_2N$  was observed but was discounted due to  $CH_2CHCNH^+$  also being present in the flow tube as an impurity ion which was formed in the ion source and injected along with  $CH_2CHCN^+$ . By careful control of the injection process, we were able to ascertain the branching ratio as 25% for reaction (2a) and 75% for reaction (2b) for the reaction in the SIFT at a reaction tube pressure of 0.35 Torr using helium as the bath gas.

What do these observations tell us about the lifetime of the  $(\text{C}_6\text{H}_6\text{N}_2^+)^*$  complex? As no collision-stabilized product is observed in the ICR, the mean lifetime of the complex,  $\tau(\text{C}_6\text{H}_6\text{N}_2^+)^*$ , is much less than the time between collisions at  $3 \times 10^{-5}$  Torr of  $\text{CH}_2\text{CHCN}$ : i.e.  $\tau \ll 430 \mu\text{s}$ . Furthermore, in the ICR, approximately 30% of all collisions undergo unimolecular dissociation back to reactants, since the measured reaction rate coefficient of  $k = 2.5 \times 10^{-9} \text{ cm}^3 \text{ S}^{-1}$  is about 70% of the collision rate.

The potential surface in the vicinity of the reaction coordinate is shown schematically in Figure 1 for this system.  $(\text{AB}^+)^*$  represents the association complex retaining the energy brought in by the two reactants. All forms of stabilization of  $(\text{AB}^+)^*$  leads to  $(\text{AB}^+)^{\ddagger}$  which retains sufficient energy to cross over the barrier and to form products ( $\text{C}^+ + \text{D}$ ). Energies of  $(\text{AB}^+)^{\ddagger}$  below  $E_{\text{B}}$  lead only to observation of the adduct and even though the complex possesses some internal energy, we represent it as  $\text{AB}^+$ . The sequence of reactions that occur may then be represented as follows:



In this scheme,  $k'_2$  (Reaction 4) and  $k_2$  (Reaction 7) are energy dependent and the value we deduce from the analysis of our data represents an average of these two  $k_2$  values.  $k_2$  decreases to zero when the available energy of  $(\text{AB}^+)^{\ddagger}$  equals the barrier height energy  $E_{\text{B}}$  of Figure 1. The lack of any

pressure independent rate coefficient from the ICR trapped mode experiments, allows us to conclude that reactions (5) and (8) (radiative stabilization) are too slow to compete with the other channels.

The behavior exhibited by this reaction is similar to that displayed by the  $\text{CH}_3^+/\text{CH}_2\text{CHCN}$  system discussed in earlier work<sup>19</sup> in which no association product was observed in the ICR at pressures of  $1 \times 10^{-4}$  Torr but which possessed a rate coefficient for bimolecular reaction close to the collision rate. In the SIFT, both  $\text{CH}_3^+$  and  $\text{CH}_2\text{CHCN}^+$  yielded the association adduct as the main product of their reaction with acrylonitrile.

Estimates for the rate coefficients  $k_{-1}, k_{-2}^{\text{av}}$  and the function  $\beta \times \tau$  for  $(\text{AB}^+)^{\ddagger}$  can be obtained by fitting the model expressed in equations (3) through (9) to the ICR and SIFT experimental data. The assumptions made in fitting the data are: the same values are chosen for  $\beta'$  in equation (6) and  $\beta$  in equation (9); the values for  $k_{-2}'$  (equation (4)) and  $k_{-2}$  (equation (7)) are averaged to a single  $k_{-2}^{\text{av}}$  value. With these assumptions, the observed bimolecular rate coefficient corresponding to total loss of  $\text{A}^+$ ,  $k_{-2}^{\text{obs}}$  for the process.



may be equated to<sup>12</sup>

$$k_{-2}^{\text{obs}} = k_{-1} (k_{-2}^{\text{av}} + \beta k_{\text{coll}}[\text{M}] / (k_{-1} + k_{-2}^{\text{av}} + \beta k_{\text{coll}}[\text{M}]) \quad (11)$$

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

Equation (11), which represents the total disappearance of  $\text{A}^+$ , has two loss components shown in the numerator: the term in  $k_{-2}^{\text{av}}$  represents loss to  $\text{C}^+ + \text{D}$  (bimolecular reaction) and the term in  $\beta k_{\text{coll}}[\text{M}]$  (termolecular reaction) represents loss to  $\text{AB}^+$ . The latter term is of course pressure-dependent when stabilization of the complex through collisions becomes important. Rewriting equation (11) to separate these two loss terms yields:

$$k_2^{C^+} = k_f k_{-2}^{av} / k_{-1} + k_{-2}^{av} + \beta k_{coll}[M] \quad (12)$$

$$k_2^{AB^+} = k_f \beta k_{coll}[M] / (k_{-1} + k_{-2}^{av} + \beta k_{coll}[M]) \quad (13)$$

The ICR data can readily be fitted to equation (12) as only the channel to  $C^+ + D$  products was seen over a pressure range  $2 \times 10^{-7}$  Torr -  $1 \times 10^{-5}$  Torr. The SIFT data has a 75% association channel (i.e.  $k_2^{AB^+} = 2.1 \times 10^{-9}$  at 0.3s Torr of He) which is described by equation (13) and a 2570 product channel (i.e.  $k_2^{C^+} = 7.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) described by equation (12). The model expressed by equations (3) through (9) and summarized in equation (12) and (13) forms the basis for iteratively fitting the experimental ICR and SIFT data using  $k_{-1}$  and  $k_{-2}^{av}$  as adjustable parameters. The fit of the data to the model is shown in Figure 2. The best estimates for  $k_{-1}$ ,  $k_{-2}^{av}$  and the function  $\beta \times \tau$  ( $\tau = 1 / (k_{-1} + k_{-2}^{av})$ ) in achieving this fit are shown in Table 1. The values of  $k_{-1}$  and  $k_{-2}^{av}$  may then be used to estimate  $k_3$ , the rate coefficient for termolecular association,

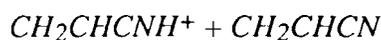


which can be expressed as<sup>12</sup>

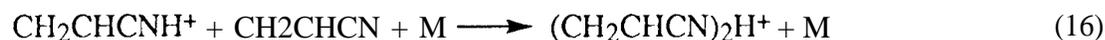
$$k_3 = k_f k_{-1} \beta k_{coll} / (k_{-1} + k_{-2}^{av})^2 \quad (15)$$

This estimate for  $k_3$  has also been included in Table 1.

Implicit in these evaluations of  $k_{-1}$ ,  $k_{-2}^{av}$  and  $k_3$  is the value chosen for the collision efficiency,  $\beta$ . Because it was not possible to measure  $\tau$  directly in the  $\text{CH}_2\text{CHCN}^+/\text{CH}_2\text{CHCN}$  system, we cannot provide unique solutions for  $k_{-1}$ ,  $k_{-2}^{av}$  and  $k_3$  that are independent of  $\beta$ . Instead we present these rate coefficients as ratios ( $k_{-1}, k_{-2}^{av}$ ) or products ( $k_3$ ) of  $\beta$ . Further discussion on collision efficiencies occurs in the treatment of the next system,



Association between  $\text{CH}_2\text{CHCNH}^+$  and  $\text{CH}_2\text{CHCN}$  to give the proton bound dimer was the only channel observed in both instruments.



The pressure variation of  $k_2$  in the ICR data for this process enables the termolecular rate coefficient to be found directly, viz.,  $k_3 = 1.2 \times 10^{-23} \text{ cm}^6 \text{ S}^{-1}$  ( $\text{M} = \text{CH}_2\text{CHCN}$ ).

In the SIFT, as in the ICR instrument, only one reaction product,  $(\text{CH}_2\text{CHCN})_2\text{H}^+$ , was formed with a pseudo bimolecular rate coefficient  $k = 1.8 \times 10^{-9} \text{ cm}^3 \text{ S}^{-1}$ . This rate coefficient measured at 0.35 Torr in a helium bath gas is significantly less than the capture rate coefficient of  $k = 3.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .<sup>18</sup> The fact that the observed rate coefficient is only one half the capture rate means that 50% of  $(\text{CH}_2\text{CHCN})_2\text{H}^+$  complexes are dissociating before they can be stabilized by the helium bath gas at 0.35 Torr.

The measurement of the rate coefficient for termolecular association in the ICR allows us to place constraints on the lifetime  $\tau$  of the collision complex  $(\text{CH}_2\text{CHCN})_2\text{H}^+$  with respect to unimolecular dissociation. Using the scheme shown in reactions (3) through (9) as discussed previously and assuming  $k_f = k_{\text{coll}} = 3.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , then 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 0.59  $\mu\text{s}$ . Actually, the product  $\beta^* \tau_{[(\text{CH}_2\text{CHCN})_2\text{H}^+]^*}$  has a value of 0.59  $\mu\text{s}$ , but  $\beta$  is less than one and therefore the lifetime is greater than 0.59  $\mu\text{s}$ . The comparison between the model and the data is shown in Figure 3 for this system.

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

### *Collision Efficiency $\beta$ and Lifetime $\tau$*

The values of  $k_3$  measured in the ICR for  $M = \text{He}$  and  $M = \text{CH}_2\text{CHCN}$  enable the relative efficiencies for collisional stabilization of  $(\text{CH}_2\text{CHCN})_2\text{H}^+$  by a helium bath gas compared to  $\text{CH}_2\text{CHCN}$ , to be found such that  $\beta_{\text{He}}/\beta_{\text{CH}_2\text{CHCN}} = 0.39$ . This value is in the range previously determined for collisional stabilization by  $\text{He}$ <sup>12-14,19-21</sup> but is at the higher end of this range. A trend appears to be developing such that molecules having large dipole moments give larger  $\beta_{\text{He}}/\beta_{\text{PG}}$  (PG = parent gas) ratios than complexes with molecules without dipole moments.

The *absolute* value for  $\beta$ , as opposed to the *relative*  $\beta$  value ( $\beta_{\text{He}}/\beta_{\text{CH}_2\text{CHCN}}$ ) deduced here, is significantly less than unity because only weak collisions with the bath gas occur.<sup>22</sup> Values of  $\beta_{\text{PG}} - 0.1$  have been found for collisions of  $(\text{AB}^+)^*$  with parent gas molecules in systems where bimolecular channels compete with collisional stabilization.<sup>22</sup> Similar competition occurs with the  $\text{CH}_2\text{CHCN}^+/\text{CH}_2\text{CHCN}$  system, but not with  $\text{CH}_2\text{CHCNH}^+/\text{CH}_2\text{CHCN}$ .

In the present experiments, it is not possible to obtain a value for  $\tau(\text{AB}^+)^*$  independently of  $\beta$ . However our experience with similar systems suggests a value for  $\beta - 0.15$  for the  $\text{CH}_2\text{CHCNH}^+/\text{CH}_2\text{CHCN}$  association, and the mean lifetime  $\tau(\text{CH}_2\text{CHCN})_2^+ - 4 \mu\text{s}$ . Slightly larger values of  $\beta$  are to be expected in systems such as  $\text{CH}_2\text{CHCNH}^+/\text{CH}_2\text{CHCN}$  because of the absence of other channels competing with collisional stabilization for depletion of  $(\text{AB}^+)^*$ .

## Conclusions

In the two ion-neutral association systems of  $\text{CH}_2\text{CHCN}$  discussed in this work, there is competition in each complex  $(\text{AB}^+)^*$  between dissociation and stabilization. The dissociation can be back to reactants or on to products. The stabilization process may in principle be radiative or collisional, but only collisional stabilization was identified in this study. The crucial parameter in determining whether or not radiative stabilization is observed is the lifetime,  $\tau$  of  $(\text{AB}^+)^*$ . The longer the lifetime, the higher the probability for IR photon emission. Factors that influence  $\tau$  strongly are the chemical complexity and binding energy of the complex as predicted by statistical theories.<sup>22,23</sup>

Our estimates of the  $(AB^+)^*$  lifetimes (Table 1) are consistent with our non-observation of radiative emission with each complex having a lifetime  $\beta \times \tau - 1 \mu\text{s}$ . These lifetimes are 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  $0.5 \mu\text{s}(\text{CH}_3\text{CN})_2\text{H}^{+11}$  to  $180 \mu\text{s}(\text{HC}_3\text{N})_2^{+24}$ . 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.<sup>25</sup>

What is not widely appreciated is that the collision efficiency parameters  $\beta$  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.<sup>19</sup> To determine  $\beta$  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  $\beta$ , we find  $\beta = 0.14$  for the parent gas ( $\text{CH}_3\text{CN}$ ) and only 0.05 for a helium bath gas.<sup>23</sup> Assuming values of  $\beta \sim 0.15$ , the lifetimes of the  $\text{CH}_2\text{CHCN}$  complexes in this study are between  $3 \mu\text{s}$  and  $15 \mu\text{s}$ .

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 mimicked 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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Table 1. Evaluation of rate coefficients in the  $\text{CH}_2\text{CHCN}^+/\text{CH}_2\text{CHCN}$  and the  $\text{CH}_2\text{CHCNH}^+/\text{CH}_2\text{CHCN}$  reactions based on the model represented in reactions (3) through (6) (with the assumption that the branching ratio for association in the  $\text{CH}_2\text{CHCN}^+/\text{CH}_2\text{CHCN}$  system is 260%).

Rate Coefficient	Units	$\text{CH}_2\text{CHCN}^+/\text{CH}_2\text{CHCN}$	$\text{CH}_2\text{CHCNH}^+/\text{CH}_2\text{CHCN}$
$k_f$	$\text{cm}^3 \text{ s}^{-1}$	$3.6 \times 10^9$	$3.6 \times 10^{-9}$
$k_{-1}/\beta$	$\text{s}^{-1}$	187,600	$1.695 \times 10^6$
$k_{-2}/\beta$	$\text{s}^{-1}$	406,100	0
$\beta \cdot \tau$	$\mu\text{s}$	1.68	0.59
$k_3$ (M= He)	$\text{cm}^6 \text{ s}^{-1}$	$1.95 \times 10^{-25}$	$8.1 \times 10^{-25}$ (M= He)

Table 2 A comparison of the reactions of  $\text{CH}_2\text{CHCN}^+$  and  $\text{CH}_2\text{CHCNH}^+$  with  $\text{CH}_2\text{CHCN}$  using ICR and SIFT techniques.

Reactant Ion	ICR			SIFT		
	Branching Ratio	Products	$k_{\text{ICR}}$ ( $10^{-9} \text{ cm}^3 \text{ S}^{-1}$ )	Branching Ratio	Products	$k_{\text{SIFT}}^a$ ( $10^{-9} \text{ cm}^3 \text{ S}^{-1}$ )
$\text{CH}_2\text{CHCN}^+$	1.0	$\text{CH}_2\text{CHCNH}^+ + \text{C}_3\text{H}_2\text{N}$	2.5 <sup>b</sup>	0.25	$\text{CH}_2\text{CHCNH}^+ + \text{C}_3\text{H}_2\text{N}$	2.8
				0.75		
$\text{CH}_2\text{CHCNH}^+$	1.0	$(\text{CH}_2\text{CHCN})_2\text{H}^+$	0.092 <sup>c</sup>	1.0	$(\text{CH}_2\text{CHCN})_2\text{H}^+$	1.8

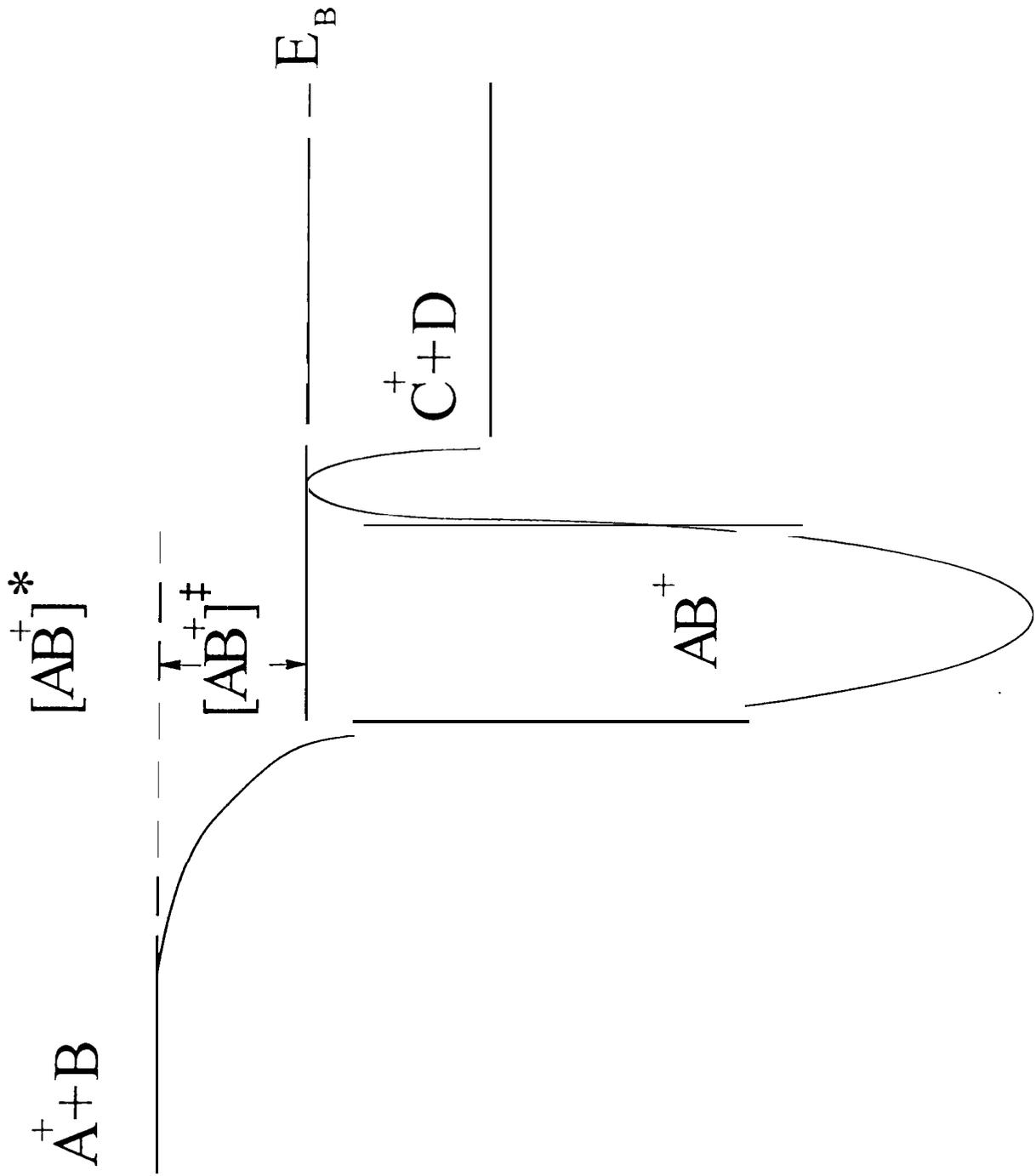
<sup>a</sup> Flow tube pressure = 0.30 Torr of helium.

<sup>b</sup> At a pressure of  $\text{CH}_2\text{CHCN}$  of less than  $3 \times 10^{-4}$  Torr.

<sup>c</sup> At a pressure of  $\text{CH}_2\text{CHCN}$  of  $3.0 \times 10^{-4}$  Torr. The rate coefficient is pressure dependent,  $k_3 = 1.2 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = \text{CH}_2\text{CHCN}$ ).

## Figure Captions

- Figure 1. A schematic diagram of the potential energy surface along the reaction coordinate for the  $A^+ + B$  reaction relative to  $(AB^+)$  having zero energy.
- Figure 2. The fit of the model expressed in equations (12) and (13) to the ICR and SIFT data for the  $CH_2CHCN^+/CH_2CHCN$  system is shown. The ICR data is represented by circles and the *SIFT* data by squares. The effective bimolecular reaction rate coefficient is plotted against  $\text{Log}(P_{CH_2CHCN})$  (solid line) or  $\text{Log}P_{He}$  (dashed line). The production of bimolecular products via equation (12) (ICR and SIFT experimental, solid symbols) and the onset of association via equation (13) (SIFT experiment, open symbols) are shown by separate curves.
- Figure 3. The variation in the apparent bimolecular rate coefficient for the  $CH_2CHCNH^+/CH_2CHCN$  system shown as a function of  $\text{Log } P$  for the two bath gases  $M = CH_2CHCN$  (solid curve) and  $M = He$  (dashed curve) from the model represented in equation (13). The ICR state is represented by circles, the SIFT data by a square.



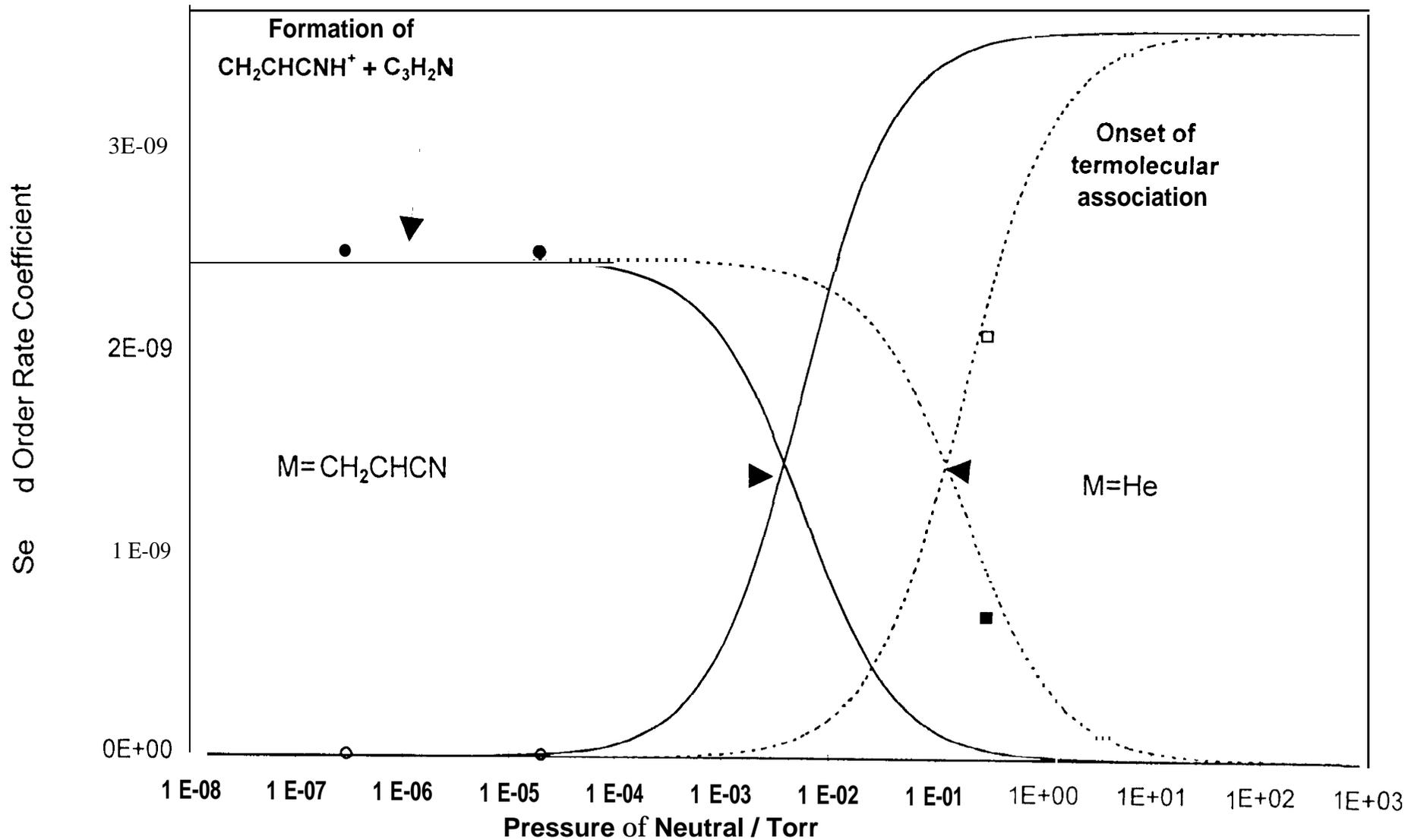


Fig 2

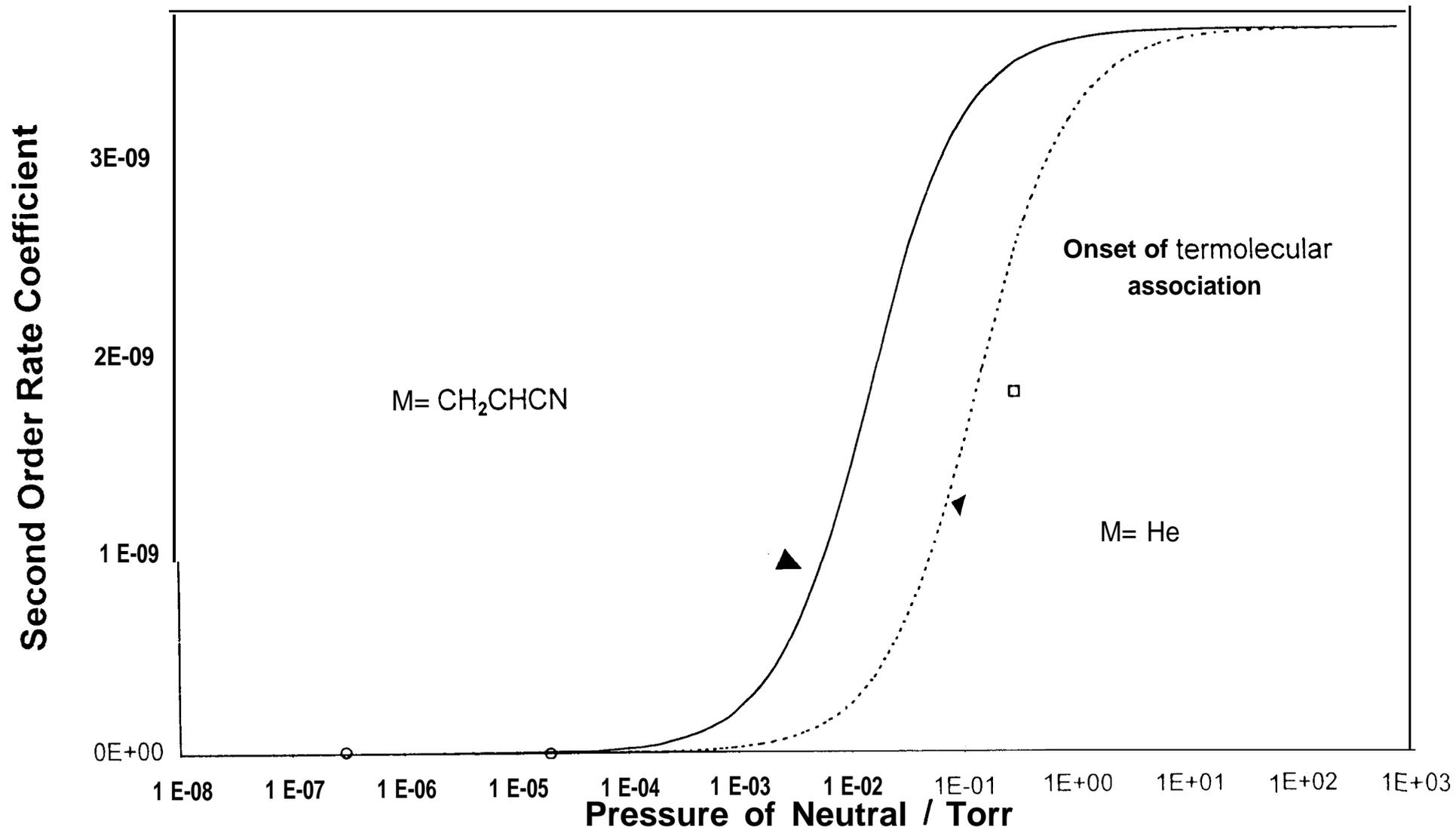


Fig 3