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A SELECTED ION FLOW TUBE STUDY OF THE KINETICS OF CN^+ REACTIONS AT 296 ± 2 K

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ABSTRACT

Rate constants and product distributions have been determined for ion/molecule reactions between CN^+ and N_2, D_2, H_2, CO, CO_2, HCN, C_2N_2, N_2O, CD_4, CH_4, D_2O, CD_3CN, Xe, O_2, C_2D_2, OCS, CH_3OH, C_2H_4, H_2S, ND_3 and NO. The measurements were performed with the selected-ion flow tube (SIFT) technique at 296 ± 2 K. Comparisons are made with recent ICR measurements. The observed reactions exhibit a wide variety of pathways including charge transfer, hydrogen atom and hydride transfer, oxygen atom transfer, nitride transfer, H_2 transfer and elimination, and adduct formation. Observations of oxygen atom transfer provide a heat of formation for NCO^+ of 1400 ± 20 kJ mol^{-1} at 298 K and $IP(NCO) = 12.9 \pm 0.5$ eV. Several of the reactions observed are of relevance to molecular synthesis by natural ion chemistry as, for example, in the atmosphere of Titan and in dense interstellar clouds.

INTRODUCTION

The gas-phase kinetics of ion/molecule reactions of CN^+ have received serious attention only recently by McEwan et al. in a systematic laboratory study using ICR techniques [1]. These authors expressed the need and provided fundamental data for the kinetics of such reactions believed to be of importance in chemical models for interstellar clouds [2,3], comets [4] and the atmosphere of Titan [5]. At the near-thermal energies and low pressures of their experiments, McEwan et al. found CN^+ ions to be highly reactive with most of the molecules they investigated. Charge transfer was reported to be a dominant product channel in many cases and multiple product channels were often observed as one might expect from the high recombination energy (14.5 eV) and high heat of formation (1803 kJ mol^{-1}) of CN^+.

In the study reported here, the selected-ion flow tube (SIFT) technique [6] has been used for similar measurements with a more extensive set of molecules at quite different operating conditions. The CN^+ ions were

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extracted from an electron ionization source operating at low pressure and allowed to thermalize by collision with helium buffer gas in a flow tube before entering a reaction region at total pressures of ca. 0.35 Torr. The total pressure in the reaction region far exceeds the ambient pressure under ICR conditions. Also, by design, the SIFT apparatus avoids complications due to the presence of other ions produced by electron ionization of the source gas which were overcome in several cases in the ICR study with a tandem ICR system [1]. The differences in operating conditions are reflected in several cases in the observed chemistry. Also, the broader scope of the present study provides further insight into CN^+ reactions and some interesting reactions of secondary product ions.

EXPERIMENTAL

The measurements were performed with the selected-ion flow tube/flowing afterglow apparatus at York University [7]. The apparatus has been modified recently with the incorporation of an axial electron ionizer and channeltron multiplier [8]. Reactant CN^+ ions were generated from cyano-

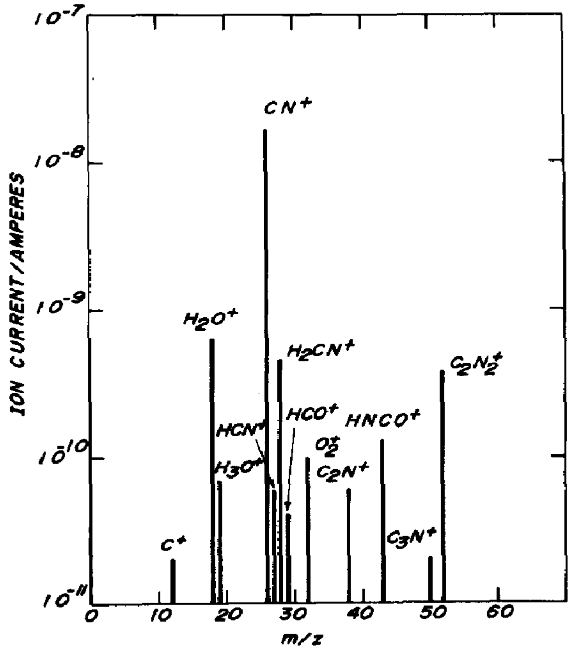


Fig. 1. SIFT spectrum for CN^+ derived from cyanogen by electron ionization at 55 eV. Ion injection energy = 12 V; buffer gas is helium at 0.32 Torr. The background spectrum arises primarily from reactions with impurities in the buffer gas and cyanogen leaking through the selection quadrupole.

gen by interaction with electrons at 45–55 eV. After selection with a quadrupole mass filter, the CN^+ ions were injected at ca. 12 V into a flowing helium gas at a total pressure of ca. 0.35 Torr. A typical SIFT spectrum for CN^+ produced and selected in this fashion and monitored by the downstream quadrupole mass spectrometer is shown in Fig. 1. The background ions at m/z 18 (H_2O^+), 27 (HCN^+), 28 (H_2CN^+), 29 (HCO^+) and 43 ($HNCO^+$) are believed to arise from the reaction of CN^+ with water impurities in the buffer gas, m/z 32 (O_2^+) from oxygen impurities and m/z 38 (C_2N^+), 50 (C_3N^+) and 52 ($C_2N_2^+$) from cyanogen which leaks from the source through the selection quadrupole. In practice, the ratio of the CN^+ signal to the signal of the major ion in the "chemical noise" was at least 30 : 1.

As has been the case in our previous studies, the reagent gases and vapours as well as the helium buffer gas were generally of high purity with a minimum purity of 99.5 mole %. Of somewhat lower purity were the gases C_2N_2 (98.5% by volume), N_2O (98.0%), OCS (97.5 mole %) and NO (99.0%). HCN was prepared according to the procedure described by Glemser [9]. All measurements were performed at an ambient temperature of 296 ± 2 K.

RESULTS AND DISCUSSION

Table 1 summarizes the rate constants and product distributions obtained in this study. Rate constants were determined as before [7] and product distributions were derived using the method described by Adams and Smith [10]. Table 1 includes all the primary product ions observed with contributions of more than 5% to the total. The branching ratios have been rounded off to the nearest 5%. The reactions are listed in Table 1 in order of decreasing ionization energy. The ensuing discussion follows a similar order, but several molecules are grouped to collect common features in their chemistry or to contrast differences. Also, comparisons are made throughout with the results of the ICR study for those molecules in common with the present study.

Reactions with N_2 and CO

A very slow reaction was observed with nitrogen to produce exclusively the adduct $CN^+ \cdot N_2$. The effective two-body rate constant at 0.34 Torr was measured to be 4.3×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and corresponds to a three-body rate constant of 3.9×10^{-28} cm^6 $molecule^{-2}$ s^{-1}. No reaction was observed between CN^+ and N_2 under the ICR conditions of McEwan et al. [1]. The bonding in the observed $CN^+ \cdot N_2$ adduct is likely to be purely electrostatic and result from ion-induced dipole interaction, but the species is

TABLE 1

Summary of rate constants (in units of 10^{-9} cm^3 molecule^{-1} s^{-1}) and product distributions measured for reactions of CN^+ with the SIFT technique at 298 ± 2 K (this work) and with the ICR technique at near-thermal energies [1]

Neutral reactant [a]	Products	Branching ratios		k_{obs}	
		This work	Previous work	This work [b]	Previous work
N_2	$CN^+ \cdot N_2$	1.0		0.0043 (He) [c]	< 0.01
[15.6]					
D_2	$DCN^+ + D$	1.0	1.0	0.81	1.10 ± 0.2
[15.5]					
H_2	$HCN^+ + H$	1.0	1.0	1.0	1.24
[15.4]					
CO	$CO^+ + CN$	0.95	1.0	0.25 (He) [c]	0.63 ± 0.1
[14.0]	$CN^+ \cdot CO$	0.05			
CO_2	$CO_2^+ + CN$	0.4	≤ 0.3	0.75	1.5 ± 0.3
[13.8]	$NCO^+ + CO$	0.3	≥ 0.7		
	$C_2O^+ + NO$	0.3			
HCN	$HCN^+ + CN$	0.85	0.80	2.1	3.1 ± 0.6,
[13.6]	$C_2N_2^+ + H$	0.15	0.20		2.8 [d]
C_2N_2	$C_2N_2^+ + CN$	0.85	1.0	1.4	2.1 ± 0.4
[13.4]	$C_3N^+ + N_2$	0.10			
	$C_2N^+ + CN_2$	0.05			
N_2O	$N_2O^+ + CN$	0.6		0.76	
[12.9]	$NCO^+ + N_2$	0.2			
	$NO^+ + CN_2$	0.2			
CD_4	$CD_3^+ + DCN$	0.45		0.58	1.1 [e]
[12.9]	$CD_4^+ + CN$	0.20			
	$DCN^+ + CD_3$	0.20			
	$D_2CN^+ + CD_2$	0.10			
	$CD_2CN^+ + D_2$	0.05			
CH_4	$CH_3^+ + HCN$	0.50	0.05	0.90	1.2 ± 0.2
[12.7]	$CH_4^+ + CN$	0.15			0.97 [e]
	$HCN^+ + CH_3$	0.15	0.35		
	$H_2CN^+ + CH_2$	0.10	0.60		
	$CH_2CN^+ + H_2$	0.10			
D_2O	$D_2O^+ + CN$	0.4	0.10	2.1	3.2 ± 0.6 [f]
[12.6]	$DCN^+ + OD$	0.4	0.50		
	$DNCO^+ + D$	0.1	0.20		
	$D_2CN^+ + O$	0.1	0.15		
	$DCO^+ + ND$		0.05		
CD_3CN	$CD_3CN^+ + CN$	0.5		3.4	
[12.2]	$CD_2CN^+ + DCN$	0.2			
	$CD_3^+ + C_2N_2$	0.2			
	$C_2D_3^+ + CN_2$	0.1			
Xe	$Xe^+ + CN$	1.0		0.16	

TABLE 1 (continued)

Neutral reactant [a]	Products	Branching ratios		k_{obs}	
		This work	Previous work	This work [b]	Previous work
[12.1]					
O_2	$O_2^+ + CN$	0.6		0.43	
[12.1]	$NCO^+ + O$	0.2			
	$NO^+ + CO$	0.2			
C_2D_2	$C_2D_2^+ + CN$	0.7	0.90	0.54	1.5
[11.4]	$DC_3N^+ + D$	0.3	0.10		
OCS	$OCS^+ + CN$	0.80		1.5	
[11.2]	$NCS^+ + CO$	0.15			
	$NC_2S^+ + O$	0.05			
CH_3OH	$CH_3O^+ + HCN$	0.6		2.6	
[10.8]	$CH_3OH^+ + CN$	0.3			
	$H_2CN^+ + CH_2O$	0.1			
C_2H_4	$C_2H_4^+ + CN$	0.7	0.55	1.0	1.6 ±0.3
[10.5]	$H_2CN^+ + C_2H_2$		0.10		
	$HCN^+ + C_2H_3$	0.25	0.25		
	$C_2H_3^+ + (HCN)$		0.10		
	$H_2C_3N^+ + H_2$	0.05			
H_2S	$H_2S^+ + CN$	0.4		1.3	
[10.4]	$HS^+ + HCN$	0.3			
	$S^+ + (H_2 + CN)$	0.3			
ND_3	$ND_3^+ + CN$	≥ 0.8	0.60	1.3	2.0 ±0.4 [g]
[10.2]	$D_2CN^+ + ND$	0.1	0.15		
	$DCN^+ + ND_2$	0.1	0.20		
	$ND_2^+ + DCN$		0.05		
NO	$NO^+ + CN$	0.75		0.76	
[9.3]	$NCO^+ + N$	0.25			

[a] The ionization potential in eV is indicated for each reactant in square brackets. Values are taken from ref. 25.

[b] The accuracy of the rate constant is estimated to be better than ±30%.

[c] In helium buffer gas at a total pressure of 0.34 Torr and density of 1.1×10^{16} molecules cm^{-3}.

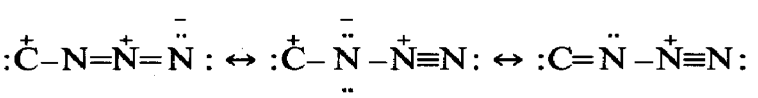
[d] From a flowing afterglow study by C.G. Freeman et al. [26].

[e] Ref. 3.

[f] Rate constant and branching ratios for the reaction with H_2O.

[g] Rate constant and branching ratios for the reaction with NH_3.

also isomeric with a covalent azide whose electronic structure may be represented by valence-bond theory as the hybrid



$$:\overset{+}{C}-N=\overset{+}{N}=\overset{\overset{-}{..}}{N}: \leftrightarrow :\overset{+}{C}-\underset{..}{\overset{\overset{-}{..}}{N}}-\overset{+}{N}\equiv N: \leftrightarrow :C=\overset{..}{N}-\overset{+}{N}\equiv N:$$

Charge transfer is endothermic with N_2 but not with CO and so, as expected, charge transfer was observed to be the major product channel with CO. A similar result was reported for the ICR measurements, however with a rate constant more than twice the value obtained in the present study. Also, at the higher total pressure of the SIFT experiments, we made the additional observation of some formation of the adduct $CN^+ \cdot CO$ for which the nature of the bonding is again uncertain.

Reactions with D_2 and H_2

Deuterium and hydrogen atom abstraction were the only primary reaction products observed with D_2 and H_2, respectively. Secondary D and H abstraction reactions established D_2CN^+ and H_2CN^+, respectively, as the ultimate product ion as is indicated in Fig. 2 for the deuterated system. Interestingly, hydride abstraction to form a proton and hydrogen cyanide as

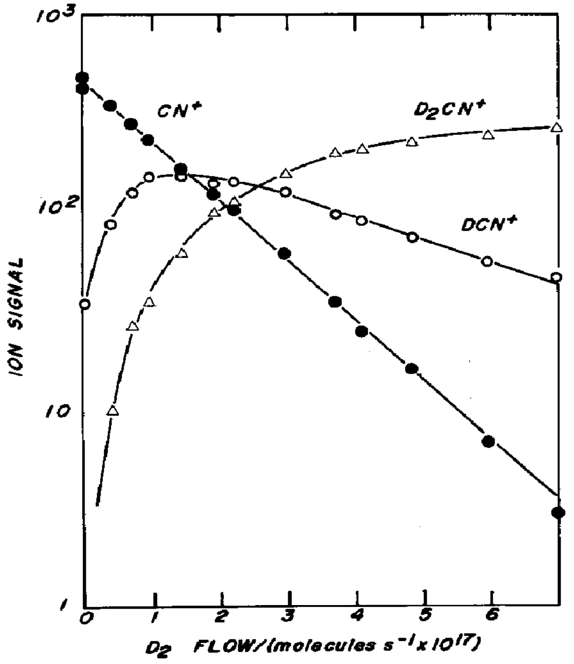


Fig. 2. The observed variation in ion signals for the addition of deuterium into the reaction region in which CN^+ has been established with the SIFT technique. $P = 0.342$ Torr, $\bar{v} = 7.3 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 296$ K. The carrier gas is helium.

primary products is slightly more exothermic than the H atom abstraction, but there was no evidence for H^+ or D^+ formation. The rate constants determined in this study for the primary reactions are both about 20% below the ICR results and about 30% below the collision rate constants derived from the Langevin expression [11]. The ratio of rate constants k_H/k_D is 1.2 ± 0.3 which is within experimental uncertainty of 1.37, the corresponding ratio of collision rate constants.

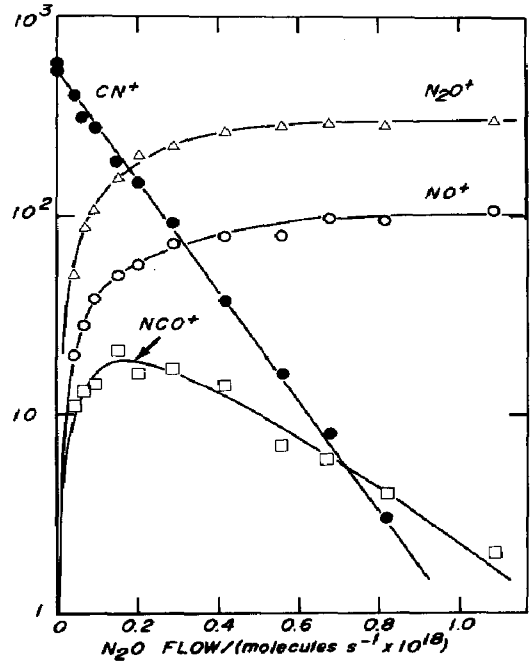
Reactions with CO_2, N_2O, O_2, OCS and NO

Charge transfer was observed to be the predominant reaction channel with all five of these molecules. Also, oxygen atom abstraction to form the NCO^+ ion was an important competing channel with all but one. With OCS, the sulphur atom was abstracted instead to form NCS^+. Another observed route resulted in C–N bond scission of the CN^+ reactant to produce $C_2O^+ + NO$ with CO_2, $NO^+ + CO$ with O_2, and $NO^+ + CN_2$ with N_2O, although the latter products may also arise from nitride abstraction. With OCS, an additional channel was observed leading to oxygen atom elimination to produce NC_2S^+.

Only the reaction of CN^+ with CO_2 was investigated in the previous ICR study [1]. Our rate constant is lower by a factor of two and there is poor agreement on the relative importance of charge transfer and oxygen atom abstraction. Also, C_2O^+ was not reported as a product in the ICR study.

The observation and non-observation of NCO^+ production by oxygen atom transfer provide useful limits to the heat of formation of NCO^+ Exothermicity for the production of NCO^+ from NO implies an upper limit to the heat of formation of NCO^+ of 1420 ± 17 kJ mol^{-1} [12]. If the failure to observe NCO^+ production from OCS is attributed to overall reaction endothermicity, a lower limit to the heat of formation of 1381 ± 21 kJ mol^{-1} may be calculated from the known heats of formation of CN^+, OCS and CS [12,13]. This bracketing leads to a value of 1400 ± 20 kJ mol^{-1} for the heat of formation of NCO^+ at 298 K and, with the known heat of formation of NCO [12], a value for the adiabatic ionization energy of NCO of 12.9 ± 0.5 eV. There appear to have been no previous measurements of IP(NCO) [14] and one theoretical study predicts an adiabatic ionization energy of 10.2 ± 0.3 eV and vertical ionization energies of 11.9 and 13.57 eV [15].

The thermochemical properties deduced from the primary oxygen atom abstraction reactions are consistent with the secondary reactions of NCO^+ observed in N_2O, O_2 and NO, and the failure to observe secondary reactions in CO_2. The derived ionization energy of NCO lies below that for CO_2, above those for NO and O_2, and is about equal to that of N_2O. The NCO^+ ion failed to charge transfer with CO_2 and reacted with NO by charge



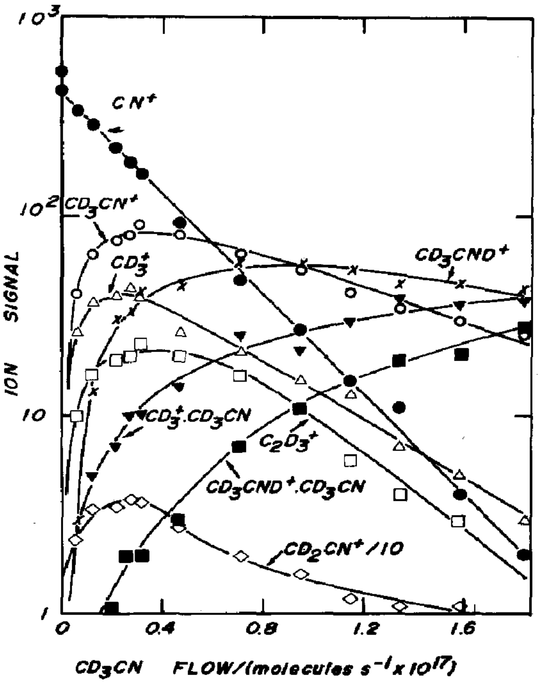


Fig. 3. The observed variation in ion signals for the addition of nitrous oxide into the reaction region in which CN^+ has been established with the SIFT technique. $P = 0.352$ Torr, $\bar{v} = 7.5 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 297$ K. The carrier gas is helium.

Fig. 4. The observed variation in ion signals for the addition of deuterated methyl cyanide into the reaction region in which CN^+ has been established with the SIFT technique. $P = 0.348$ Torr, $\bar{v} = 7.4 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 296$ K. The carrier gas is helium.

transfer as expected. Reactions were also observed with O_2 and N_2O as is indicated in Fig. 3 for N_2O. The product distribution analyses also suggested charge transfer to be the major channel with these two molecules, but some production of NO^+ could not be excluded.

Reactions with HCN and CD_3CN

The CN^+ ion was observed to react with HCN to produce predominantly HCN^+, which may arise by charge transfer and also by hydride transfer. The background ion at *m/z* 52 ($C_2N_2^+$) was also observed to react with HCN, but there was an early inflection in its decay, which was shown by curve-fitting to be consistent with a 15% production of $C_2N_2^+$ by CN^+. These observations are in accord with the previous ICR study [1]. We have shown in separate experiments that $C_2N_2^+$ reacts rapidly with HCN ($k = 1.8 \times 10^{-9}$ cm³ molecule^{-1} s^{-1}) to produce $C_2N_2H^+$ and then H_2CN^+ in a secondary proton-transfer reaction of $C_2N_2H^+$ with HCN.

The results with CD_3CN were more complex, as is illustrated in Fig. 4.

Primary reaction channels were observed to lead to CD_3CN^+ by charge transfer, CD_2CN^+ by deuteride transfer, $C_2D_3^+$ by nitride transfer, and CD_3^+ by cyanide transfer (dissociative charge transfer is endothermic). CD_3^+ reacted further with CD_3CN to form an adduct which is isomeric with deuterated ethyl cyanide, $C_2D_5CND^+$. The ions $C_2D_3^+$, CD_3CN^+ and CD_2CN^+ all reacted further to establish CD_3CND^+ which then reacts further to form the adduct $CD_3CND^+ \cdot CD_3CN$.

Reaction with C_2N_2

The CN^+ ion was observed to react rapidly with cyanogen, primarily by charge transfer with a rate constant about 30% lower than the value reported by McEwan et al. [1]. Also, two minor channels not observed in the ICR studies appeared to compete with charge transfer: elimination of N_2 with formation of C_3N^+ and nitride transfer to CN^+ to form C_2N^+ and CN_2. All three of the primary product ions were observed to add C_2N_2 in the formation of the cluster ions $C_2N_2^+ \cdot C_2N_2$, $C_3N^+ \cdot C_2N_2$ and $C_2N^+ \cdot C_2N_2$, as is shown in Fig. 5.

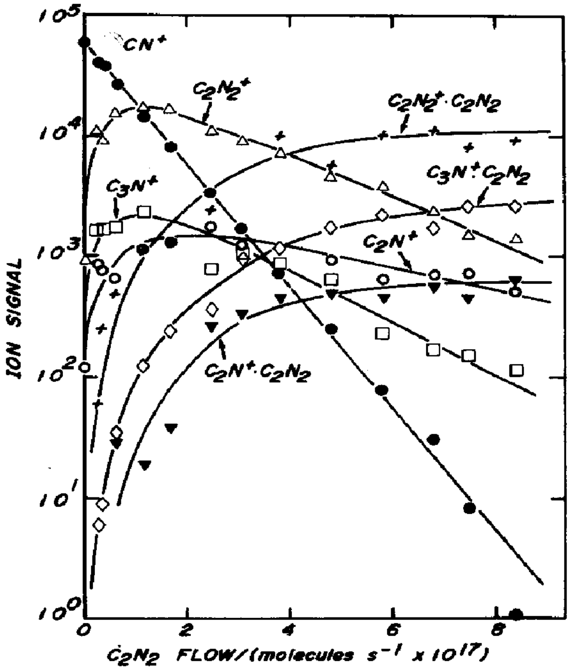


Fig. 5. The observed variation in ion signals for the addition of cyanogen into the reaction region in which CN^+ has been established with the SIFT technique. $P = 0.293$ Torr, $\bar{v} = 7.1 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 295$ K. The carrier gas is helium.

Reactions with CD_4 and CH_4

Five product channels were observed with CD_4 and CH_4. Use of the two isotopic molecules allowed the identification of product ions with CH_4 at *m/z* 15 as CH_3^+ and not NH^+, at 27 as HCN^+ and not $C_2H_3^+$, and at 28 as H_2CN^+ and not $C_2H_4^+$ and with CD_4 at *m/z* 20 as CD_4^+ and not ND_3^+ and 28 as DCN^+ and not $C_2D_2^+$. Hydride transfer was observed to be the dominant product channel. Charge transfer and hydrogen atom transfer together proceeded in almost comparable amounts. Two other channels involving H_2 transfer and condensation accompanied by H_2 elimination were observed to contribute as minor channels.

An earlier SIFT study in our laboratory with CN^+ signals of lower intensity had identified only the major channel leading to CH_3^+ and the minor channel leading to H_2CN^+ [3]. The previous ICR measurements by McEwan et al. indicated that H_2CN^+ was the major channel of the reaction of CN^+ with CH_4 [1] while, still earlier, Huntress reported CH_2CN^+ as the only product for this reaction [16]. Our SIFT measurements show that H_2CN^+ is primarily a secondary product arising from the secondary reaction between HCN^+ and CH_4 [3] and that CH_2CN^+ is only a minor product.

Reactions with D_2O, H_2S and CH_3OH

At least five product channels were observed with D_2O, as is indicated in Table 1. Two additional products which appeared to be produced in trace amounts ($< 5\%$ of the total) were D_2CO^+ and OD^+. In comparison, only three product channels were observed with H_2S and CH_3OH. Charge transfer was a large channel with all three molecules, but otherwise the product distributions showed distinct differences. Deuterium atom transfer predominated over deuteride transfer with D_2O, while hydride transfer predominated over hydrogen atom transfer with both H_2S and CH_3OH. With CH_3OH, hydride transfer appeared to be the major channel. Dissociative charge transfer to produce CH_3O^+ or SH^+ from H_2S is endothermic. On the other hand, dissociative charge transfer with H_2S to form S^+ is exothermic by about 70 kJ mol^{-1} and appears to be responsible for the production of this ion. The corresponding channel to produce O^+ is endothermic with both D_2O and CH_3OH. Other products observed with D_2O include deuterium atom elimination (to produce $DNCO^+$), D_2 transfer (to produce D_2CN^+) and, interestingly, C–N bond scission (to produce $DCO^+ + ND$ and $D_2CO^+ + N$).

Extensive secondary ion/molecule reactions were observed with all three molecules. In the reactant flow regime of the present experiments, well-known chemistry establishes D_3O^+ and D_2CN^+ as terminal ions with D_2O. Sec-

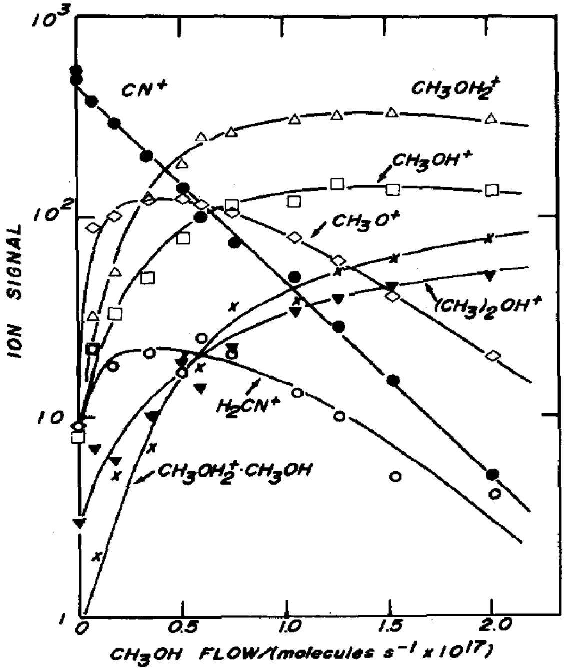


Fig. 6. The observed variation in ion signals for the addition of methanol vapour into the reaction region in which CN^+ has been established with the SIFT technique. $P = 0.357$ Torr, $\bar{v} = 7.4 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 298$ K. The carrier gas is helium.

ondary reactions of S^+, SH^+ and H_2S^+ with H_2S are known to establish H_3S^+ and HS_2^+ as terminal ions [17]. The secondary ion chemistry observed with CH_3OH is included in Fig. 6. The $CH_3OH_2^+$ ion is established by proton-transfer reactions of CH_3O^+, CH_3OH^+ and H_2CN^+ with CH_3OH. Further reaction with CH_3OH produces the cluster ion $CH_3OH_2^+ \cdot CH_3OH$ and $(CH_3H)_2OH^+$ [18].

All five of the product ions observed with D_2O were identified previously in the ICR study of the H_2O reaction [1]. There are some differences in the product distributions as shown in Table 1. Most notably, the ICR study indicated a smaller contribution due to charge transfer and was able to distinguish between the channels leading to D_2CN^+ and DCO^+ with D_2O.

Reactions with C_2D_2 and C_2H_4

The CN^+ ion was observed to react with C_2D_2 predominantly by charge transfer and by D atom elimination to produce what is likely to be ionized cyanoacetylene. Both channels were observed in the ICR studies and with a similar product distribution. Our rate constant is a factor of 3 lower than the approximate value reported by McEwan et al. [1].

There is good agreement between the ICR and SIFT observations of the reaction with C_2H_4. Due to peak overlap, we could not distinguish between $C_2H_4^+$ and H_2CN^+ or between $C_2H_3^+$ and HCN^+. All four of these product ions were identified by the ICR measurements with C_2H_4 and C_2D_4. When summed, the ICR branching ratios shown in Table 1 are in good agreement with the SIFT results. Our SIFT studies also indicated a minor primary reaction channel (5%) leading to the formation of $H_2C_3N^+$, which may be protonated cyanoacetylene.

Reaction with Xe

This reaction is somewhat unique in that it involves the transfer of an electron from an atom to a molecular ion. The rates of such reactions are known to be specific to details of energy resonance and Franck–Condon factors [19]. The relatively high rate of charge transfer with CN^+ may be accounted for by the possibility of accidental resonance with several bound states of the neutral product CN. The total excess energy of 2.4 ± 0.2 eV for this reaction is sufficient to populate the ground electronic state, $CN(X^2\Sigma^+, v \approx 9)$, or the first excited electronic state, $CN(A^2\Pi_i, v \approx 5)$. Formation of the electronically excited product would make this charge transfer reaction a potential source for the study of the red system in the emission spectroscopy of CN [20].

Reaction with ND_3

Four product ions were observed for the reaction with NH_3 in the ICR study and rapid secondary reactions of these four ions introduced difficulties in the determination of the product distribution [1]. The observations recorded with the SIFT apparatus for ND_3 were similar and the presence of reactive background signals at m/z 18 (H_2O^+) and 28 (H_2CN^+) introduced additional difficulties in the assessment of individual branching ratios for ND_2^+ and DCN^+, respectively. Irrespective of these uncertainties, the data clearly indicate charge transfer to be the predominant channel. The other minor channels observed correspond to deuterium atom transfer to produce DCN^+ and deuteride transfer to form DCN and ND_2^+, which may react by D^+ transfer before separation to produce also D_2CN^+ and ND. Nitride transfer to produce D_3^+ and CN_2 is also exothermic, but is prevented, presumably by the extensive bond cleavage and formation required to bring it about. There was no evidence for any formation of D_3^+ as a product ion.

CONCLUSIONS

The measurements reported here show that CN^+ ions react with simple inorganic and organic molecules in the gas phase at room temperature in a variety of different ways, generally with high reactivity. The observed reaction channels include charge transfer, dissociative charge transfer, hydrogen atom transfer, oxygen atom transfer or elimination, hydride transfer, nitride transfer, H_2 transfer or elimination, and adduct formation.

Charge transfer was observed to be a reaction channel with all of the 18 molecules (including xenon) with an ionization energy less than that of CN (14.5 eV). In most of these cases, charge transfer was the predominant channel.

The observation and non-observation of NCO^+ production by oxygen atom transfer have provided a heat of formation for NCO^+ of 1400 ± 20 kJ mol^{-1} at 298 K and an adiabatic ionization energy for NCO of 12.9 ± 0.5 eV.

Hydride transfer to form HCN was observed to predominate over hydrogen atom transfer to form HCN^+ with the molecules H_2S, CH_3OH, CH_4 and CH_3CN for which hydride transfer is much more exothermic (by more than 330 kJ mol^{-1}). With H_2O, hydrogen atom transfer predominates and the two channels have more equal exothermicities. With H_2, hydride abstraction would lead to proton production which was not observed. The two channels were not observed with C_2H_2. With NH_3 the two channels were minor (< 10%) and with C_2H_4 they could not be distinguished.

With nitrogen-containing compounds nitride transfer to form CN_2 was observed only when exothermic but with one exception. The reaction is exothermic with C_2N_2, N_2O, CD_3CN and ND_3 and endothermic with N_2, HCN and NO. The exothermic reaction with ND_3 to produce D_3^+ was not observed presumably because of the extensive bond redisposition which would be required. Nitrogen atom transfer to form CN_2^+ was not observed as a competing channel.

The CN^+ ion was observed to form adducts with N_2 and CO in helium buffer gas at the total pressures used in these experiments. The association reaction with N_2 is likely to be the dominant loss process for CN^+ in the atmosphere of Titan, which is composed predominantly of molecular nitrogen [21]. Our measurements also suggest that the presence of cyanogen in the atmosphere of Titan [22] may lead to adducts of the type $C_2N_2^+ \cdot (C_2N_2)_n$, $C_3N^+ \cdot (C_2N_2)_n$ and $C_2N^+ \cdot (C_2N_2)_n$. The nature of the bonding in these ions, their structures, and their role as reactive intermediates and fate upon electron–ion recombination remain to be explored.

Several of the observed two-body reactions are of relevance to molecular synthesis by means of ion chemistry as in dense interstellar clouds for example, where CN^+ may be formed from $CH^+ + N$ or $C^+ + NH$ [23]. The reaction of CN^+ with HCN initiates a sequence of reactions which can lead to the synthesis of cyanogen

$$CN^+ \xrightarrow{HCN} C_2N_2^+ \xrightarrow{H_2} C_2N_2H^+ \xrightarrow[EIR]{PT} C_2N_2$$

The final neutralization step may proceed by proton transfer (PT) or electron–ion recombination (EIR). The reaction of CN^+ with CH_4 may initiate the following sequence of reactions leading ultimately to the production of methyl cyanide.

$$CN^+ \xrightarrow{CH_4} CH_2CN^+ \xrightarrow{H_2,H_2} CH_4CN^+ \xrightarrow[EIR]{PT} CH_3CN$$

Reaction of CN^+ with methyl cyanide will lead directly to cyanogen as one of the channels

$$CN^+ + CH_3CN \rightarrow CH_3^+ + C_2N_2$$

The reaction of CN^+ with H_2O can lead directly to NCO, which has been discussed as a potential interstellar species [24]

$$CN^+ \xrightarrow{H_2O} HNCO^+ \xrightarrow[EIR]{PT} NCO$$

Finally, the reactions of CN^+ with C_2H_2 and C_2H_4 may lead to formation of cyanoacetylene, which is of interest in interstellar synthesis [3]

$$CN^+ \xrightarrow{C_2H_2} HC_3N^+ \xrightarrow{H_2} H_2C_3N^+ \xrightarrow[EIR]{PT} HC_3N$$

$$CN^+ \xrightarrow{C_2H_4} H_2C_3N^+ \xrightarrow[EIR]{PT} HC_3N$$

A final comment should be made on the comparisons with the results of the previous ICR study of McEwan et al. [1]. The rate constants obtained with the SIFT instrument are systematically lower than those reported in the ICR study (see Table 1). In many cases, there is good agreement in the branching ratios of the observed products, but there are several important exceptions. Adduct formation with N_2 and CO was not reported in the ICR study, which was made at much lower pressures. Serious differences exist in the branching ratios for the products of the reactions with CO_2 and CH_4, which, at least in the latter case, may be attributable to secondary ion chemistry.

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