International Journal of Mass Spectrometry and Ion Physics, 36 (1980) 259—270
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

STUDIES OF REACTIONS INVOLVING $C_2H_x^+$ IONS WITH HCN USING A MODIFIED SELECTED ION FLOW TUBE

G.I. MACKAY, G.D. VLACHOS, D.K. BOHME and H.I. SCHIFF

Department of Chemistry and Centre for Research in Experimental Space Science, York University, 4700 Keele Street, Downsview, Ontario M3J 1P3 (Canada)

(Received 8 April 1980)

ABSTRACT

A modified version of the selected ion flow tube is described. Its application to the study of the reactions of $C_2H_x^+$ ions with HCN eliminates the complications encountered with attempts to study some of these reactions with the flowing afterglow technique.

Proton transfer is the only process observed for reactions of $C_2H_3^+$ and $C_2H_5^+$ and is the dominant channel for the $C_2H_7^+$ reaction. C_2^+ reacts exclusively by condensation while C_2H^+ reacts, with nearly equal probability, by proton and hydrogen atom transfer. The second-order reactions of all the ions, with the exception of $C_2H_2^+$, occur with probabilities greater than 65% of their theoretical values.

Three-body association is the dominant channel for the $C_2H_2^+$ reaction, with proton transfer and condensation occurring at less than 1% of the theoretical collision rate.

Clustering is the only reaction observed for $C_2H_4^+$, but, in this case, it is the only known exothermic channel.

INTRODUCTION

A potent method for studying ion—molecule reactions at thermal energies is the flowing afterglow (FA) technique. It was pioneered at the NOAA laboratories in Boulder [1] and has been used here to test reaction rate theories and to obtain thermodynamic data for neutral and ionic species [2].

In some cases, however, complications are encountered which seriously limit the application of the method. These complications arise mainly from the manner in which the ion under study is produced. This introduces ions other than the reactant ion and neutral species other than the reactant neutral species into the reaction volume. The presence of these other species can lead to erroneous rate data if they react to reform the reactant ion in the flow tube. They can also obfuscate the product branching ratio of the reaction under study by reacting with one another or with the neutral reactant to form the same product ions.

An interesting example is provided by the reaction of $C_2H_2^+$ with HCN, a reaction of considerable importance in models of interstellar clouds [3,4]. The overall rate constant for the reaction obtained by the FA technique [5] differs by an order of magnitude from that obtained by ion-cyclotron

0020-7381/80/0000—0000/$02.25

resonance [6]. Moreover, the two techniques give very different branching ratios for the products of this reaction. These discrepancies suggested that some of the complications inherent in the FA method were encountered with this reaction.

Virtually all these difficulties can be circumvented by use of the selected ion flow tube (SIFT) first developed by Adams and Smith [7]. The present paper describes a modified version of this technique and its application to clarifying the reaction of $C_2H_2^+$ with HCN, as well as the reactions of other $C_2H_x^+$ ions with the same neutral molecule, some of which are also of astrophysical interest [3,4].

EXPERIMENTAL

The distinctive feature of the SIFT technique is an ion source capable of delivering to the reaction volume a single ionic species along with only insignificant amounts of neutral species. In the present version this is accomplished with an apparatus shown schematically in Fig. 1. The apparatus has four regions, each operating at a different pressure. Ions are produced in a small reaction flow tube and the desired ions are selected in the second region by a quadrupole mass filter. The selected ion beam is then injected into a conventional reaction flow tube from which reactant and product ions are continuously sampled into the analysis region.

The source region is enclosed by an aluminium tube 25 cm long with an internal diameter of 4.2 cm. Carrier gas (He or H_2) is added at one end of the tube and neutral gas(es) through one or both inlets located 10 and 18 cm from the exit orifice. The thoriated iridium filament of the ion gun can be biased up to —250 V relative to a surrounding grid envelope held at the wall potential; this filament assembly can be moved axially along the entire length of the tube. Thus a neutral gas can be added either upstream or downstream of the filament: alternatively one neutral gas can be added upstream and another downstream. This arrangement, essentially a miniature

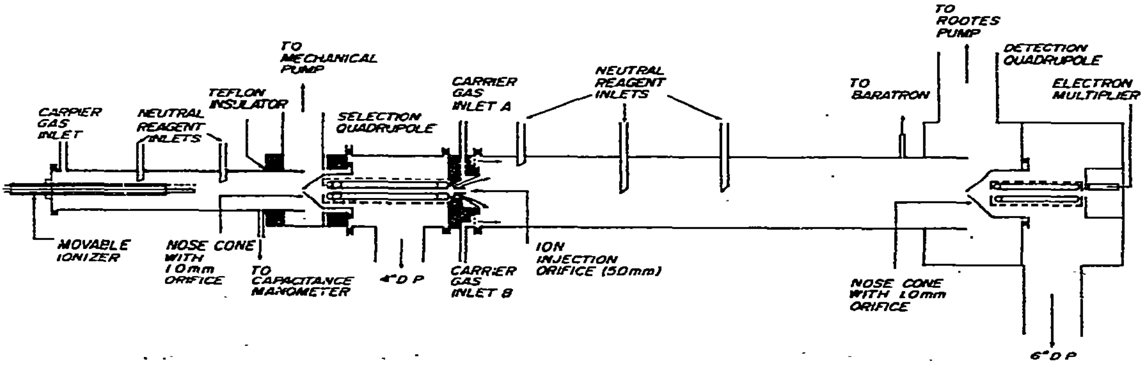

Fig. 1. A schematic diagram of the selected ion flow tube (SIFT) apparatus.

FA system, provides great versatility in manipulating the ion chemistry from which a desired ion can be formed.

The total pressure within this source region is maintained in the range 0.2—0.6 torr by a rotary pump. The residence time of an ion in this region is ca. 25 ms, corresponding to ca. 10^5 collisions, which is ample for thermalization. Ions are extracted by pressure gradient into the selection region through a hole, 1 mm in diameter, in a 0.127-mm thick Mo plate. The nose cone holding this plate can be biased electrically to increase the extraction efficiency. The pressure in the selection region is maintained at less than 10^{-4} torr by a 4-in. diffusion pump. Ions are selected with a quadrupole mass filter equipped with Brubaker pre and post filters [8].

The mass-selected ion beam enters the reaction volume through a 5.0-mm orifice in the center of a stainless-steel cone. The ion beam is made to flow against a pressure gradient by the pumping action of a Venturi gas aspirator, shown in detail in Fig. 2. The aspirator gas (normally He) flows through an annular ring surrounding the orifice, with a 2.5×10^{-2}-mm gap, and also serves as the carrier gas in the reaction volume. A flow of 50—300 STD cm^3 s^{-1} through the aspirator jet produces a pressure in the range 0.1—0.5 torr in the reaction volume and a decrease in pressure of more than an order of magnitude in the ion-selection region, even in the absence of the diffusion pump.

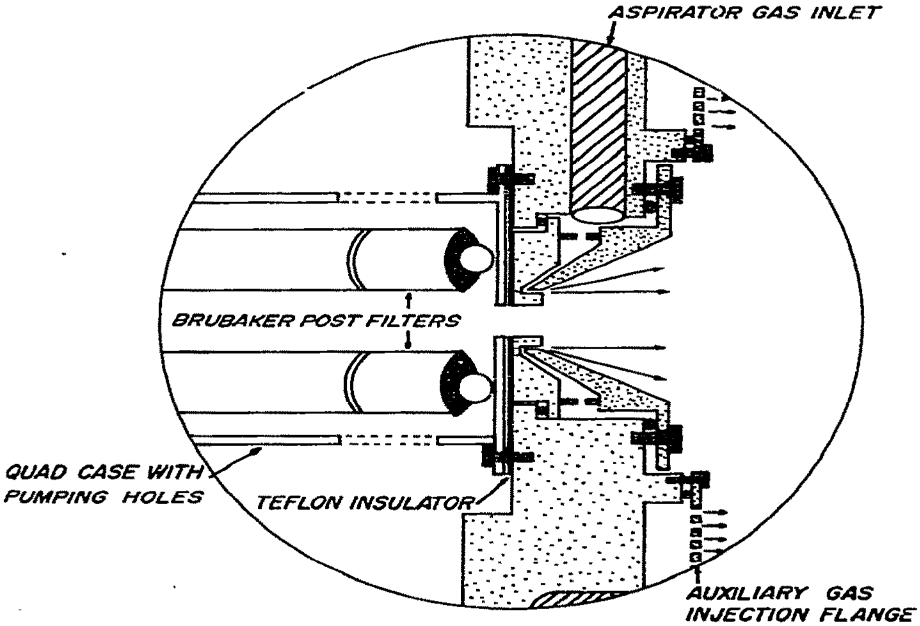

Fig. 2. An expanded schematic diagram of the ion injection aspirator. The arrows indicate the direction of gas flow.

The reaction and analytical regions are similar to those described previously for the conventional flowing afterglow technique. The reaction volume is contained in a stainless-steel tube of length 85 cm and internal diameter 8.9 cm. A small central portion of the gas flow is continuously sampled through a 1-mm hole and analyzed by a quadrupole mass spectrometer.

The reaction volume is held at ground potential and is isolated electrically from the source and the quadrupole axis potential of the ion-selection region which can be biased from +150 to —150 V to assist in ion extraction. In practice, biases less than 30 V are used to minimize break-up of ions in the injection orifice.

The kinetic analysis assumes that laminar flow conditions are established in the reaction region. To test this assumption the well-established reaction of H_3^+ with CO was studied as a function of He flow rate through the aspirator jet. The open circles of Fig. 3 show that the calculated rate constant remained invariant only up to a reaction volume pressure of 0.35 torr. Presumably, turbulent flow develops at higher He flow rates through the aspirator jet. To extend the range, additional He is introduced through a series of 100 holes, each 1 mm in diameter, which are uniformly distributed over the plate containing the aspirator jet and the inlet cone (Fig. 2). The open squares in Fig. 3 represent rate constants obtained under these conditions. The average value of $(1.98 \pm 0.40) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} is in excellent agreement with the value of $(2.0 \pm 0.4) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} obtained from FA measurements [9]. This indicates that laminar flow can indeed be

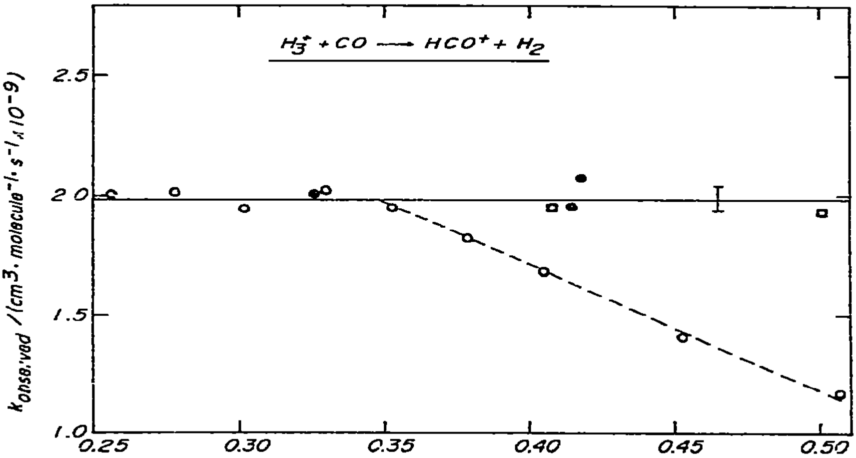

Fig. 3. The variation in the measured rate constant for the reaction $H_3^+ + CO \rightarrow HCO^+ + H_2$ as a function of pressure in the reaction region of the SIFT apparatus. (○) Total gas through aspirator; (□) 0.3 torr through aspirator, remainder through auxiliary gas inlet flange; (●) flowing afterglow results.

extended by this expedient. The agreement also confirms the validity of the data analysis, which was similar to that used for the FA method [10]. Such confirmation was necessary since ambipolar diffusion is not the primary diffusion-loss process when the apparatus is operated in the SIFT mode. Additional studies made with the well-established reactions of H_3^+ with H_2O and of H_2O^+ with H_2 also resulted in rate constants which agreed, within experimental error, with those reported in the literature and those obtained when the present apparatus was operated in the FA mode.

The apparatus can also be operated in the conventional FA mode by using an alternative ionizer located in the reaction volume 10 cm downstream of the ion-selection region. The grid of this ionizer also serves to measure the ion current entering the reaction tube when the apparatus is operating in the SIFT mode. Typical ion count rates in the SIFT mode are 5×10^3 s^{-1} and in the FA mode 500×10^3 s^{-1}. The suprisingly high ion currents obtainable under SIFT conditions may be due, in part, to the smaller loss of ions in the reaction volume owing to the absence of electrons.

RESULTS

Reaction of $C_2H_2^+$ with HCN

The reaction of $C_2H_2^+$ with HCN was studied with the apparatus operating both in the FA and in the SIFT mode. The $C_2H_2^+$ ions were formed in both cases by introduction of C_2H_2 into a weak helium plasma. Typical results obtained with the FA method are shown in Fig. 4. In addition to $C_2H_2^+$ the source also produces C_2H^+ and, as a result of secondary reactions, the ions $C_4H_2^+$ and $C_4H_3^+$. All these ions react with HCN. The product ion H_2CN^+ may be formed by reaction of HCN with one or more of the source ions. The product ions at masses 52 and 53 (not resolved in this experiment), shown below to be $H_2C_3N^+$ and $C_2H_2^+ \cdot HCN$, may also be formed by reactions of HCN with $C_4H_2^+$ and $C_4H_3^+$ as well as with $C_2H_2^+$. The product at mass 27 could be either $C_2H_3^+$ or HCN^+; however, no exothermic channels exist for the production of either of these ions by reaction of any of the source ions with HCN. The most likely explanation is Penning ionization of HCN to HCN^+ by metastable He^* atoms. Sufficient C_2H_2 was added to the helium plasma to remove all the He^+ ions in the source region, but not enough to remove all the He^* metastable species. Increasing the flow of C_2H_2 to the source region to reduce He^* did decrease the ion current at mass 27 but unfortunately also decreased the reactant $C_2H_2^+$ concentration below desirable levels (and increased $C_4H_2^+$ and $C_4H_3^+$).

The presence of HCN^+ further complicates the interpretation of product ratios since this ion also produces H_2CN^+ by the rapid reaction:

$$HCN^+ + HCN \rightarrow H_2CN^+ + CN \qquad (1)$$

Figure 4 shows that the $C_2H_2^+$ signal appears to decrease exponentially with

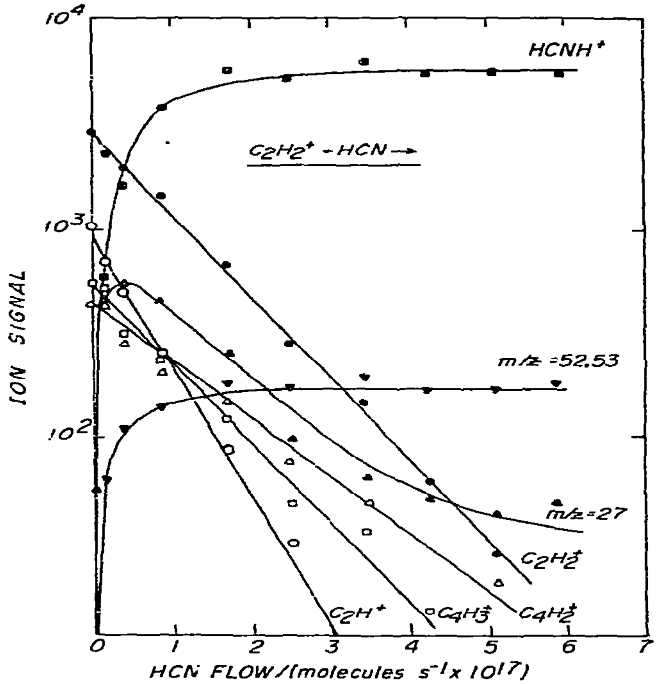

Fig. 4. The observed variation in the ion signals detected on addition of HCN into an He—C_2H_2 plasma with the apparatus in the flowing afterglow mode. $P = 0.451$ torr, $\bar{v} = 7.8 \times 10^3$ cm s^{-1}, $L = 85$ cm, and $T = 298$ K.

HCN flow. From the slope of this curve a value of $k = 5.9 \times 10^{-10}$ cm^3 s^{-1} can be calculated. There are, however, a number of reasons why this slope could yield an incorrect value for the rate constant of the reaction of $C_2H_2^+$ with HCN. C_2H^+ reacts with HCN and HCN^+ reacts with the C_2H_2 present in this system to generate $C_2H_2^+$. These extended sources have the effect of giving an erroneously low rate constant. On the other hand the He^* metastable atoms and C_2H^+ which also serve as extended sources of $C_2H_2^+$ in the absence of HCN are progressively removed as the HCN flow is increased, having the effect of increasing the perceived rate constant. These results can be compared with those shown in Fig. 5 obtained using the SIFT method. Under SIFT conditions $C_2H_2^+$ is the only ionic species present in the reaction volume in the absence of the added HCN neutral. The absence of an ion at mass 27 when HCN is added indicates that He metastable species are not transmitted from the source region to the reaction volume.

The product ions can thus be unequivocally attributed to the primary reaction of $C_2H_2^+$ with HCN, viz.

$$C_2H_2^+ + HCN \xrightarrow{He} C_2H_2^+ \cdot HCN \qquad (2a)$$

$$\rightarrow H_2C_3N^+ + H \qquad (2b)$$

$$\rightarrow HCNH^+ + C_2H \qquad (2c)$$

The major product under the operating conditions adopted is the cluster ion $C_2H_2^+ \cdot HCN$. The ratio of H_2CN^+ to the sum of $H_2C_3N^+$ and $C_2H_2^+ \cdot HCN$ (masses 52 and 53) is very different from the ratio obtained with the FA (Fig. 4) which shows clearly that, under FA conditions, these product ions were also formed from reactions involving more than one of the primary ions present initially.

The rate constant for the reaction of $C_2H_2^+$ with HCN obtained from five experiments with the SIFT apparatus is $(3.9 \pm 0.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} compared with the value of $(6.2 \pm 1.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} obtained from four experiments performed with the apparatus operated in the FA mode. This difference clearly indicates the occurrence of secondary processes reforming $C_2H_2^+$ in the FA experiments.

The cluster ion formation accounts for 90% of the products, a fraction which does not change with pressure over the limited range, 0.3—0.5 torr,

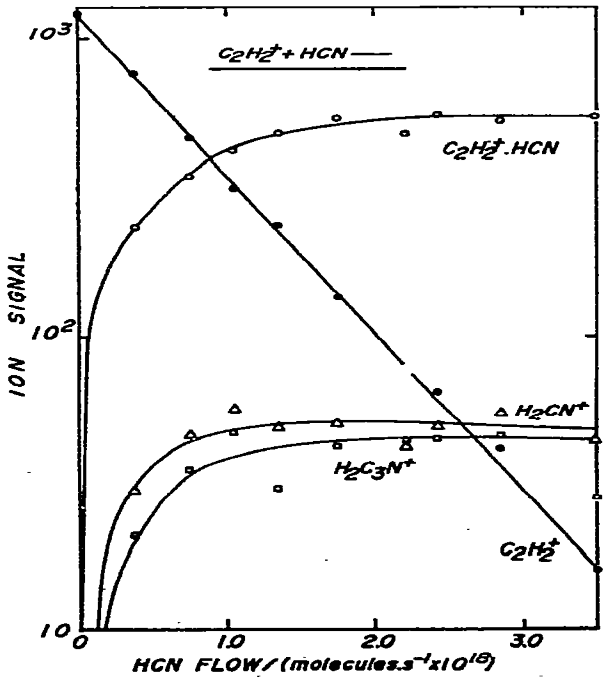

Fig. 5. The observed variation in the ion signals detected on addition of HCN into the reaction region of the SIFT apparatus in which $C_2H_2^+$ is initially the only positive ion present in the He buffer gas in measurable concentration. $P = 0.677$ torr, $\bar{v} = 8.2 \times 10^3$ cm^{-1}, $L = 48$ cm, and $T = 298$ K.

available in these experiments. The third-order reaction appears to be saturated above 0.3 torr, and its rate constant is therefore greater than 4 × 10^{-26} cm^6 $molecule^{-2}$ s^{-1}.

The SIFT apparatus was also used to study the reactions of other $C_2H_x^+$ ions with HCN.

Reactions of C_2H^+ and C_2^+

These ions were generated in the same manner as described above for $C_2H_2^+$.

Two product ions were found in the reaction with C_2H^+, one at mass 28 and the other at mass 26. The ion at mass 26 must be $C_2H_2^+$ since there are no exothermic reactions capable of producing CN^+. This observation confirms the presence of a secondary source of $C_2H_2^+$ in the FA experiments just described. The product at mass 28 can be unequivocally identified as H_2CN^+ since it is the only ion of this mass which can be formed by a primary process from the reactants. Therefore, the primary reactions appear to be hydrogen atom transfer and proton transfer:

$$C_2H^+ + HCN \rightarrow C_2H_2^+ + CN \quad (3a)$$

$$\rightarrow H_2CN^+ + C_2 \quad (3b)$$

with close to equal probability.

No product at mass 50 was observed, indicating that the rearrangement reaction

$$C_2H^+ + HCN \rightarrow C_3N^+ + H_2 \quad (4)$$

does not occur. At higher HCN flows the secondary reactions of $C_2H_2^+$ to form $H_2C_3N^+$ and $C_2H_2^+ \cdot HCN$ are observed.

A single product at mass 50 was observed when C_2^+ was reacted with HCN. This is due to the hydrogen atom elimination process

$$C_2^+ + HCN \rightarrow C_3N^+ + H \quad (5)$$

Reactions of $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$ and $C_2H_7^+$

The $C_2H_3^+$, $C_2H_4^+$ and $C_2H_5^+$ ions were produced by introduction of C_2H_6 into a weak helium plasma and selected for individual study by the SIFT apparatus. The $C_2H_7^+$ ions were produced by proton transfer from HCO^+ to C_2H_6. Dissociative proton transfer from HCO^+ and H_3^+ was also used as an alternative source for $C_2H_5^+$.

Proton transfer was the only channel observed in the reactions of $C_2H_3^+$ and $C_2H_5^+$ with HCN. A result for the latter reaction is shown in Fig. 6. Although proton transfer was the major channel in the reaction of $C_2H_7^+$ with HCN, an additional product at mass 42 was also observed in amounts corre-

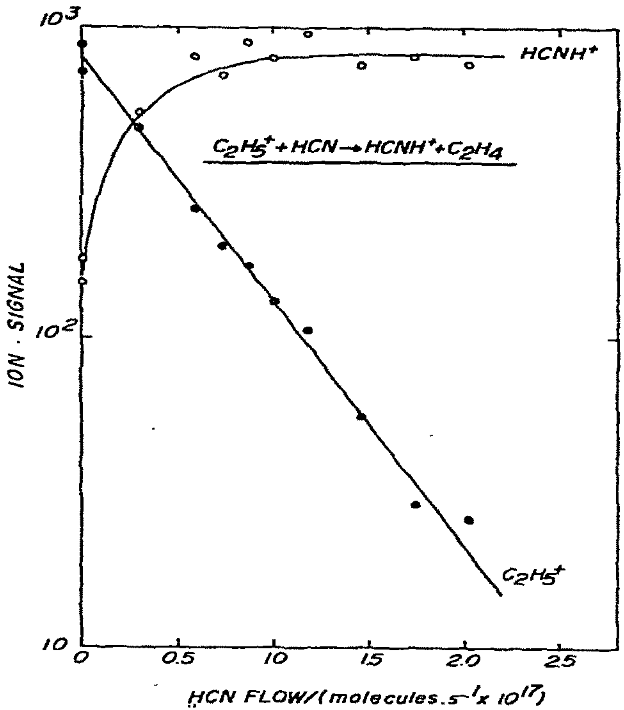

Fig. 6. The observed variation in the $C_2H_5^+$ signal on addition of HCN into the reaction region of the SIFT apparatus. The initial signal at $m/z = 28$ is thought to arise from the collisional break-up of $C_2H_5^+$ into $C_2H_4^+$. $P = 0.378$ torr, $\bar{v} = 8.2 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 298$ K.

sponding to about 10% of the total reaction. CH_3CNH^+ appears to be the only ion of this mass which would be a reasonable product of the reaction.

Rate constants

The rate constants obtained using the SIFT apparatus are given in Table 1 along with the theoretical values calculated from the modified AADO theory [11]. The precision of the measurements is better than 10% and the accuracy of the rate constant is believed to be ±25%.

The reaction of C_2^+ with HCN proceeds exclusively by condensation with H atom elimination to form C_3N^+ with a rate constant close to the theoretical limit. The occurrence of this reaction together with available heats of formation [15] indicate the heat of formation of C_3N^+ to be less than 455 kcal mol^{-1} at 298 K. In contrast, the reaction of C_2H^+ with HCN shows no evidence for condensation to form C_3N^+ or C_3NH^+. Instead it proceeds, with nearly equal probabilities, by proton transfer and by hydrogen atom transfer. The overall rate constant is also close to the theoretical value.

TABLE 1

Rate constants and product distributions at 299 ± 1 K for reactions of $C_2H_x^+$ ions with HCN

Reaction	Product distribution	k_{exp} [a]	k_{AADO} [b]	k_{exp}/k_{AADO}
$C_2^+ + HCN \rightarrow C_3N^+ + H$	1.0	2.8 ± 0.6	3.64	0.77
$C_2H^+ + HCN \rightarrow C_2H_2^+ + CN$	0.5	2.8 ± 0.6	3.60	0.77
$\rightarrow HCNH^+ + C_2$	0.5			
$C_2H_2^+ + HCN \xrightarrow{He} C_2H_2^+ \cdot HCN$	0.87	0.39 ± 0.08 [c]	3.56	0.11
$\rightarrow H_2C_3N^+ + H$	0.08			
$\rightarrow HCNH^+ + C_2H$	0.05			
$C_2H_3^+ + HCN \rightarrow HCNH^+ + C_2H_2$	1.0	2.9 ± 0.6	3.53	0.82
$C_2H_4^+ + HCN \rightarrow C_2H_4^+ \cdot HCN$	1.0	0.087 ± 0.017	3.50	0.025
$C_2H_5^+ + HCN \rightarrow HCNH^+ + C_2H_4$	1.0	2.7 ± 0.5	3.47	0.78
$C_2H_7^+ + HCN \rightarrow HCNH^+ + C_2H_6$	0.9	2.2 ± 0.4	3.41	0.65
$\rightarrow CH_3CNH^+ + CH_4$	0.1			

[a] The measured rate constants in units of 10^{-9} cm^3 molecule^{-1} s^{-1} together with their estimated uncertainties.

[b] Rate constants in units of 10^{-9} cm^3 molecule^{-1} s^{-1} derived using the angular-momentum-conserved average dipole orientation theory $\overline{\cos\theta}$ model [11]: $\alpha = 2.59$ Å^3 [12], $\mu_D = 3.98$ D [13], $C = 0.264$ and $I = 18.83 \times 10^{-40}$ g cm^2 [14].

[c] The two-body rate constant was independent of pressure in the range P(He) = 0.395—0.521 torr.

Condensation and proton transfer are both slow channels in the reaction of $C_2H_2^+$ with HCN. In the presence of 0.3—0.5 torr of helium the dominant channel is three-body association which, in this pressure range, appears to be saturated. The combined effective rate constant is about 12% of the theoretical value.

The rate constants for the two second-order channels are similar to those reported by Huntress and Anicich [6] using the ICR method. These workers did not observe the association channel, which is understandable, since the ICR system operates at a total pressure of only about 10^{-5} torr. However, more recent work with the same apparatus [16] led to a higher overall rate constant of 2×10^{-10} cm^3 molecule^{-1} s^{-1} and a higher ratio of k_{2b}/k_{2c}, which they believe is due to the associative complex breaking into $H_2C_3N^+$ and H under their low-pressure conditions.

Freeman et al. [5], using the FA technique, obtained an overall rate constant of 7.1×10^{-10} cm^3 molecule^{-1} s^{-1} but did not give uncertainty estimates. This value agrees with the value of $(6.2 \pm 1.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} which we obtained using the FA method. Freeman et al. did not report the three-body channel (2a), perhaps because their resolution was insufficient to separate (2a) and (2b). However, the overall rate constant obtained by our SIFT technique is $(3.9 \pm 0.8) \times 10^{-10}$, appreciably lower than either of the FA values which we believe to be incorrect for the reasons given above. Moreover, the branching ratio of $k_{2b}/k_{2c} = 5.7$ reported by Freeman et al. is very different from the value close to unity which is found using the SIFT. This difference may be due not only to their inability to distinguish between reactions (2a) and (2b) but also to the complications arising from secondary reactions in the FA system.

Proton transfer is the only exothermic channel, to the best of our knowledge, for the reactions of $C_2H_3^+$ and $C_2H_5^+$ with HCN. There are three exothermic channels available for the reaction of $C_2H_7^+$. One, to yield $C_3H_5^+$ and NH_3, requires drastic rearrangement and is not observed. A second channel corresponds to CH_4 elimination but proton transfer dominates this channel by a factor of about 10. Rate constants for proton transfer for these three ions are close to theoretical.

There do not appear to be any exothermic reactive channels available for the reaction of $C_2H_4^+$ with HCN and clustering is the only process observed. The corresponding third-order rate constant is approximately 8×10^{-27} cm^6 molecule^{-2} s^{-1}.

SUMMARY

This study serves as a good example of the versatility and advantages of the SIFT technique for investigating complex ion—molecule reactions. It has permitted the use of the same weak plasma source to generate a number of $C_2H_x^+$ ions and to study the reaction of each of these ions separately. Had this separation not been possible, complications would have resulted from having all the ions, as well as helium metastable species and source gas neutral molecules, simultaneously present in the reaction region. We have exploited the advantages of the SIFT technique in unravelling other complex reactions of interest in interstellar ion chemistry which we will report shortly.

ACKNOWLEDGEMENT

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

REFERENCES

1 E.E. Ferguson, F.C. Fehsenfield and A.L. Schmeltekopf, Adv. At. Mol. Phys., 5 (1969) 1.
2 H.I. Schiff and D.K. Bohme, Int. J. Mass Spectrom. Ion Phys., 16 (1975) 167.
3 G.F. Mitchell, J.L. Ginsburg and P.J. Kuntz, Astrophys. J. Suppl., 38 (1978) 39.
4 H.I. Schiff and D.K. Bohme, Astrophys. J., 232 (1979) 740.
5 C.G. Freeman, P.W. Harland and M.J. McEwan, Astrophys. J. (Letters), 19 (1978) 133.
6 W.T. Huntress and V.G. Anicich, Astrophys. J., 208 (1976) 237.
7 N.G. Adams and D. Smith, Int. J. Mass Spectrom. Ion Phys., 21 (1976) 349.
8 W.M. Brubaker, Advances in Mass Spectrometry, Vol. 4, Elsevier, Amsterdam, 1968.

9 S.D. Tanner, G.I. Mackay, A.C. Hopkinson and D.K. Bohme, Int. J. Mass Spectrom. Ion Phys., 29 (1979) 153.
10 D.K. Bohme, R.S. Hemsworth, H.W. Rundle and H.I. Schiff, J. Chem. Phys., 58 (1973) 3504.
11 T. Su, E.C.F. Su and M.T. Bowers, J. Chem. Phys., 69 (1978) 2243.
12 J.O. Hirschfelder, C.F. Curtis and R.B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, 1967.
13 R.D. Nelson, D.R. Lide and R.A. Maryott, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 10, 1967.
14 G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 3, Van Nostrand—Reinhold, Toronto, 1966.
15 J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxl and F.H. Field, Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, NSRDS-NBS 26, U.S. Government Printing Office, Washington, DC, 1969.
16 M.J. McEwan and W.T. Huntress, reported at the I.A.U. Symposium No. 87 on Interstellar Molecules, Mont Tremblant, 1979.