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FLOW TUBE STUDIES OF REACTIONS OF CYANOGEN WITH IONS SELECTED FROM CYANOGEN

A.B. RAKSIT and D.K. BOHME

Department of Chemistry and Centre for Research in Experimental Space Science, York University, Downsview, Ont. M3J 1P3 (Canada)

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ABSTRACT

The selected-ion flow tube (SIFT) technique has been applied at 296 ± 2 K to a study of the ion chemistry of cyanogen, C_2N_2, initiated by the ionization of C_2N_2. The ions are derived from C_2N_2 in a separate source and are then allowed to react with C_2N_2 essentially in isolation. All of the ions N^+, N_2^+, C^+, C_2^+, CN^+, C_2N^+ and $C_2N_2^+$ were observed to react rapidly with C_2N_2 with nearly unit efficiency. The reaction paths were of a varied nature and led to the product ions C_2N^+, $C_2N_2^+$, C_3N^+, C_4^+, N_3^+ and CN_2^+. Addition of C_2N_2 was a predominant feature of the secondary ion chemistry which established polymeric ions of the type $(C_{2n}N_{2n-4})^+$ with $n = 2$ and 3, $(C_{n+2}N_n)^+$ with $n = 2$ to 5, $(C_{2n}N_{2n-1})^+$ with $n = 2$ and 3, and $(CN)_n^+$ with $n = 3$ to 6. The results are compared with previous mass spectrometer ion source measurements at lower pressures and with mass spectra obtained for the electron-induced radiolytic polymerization of C_2N_2. Their relevance to the ion chemistry in the atmosphere of Titan is also discussed briefly.

INTRODUCTION

The energetics and chemistry of the ionic derivatives of cyanogen have been the subject of a number of mass spectrometric investigations. The different carbon- and nitrogen-containing ions formed by electron impact and photoionization of cyanogen have been identified at low pressures primarily to determine their appearance energies and to deduce their heats of formation [1]. Ions derived from ion/molecule reactions with C_2N_2 which begin to operate in a mass spectrometer ion source at intermediate pressures have been investigated in detail by Inoué and Cottin for a range in pressure from 10^{-4} to 2×10^{-2} Torr [2]. Also, an attempt was made by these authors to unravel the identity of individual ion/molecule reactions from appearance energy measurements coupled with observations of variations of ion intensity with pressure. Interesting polymeric ions with various proportions of carbon and nitrogen have been observed at still higher pressures in the electron-induced radiolytic polymerization of C_2N_2 at ca. 1 Torr [3].

Here, we report the application of the selected-ion flow tube (SIFT) technique to a study of the ion chemistry of cyanogen. With the SIFT technique, ions may be derived from C_2N_2 in a separate source by electron impact, selected with a quadrupole mass spectrometer, and then allowed to react in a flowing helium carrier gas to which C_2N_2 is added downstream. The selected reactions proceed in the flow tube without significant interference from competing extraneous ion/molecule reactions. Reactant and product ions are readily identified downstream with the aid of a second quadrupole mass spectrometer.

The measurements were motivated in part by the recent revelation of the presence of C_2N_2 in the atmosphere of Titan where ion chemistry is driven by energetic magnetospheric electrons, solar radiation below 100 Å and cosmic ray bombardment [4,5]. Also, there is a standing interest here in the elucidation of the ion chemistry of organonitrogen molecules proceeding in other extraterrestrial environments such as interstellar gas clouds [6].

EXPERIMENTAL

The measurements were performed with the selected-ion flow tube/flowing afterglow apparatus in the Ion Chemistry Laboratory at York University [7,8]. An axial electron impact ionizer (Extranuclear, Model 041-3) was used

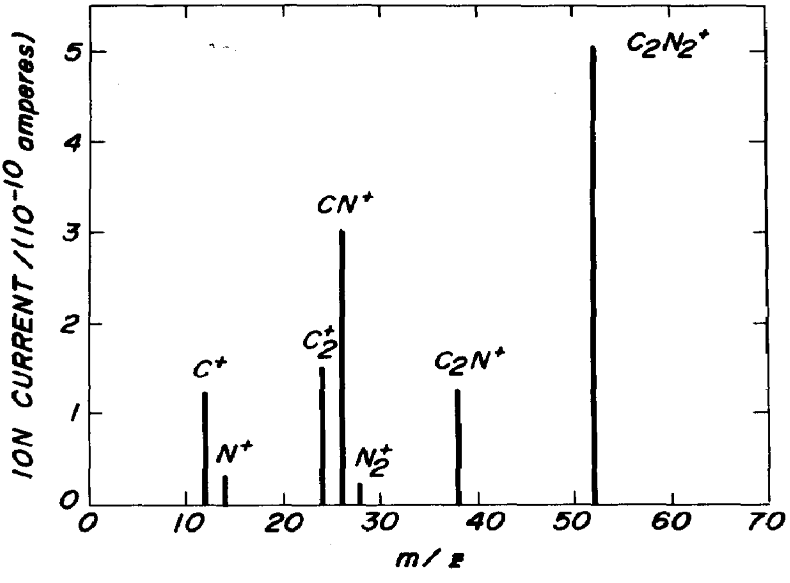

Fig. 1. SIFT spectrum for ions derived from C_2N_2 by electron impact at 45 eV. Ions are injected at 8.5 V, the buffer gas is helium at 0.353 Torr. Background ions due to impurities are present at levels less than 1% full scale.

as the ion source. The reagent ions C^+, C_2^+, CN^+, C_2N^+ and $C_2N_2^+$ were derived from cyanogen while N^+ and N_2^+ were derived from N_2. The SIFT spectrum obtained for cyanogen at a relatively low ion injection energy (8.5 V) is shown in Fig. 1. At 12.5 V, the currents were enhanced by a factor of approximately 100 without any significant distortions in relative ion signals. Helium was used as the carrier gas in all the experiments. The cyanogen was of commercial grade (Matheson, 98.5% min. by volume in the liquid phase). Separate measurements using H_3^+ as a chemical ionization reagent indicated a purity for this gas of more than 99%. All measurements were made at an ambient temperature of 296 ± 2 K.

RESULTS AND DISCUSSION

Table 1 summarizes the reaction rate constants and product distributions obtained in this study for the observed primary reactions of ions with C_2N_2. Rate constants and product distributions were determined in the manner described previously [7,9]. Table 1 includes all the primary product ions observed with contributions of more than 5% to the total. The branching

TABLE 1

Summary of rate constants (in units of 10^{-9} cm^3 molecule^{-1} s^{-1}) and product distributions measured for reactions of C_2N_2 with ions derived from C_2N_2 using the SIFT technique at 296 ± 2 K

Reactant ion	Products	Branching ratio	k_{exp} [a]	k_c [b]
C^+	$C_2N^+ + CN$	1.0	1.9	1.8
C_2^+	$C_2N^+ + C_2N$	0.5	1.5	1.4
	$C_3N^+ + CN$	0.3		
	$C_4^+ + N_2$	0.2		
CN^+	$C_2N_2^+ + CN$	0.85	1.4	1.3
	$C_3N^+ + N_2$	0.10		
	$C_2N^+ + CN_2$	0.05		
C_2N^+	$C_2N^+ \cdot C_2N_2$	1.0	0.15 (He) [c]	1.2
$C_2N_2^+$	$C_2N_2^+ \cdot C_2N_2$	1.0	0.49 (He) [c]	1.1
N^+	$C_2N^+ + N_2$	0.7	1.4	1.7
	$C_2N_2^+ + N$	0.3		
N_2^+	$C_2N_2^+ + N_2$	≥ 0.95	0.86	1.3
	$N_3^+ + CN_2$ $CN_2^+ + N_3$	≤ 0.05		

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

[b] Collision rate constants derived from the average quadrupole orientation theory [10].

[c] Effective second-order rate constant in helium buffer gas at a total pressure of 0.33 Torr and concentration of 1.1×10^{16} atoms cm^{-3}.

ratios have been rounded to the nearest 5%. The experimental rate constants are compared with collision rate constants, k_c, derived from the average quadrupole orientation (AQO) theory [10] with a polarizability for C_2N_2 of 5.01 Å^3 [11] and a rotation average quadrupole moment of -4.5×10^{-26} e.s.u. cm^2 [10].

C^+, C_2^+

The C^+ ions were observed to react with C_2N_2 to produce C_2N^+ exclusively in a rapid bimolecular reaction with a rate constant close to the collision limit. The C^+ ions were shown in separate experiments to be predominantly (95%) in the ^2P ground state by virtue of their failure to react with CO [12]. Formation of C_2N^+ is exothermic with ground state C^+ for a heat of formation for C_2N^+ of less than 401 kcal mol^{-1}. Reasonable routes are available for the formation of both the CCN^+ and CNC^+ isomers: the CCN^+ isomer may be formed by N^- transfer or by CN transfer to C^+, while the CNC^+ isomer may be formed by NC transfer to C^+. However, available thermochemical information suggests that the CNC^+ isomer is preferred.

The reported experimental heats of formation for C_2N^+ are in the range 364–421 kcal mol^{-1} [1]. According to Haese and Woods [13], these values may be resolved into values of 364 ± 12 and 421 ± 12 kcal mol^{-1} for the heats of formation of the CNC^+ and CCN^+ isomers, respectively. Haese and Woods have examined the molecular structures of CNC^+ and CCN^+ with double zeta self-consistent field calculations and predict that the CCN^+ structure is less stable. Their calculations have led to values of 372 ± 20 and 421 ± 25 kcal mol^{-1} for the heats of formation of the two isomers. On the basis of these experimental and theoretical results we conclude that the reaction of ground state C^+ with C_2N_2 will be specific towards formation of the CNC^+ isomer. Formation of the CCN^+ isomer appears to be endothermic.

More variety was observed in the product spectrum for the reaction of C_2^+ with C_2N_2 which is displayed in Fig. 2. The main channel was again production of C_2N^+ and in this case the formation of both isomers appears to be exothermic. The CCN^+ structure may be preferred on mechanistic grounds if the reaction proceeds by end-on attack with an N atom or N^- transfer to C_2^+ or even if a four-centred intermediate is formed by side-on attack. The C_3N^+ and C_4^+ ions were observed to be the other major product ions. The C_3N^+ may be formed as C_2NC^+ by NC transfer from C_2N_2 in analogy with the formation of CNC^+ from C^+. The C_4^+ arises with elimination of N_2 which appears to be exothermic by about 24 kcal mol^{-1} with the known heats of formation of C_2^+ and C_4^+ [1]. The C_4N^+ ion was observed to be produced in only trace amounts ($\leq 1\%$). A $C_4N_2^+$ ion, possible corresponding to the adduct $C_2^+ \cdot C_2N_2$, was also observed in the product spectrum but an analysis of the product ion variation indicated that it was mainly a secondary ion. Separate experiments with C_3N^+ derived from cyanoacetylene indicated that $C_4N_2^+$ can arise from the CN transfer reaction

$$C_3N^+ + C_2N_2 \rightarrow C_4N_2^+ + CN \tag{1}$$

Formation of $C_4N_2^+$ from C_2N^+ is endothermic. Its formation from C_4^+ appears to be only slightly exothermic and unlikely on mechanistic grounds.

The chemical connection between C_2^+ and C_3N^+ in C_2N_2 was first revealed by Inoué and Cottin in their mass spectrometer ion source experiments [2] which yielded a rate constant for this channel of 4.4×10^{-10} cm^3 molecule^{-1} s^{-1} in good agreement with our result. These authors also reported C_4^+ and C_4N^+ as minor products with values for rate constants of 3.4 and 1.8×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. Our value for C_4^+ production is about 10 times greater while our observation of traces of

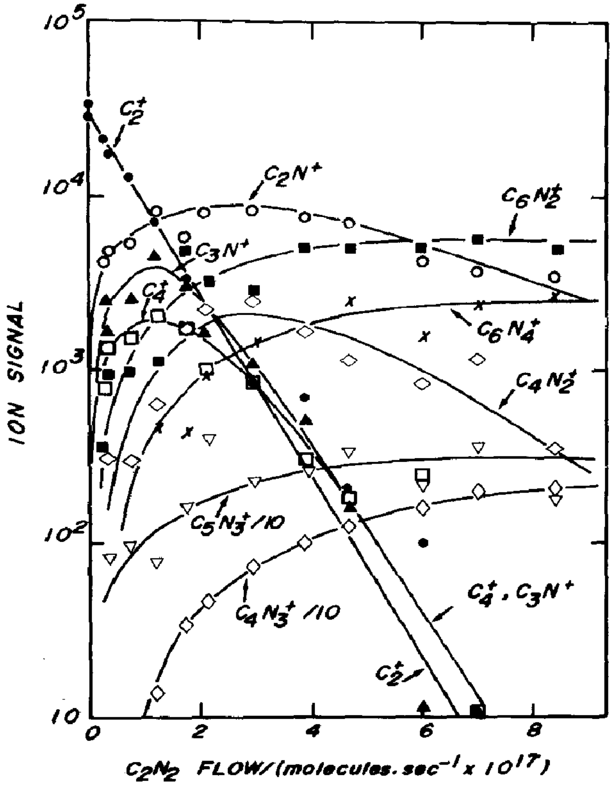

Fig. 2. The observed variations in ion signals detected upon the addition of C_2N_2 into the reaction region of the SIFT apparatus in which C_2^+ is initially established in helium buffer gas. C_2^+ is derived from C_2N_2 at an electron energy of 51 eV. The conditions in the reaction region were: $P = 0.332$ Torr, $\bar{v} = 7.4 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 295$ K.

C_4N^+ is consistent with the latter result within our experimental uncertainty. Inoué and Cottin did not report C_2N^+ as a primary product. The ions were observed to be produced in their ion source but their origin was ascribed exclusively to the reaction of CN^+ with C_2N_2.

Figure 2 also illustrates the plethora of secondary reactions which are initiated by the products of the C_2^+ reaction. Most of the secondary reactions appear to be of a termolecular nature involving the addition of C_2N_2 with He acting as the stabilizing third body. The reactions which contribute to the secondary ion chemistry shown in Fig. 2 are believed to be

$$C_2N^+ + C_2N_2 + He \rightarrow C_4N_3^+ + He \tag{2}$$

$$\begin{aligned} C_3N^+ + C_2N_2 + He &\rightarrow C_5N_3^+ + He \\ &\rightarrow C_4N_2^+ + CN \end{aligned} \tag{3}$$

$$C_4^+ + C_2N_2 + He \rightarrow C_6N_2^+ + He \tag{4}$$

$$C_4N_2^+ + C_2N_2 + He \rightarrow C_6N_4^+ + He \tag{5}$$

Reactions (2) and (3) have been studied separately and are discussed later in the text.

Measurements of the $C_4N_3^+/C_2N^+$ ratio as a function of electron energy in the mass spectrometer ion source experiments of Inoué and Cottin had suggested a direct chemical connection between C_2N^+ and $C_4N_3^+$ but Inoué and Cottin did not propose a mechanism [2]. They did suggest that both C_3N^+ and C_4^+ react with C_2N_2 by CN transfer to produce $C_4N_2^+$ and C_5N^+ but not by C_2N_2 addition to produce $C_5N_3^+$ and $C_6N_2^+$. The latter two ions were observed in their mass spectrometer ion source experiments but their origin was ascribed to reactions of C_5N^+ with C_2N_2. There was no indication of the formation of C_5N^+ under our experimental conditions. The origin of $C_6N_4^+$ observed by Inoué and Cottin was ascribed by these authors to the bimolecular reactions of $C_6N_2^+$ and $C_5N_3^+$ with C_2N_2. The termolecular reactions (4) and (5) are more consistent with the observations represented in Fig. 2 but must be regarded as speculative until they are investigated separately.

CN^+, C_2N^+, $C_2N_2^+$

We have reported elsewhere in a study of CN^+ ion chemistry that CN^+ was observed to react rapidly with C_2N_2 in our SIFT apparatus primarily to produce $C_2N_2^+$ by charge or CN transfer and also by elimination of N_2 to form C_3N^+, and apparently by N^- transfer to form CN_2 and C_2N^+ [14]. The overall efficiency of this reaction is approximately unity as the collision rate constant is equal to the measured reaction rate constant. McEwan et al.

[15] measured a rate constant of $(2.1 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} in an ICR study of this reaction and observed only the charge transfer channel. Also, there was no indication either in our SIFT experiments or the ICR study of the formation of an ion with m/z 64 ($C_3N_2^+$). Formation of $C_3N_2^+$ was proposed as a minor channel, $k = 4.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, by Inoué and Cottin on the basis of their appearance energy and pressure dependence measurements [2]. The authors also reported a rate constant of 6.2×10^{-10} cm^3 molecule^{-1} s^{-1} for the formation of C_2N^+ from CN^+ and C_2N_2.

The C_2N^+ and $C_2N_2^+$ ions were both observed to react efficiently with C_2N_2 in our SIFT apparatus primarily by addition to form $C_4N_3^+$ and $C_4N_4^+$, respectively, with effective second-order rate constants equal to 13% and 48% of the corresponding collision rate constant. In both cases the addition of a second molecule of cyanogen to form $C_6N_5^+$ and $C_6N_6^+$, respectively, was also observed. Data for the reaction with $C_2N_2^+$ are shown in Fig. 3: the results indicate that $C_3N_3^+$ and $C_5N_5^+$ also appeared as

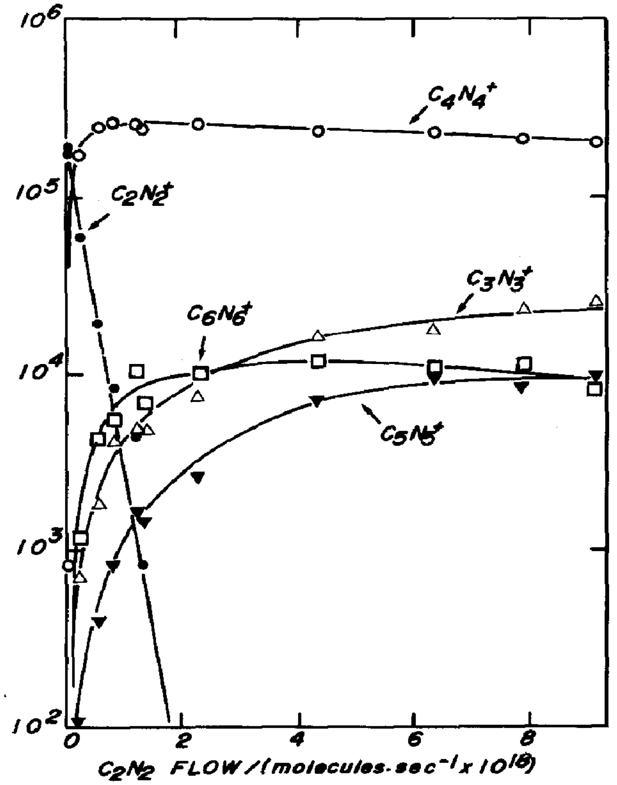

Fig. 3. The observed variations in ion signals recorded for the addition of C_2N_2 into the reaction region of the SIFT apparatus in which $C_2N_2^+$ is initially established in helium buffer gas. $P = 0.312$ Torr, $\bar{v} = 7.2 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 295$ K. $C_2N_2^+$ is derived from C_2N_2 at an electron energy of 25 eV.

secondary product ions. Their ion signal variations are consistent with their formation from $C_4N_4^+$ via the reaction

$$\begin{aligned} C_4N_4^+ + C_2N_2 &\rightarrow C_3N_3^+ + C_3N_3 \\ &\rightarrow C_5N_5^+ + CN \end{aligned} \tag{6}$$

but other reactions may contribute as, for example, the addition of C_2N_2 to $C_3N_3^+$. Again, the reaction of $C_4N_4^+$ should be studied separately to resolve the exact nature of the chemistry.

N^+, N_2^+

In order to increase their signal intensities, the N^+ and N_2^+ ions were both derived by electron impact ionization from N_2 at 40 eV rather than C_2N_2. Results obtained for the reaction of N^+ with C_2N_2 are shown in Fig. 4. Production of C_2N^+ and $C_2N_2^+$ were the two observed reaction channels.

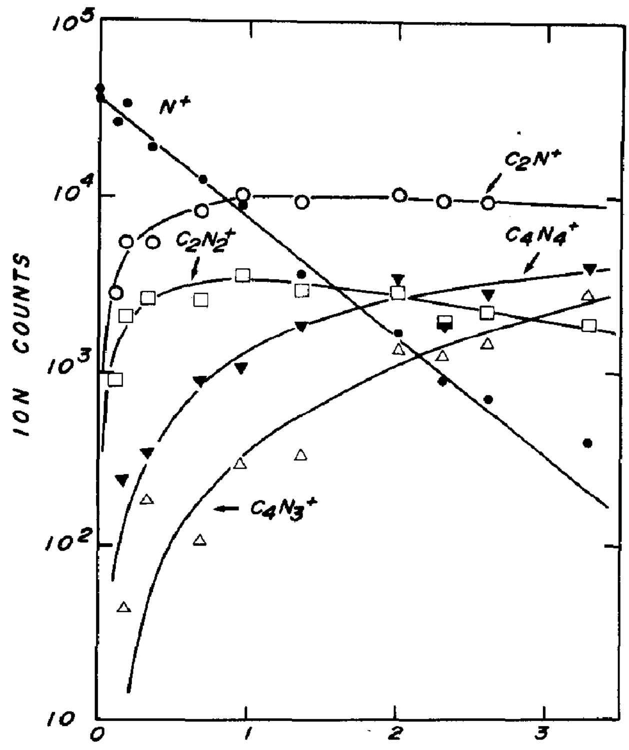

Fig. 4. The observed variations in ion signals recorded for the addition of C_2N_2 into the reaction region of the SIFT apparatus in which N^+ is initially established in helium buffer gas. $P = 0.317$ Torr, $\bar{v} = 6.9 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 297$ K. N^+ is derived from N_2 at an electron energy of 40 eV.

With C_2N^+ the neutral product must be N_2 since formation of two N atoms is endothermic. The total rate constant and the product distribution for the reaction of N^+ is listed in Table 1. The reaction rate constant is equal to the collision rate constant to within the experimental uncertainty. The exothermicity for the formation of C_2N^+ is sufficient to produce either isomer but formation of CCN^+ is likely to be preferred on mechanistic grounds. It may proceed by end-on attack with N^- transfer to form N_2. Formation of CNC^+ would require insertion with less favourable N_2 elimination. The $C_2N_2^+$ ion is likely to arise by charge transfer. Both C_2N^+ and $C_2N_2^+$ were observed to react further with C_2N_2 in the manner already described.

The N_2^+ ion was observed to react with near unit efficiency by charge transfer. The $C_2N_2^+$ product ion subsequently formed $C_4N_4^+$ and $C_6N_6^+$ by stepwise addition of cyanogen. A complication arose at high additions of C_2N_2 at which the *m/z* 28 signal began to rise but this behaviour could be accounted for by the presence of an HCN impurity in C_2N_2 and its protonation by the impurity ions H_3O^+, N_2H^+ and H_2O^+. There was

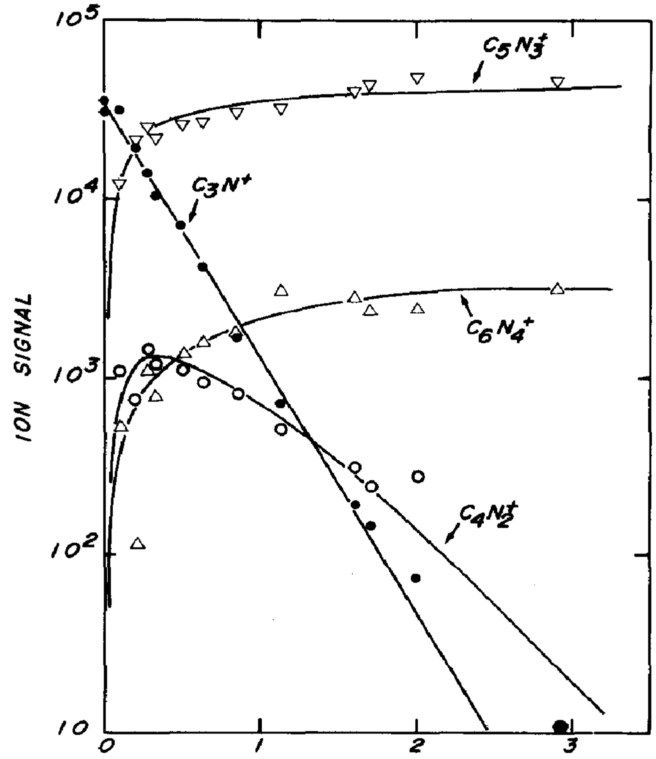

Fig. 5. The observed variations in ion signals for the addition of C_2N_2 into the reaction region of the SIFT apparatus in which C_3N^+ is initially established in helium buffer gas. $P = 0.314$ Torr, $\bar{v} = 7.2 \times 10^3$ cm s^{-1}, $L = 46$ cm and $T = 296$ K. C_3N^+ is derived from cyanoacetylene at an electron energy of 50 eV.

evidence for the occurrence of minor channels ($\leq 5\%$) leading to formation of N_3^+ and C_2N^+. The N_3^+ ion did not react rapidly with C_2N_2, while C_2N^+ reacted further in the manner already described.

C_3N^+

The C_3N^+ ion was derived from cyanoacetylene by electron impact at 50 eV. The ion presumably has the $CCCN^+$ structure rather than the $CCNC^+$ structure whose formation would require a curious rearrangement. Results for its reaction with C_2N_2 are shown in Fig. 5. The reaction proceeded with an effective second-order rate constant of $(4.5 \pm 1.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} which is equal to about 50% of the corresponding collision rate constant. Two channels were observed in helium buffer gas. The predominant channel led to the formation of $C_5N_3^+$ which results by addition of C_2N_2. A second molecule of C_2N_2 was observed to add at higher flows of C_2N_2. Some primary production of $C_4N_2^+$ was also observed for the reaction of C_3N^+ with C_2N_2. The $C_4N_2^+$ ion reacted quite rapidly with C_2N_2 to form $C_6N_4^+$ by C_2N_2 addition and conceivably also to form $C_5N_3^+$. The latter channel would be masked by the $C_5N_3^+$ produced directly from C_3N^+.

CONCLUSIONS

The ions N^+, N_2^+, C^+, C_2^+, CN^+, C_2N^+ and $C_2N_2^+$ which may be derived from cyanogen by ionization were all observed to react rapidly with the parent molecule with nearly unit efficiency at 296 K. The observed primary products were varied. They included C_2N^+, $C_2N_2^+$, C_3N^+, C_4^+, N_3^+ and CN_2^+.

The $C_2N_2^+$ ion was observed as a predominant product with the molecular ions N_2^+ and CN^+. Both of these ions have an electron recombination energy greater than the ionization energy of C_2N_2 (13.37 eV) so that charge transfer is exothermic. However, the charge transfer mechanism is not established unambiguously since other routes are possible for the production of $C_2N_2^+$. For example, CN transfer may contribute to the formation of $C_2N_2^+$ in the reaction of C_2N_2 with CN^+. No attempts were made here to resolve mechanisms as might be possible, for example, with isotope labelling experiments. The $C_2N_2^+$ ion was observed as a minor product in the reaction of the atomic ion N^+ with C_2N_2. In this case, formation of C_2N^+ and the stable N_2 molecule is much more exothermic than the competing formation of $C_2N_2^+$. We have reported elsewhere measurements for the reactions of atomic ions He^+ and Xe^+ with C_2N_2 [16]. There is no ambiguity about the charge transfer mechanism in these cases. The He^+ ion reacts by dissociative charge transfer. In the case of Xe^+, charge transfer is exothermic and was observed only with the 1/2 spin state. The 3/2 spin state was shown to react only by C_2N_2 addition [16].

Charge transfer is endothermic with C^+ and C_2^+. These two ions produced C_2N^+ and C_3N^+, respectively, which is indicative of C–C bond scission in C_2N_2. Available heats of formation suggest that the reaction with C^+ is specific towards formation of the CNC^+ isomer, while C_2^+, by analogy, may seek out the C_2NC^+ isomer. With C_2^+, formation of C_2N^+ was predominant. The C_2N^+ ion may arise by N^- transfer in analogy with the reaction of N^+ with C_2N_2. Formation of the C_4^+ product ion was unexpected as it involves a curious elimination of N_2. Both the structure and mechanism of formation of C_4^+ remain to be elucidated.

The C_2N^+ and $C_2N_2^+$ ions were observed to react only by C_2N_2 addition even though exothermic bimolecular channels appear to be possible. For example, the reaction

$$C_2N_2^+ + C_2N_2 \rightarrow C_4N_2^+ + N_2 \tag{7}$$

is exothermic by 70 kcal mol^{-1} according to available heats of formation [1]. Also, the reaction

$$C_2N^+ + C_2N_2 \rightarrow C_4N^+ + N_2 \tag{8}$$

is likely to be exothermic with the less stable CCN^+ isomer of C_2N^+. However, both reactions (7) and (8) involve curious eliminations of N_2 which appear to be kinetically unfavourable. C_2N^+ was observed to form the adduct $C_4N_3^+$ irrespective of whether it was produced from C_2N_2 directly by electron impact or by chemical reaction with N^+ or C_2^+, in which case the CCN^+ isomer is likely to be preferred, or with C^+, in which case the CNC^+ isomer is expected to be preferred.

Addition of cyanogen was also the predominant feature of the secondary ion chemistry observed. This chemistry is summarized in Fig. 6 and was seen to establish polymeric ions of the type $(C_{2n}N_{2n-4})^+$ $n = 2$ and 3, $(C_{n+2}N_n)^+$ with $n = 2$ to 5, $(C_{2n}N_{2n-1})^+$ with $n = 2$ and 3, and $(CN)_n^+$ with $n = 3$ to 6. The nature of the bonding and the structures of these ions was not elucidated. However, with its high polarizability, C_2N_2 may well be bonded electrostatically to the base ion as in $C_4^+ \cdot C_2N_2$, $C_3N^+ \cdot C_2N_2$ and $C_3N^+ \cdot (C_2N_2)_2$, $C_4N_2^+ \cdot C_2N_2$, $C_2N^+ \cdot C_2N_2$ and $C_2N^+ \cdot (C_2N_2)_2$, $C_2N_2^+ \cdot C_2N_2$ and $C_2N_2^+ \cdot (C_2N_2)_2$, respectively. At higher pressures of C_2N_2 we would then expect further growth to larger cluster ions.

Ions with integral multiplicities of CN up to 10 and other ions of varying proportions of C to N were observed as transient species in the radiolytic polymerization of C_2N_2 enhanced by Xe^+ [3]. The ultimate neutralization of these polymeric ions by electron–ion recombination will establish more complex organonitrogen molecules perhaps including paracyanogen.

Paracyanogen is a brown polymer [17] which has been observed to be formed as a faint cloud in the photochemical polymerization of C_2N_2 [18]. Formation of paracyanogen could conceivably occur in Titan's atmosphere and contribute to the colouring of the dust-covered cloud layer which has been observed [19]. While the ionization rate in Titan's atmosphere is likely to be insufficient to compete with neutral photochemistry, the results of the measurements reported here suggest that chemical evolution by ion/molecule reactions with C_2N_2 may also contribute.

Most of the ions derived in this study from the isolated ion/molecule reactions with C_2N_2 were observed at the lower pressures of the mass spectrometer experiments of Inoué and Cottin [2]. The only exceptions were $C_7N_5^+$, $C_6N_5^+$ and $C_5N_5^+$. The former two ions and possibly $C_5N_5^+$ arise from C_2N_2 addition to $C_5N_3^+$, $C_4N_3^+$ and $C_3N_3^+$, respectively, and so are expected to be enhanced at the higher pressures employed in the measurements reported here. The $C_5N_5^+$ ion may also arise from $C_4N_4^+$ but appears as a minor channel in our experiments at high flows of C_2N_2. Several ions observed in the ion source experiments were not apparent in the SIFT measurements. These include $C_3N_2^+$, C_4N^+ and C_5N^+ as well as $C_5N_4^+$, $C_6N_3^+$ and $C_7N_3^+$ which are likely to be derivative ions formed by C_2N_2 addition, viz. $C_3N_2^+ \cdot C_2N_2$, $C_4N^+ \cdot C_2N_2$ and $C_5N^+ \cdot C_2N_2$. Inoué and Cottin [2] have postulated that $C_3N_2^+$, C_4N^+ and C_5N^+ are derived from

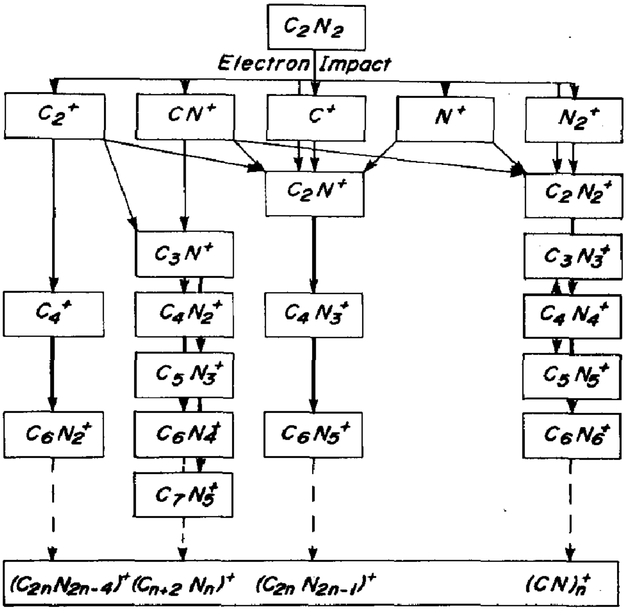

Fig. 6. Summary of the ion/molecule reactions initiated by the seven ions which may be derived from cyanogen by electron impact. The heavy arrows refer to C_2N_2 addition reactions.

CN^+, C_2^+ and C_4^+, respectively. The energetics of these processes is uncertain but it is possible that these reaction paths are all endothermic and are observed in the ion source experiments only because of residual excitation of the reactant ions which is removed in the SIFT experiment prior to reaction by collisions with the buffer gas.

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