Studies of the initial steps in the polymerization of C_2N_2 induced by Xe^+

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A Selected-Ion Flow Tube (SIFT) apparatus has been used to produce Xe^+ by electron impact and to study its reactions with C_2N_2. The $^2P_{3/2}$ and $^2P_{1/2}$ spin states of Xe^+ were observed to react differently: by C_2N_2 addition to form $Xe^+\cdot C_2N_2$ and by charge transfer to form $C_2N_2^+$, respectively. Further ion–molecule reactions with C_2N_2 were observed to establish polymeric ions of the type $(C_2N_2)_x^+$. The results indicate that the simple charge transfer model may be sufficient to account for the rate enhancement observed in the radiolytic polymerization of C_2N_2/Xe mixtures.

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On a utilisé un tube à écoulement sélecteur d'ions (TESI) pour produire des ions Xe^+ par impact électronique et pour étudier leurs réactions avec le C_2N_2. On a observé que les états de spin $^2P_{3/2}$ et $^2P_{1/2}$ du Xe^+ réagissent différemment alors qu'ils donnent respectivement une addition du C_2N_2 pour former l'ion $Xe^+\cdot C_2N_2$ et un transfert de charge qui conduit à l'ion $C_2N_2^+$. On a observé que d'autres réactions ion–molécule avec le C_2N_2 conduisent à des ions polymères de type $(C_2N_2)_x^+$. Les résultats indiquent que le modèle simple de transfert de charge peut être suffisant pour expliquer l'augmentation de la vitesse réaction observée lors de la polymérisation par radiolyse de mélanges de C_2N_2/Xe.

[Traduit par le journal]

Introduction

The rate of radiolytic polymerization of C_2N_2 is known to be enhanced by noble gases approximately in proportion to the stopping power of the noble gas (1). This increase in rate has been explained in terms of an initial charge transfer reaction involving the rare gas ion for those noble gases which have a higher ionization energy than C_2N_2 (2). Xenon has been viewed as an exception because of its relatively low ionization energy and it has been argued that the simple charge transfer theory cannot explain the observations with xenon additive (3). An alternative mechanism has been proposed in which a complex of the type $[XeC_2N_2]^+$ is invoked as an intermediate in a sequence of steps [1] to [3]

[1] $Xe \rightarrow Xe^+ + e^-$

[2] $Xe^+ + C_2N_2 \rightarrow [XeC_2N_2{}^*]^+$

[3] $[XeC_2N_2{}^*]^+ + C_2N_2 \rightarrow (C_nN_m)^+ + \cdot C_pN_q + Xe$

where n and m equal 1 to 4 but n is not necessarily equal to m, $p = 4 - n$ and $q = 4 - m$ (1, 3). Neutral cyanogen can continue to react with the ionic species produced in step [3] to form polymeric ions which ultimately can lead to neutral products by ion–ion or ion–electron recombination. The addition complex $[XeC_2N_2]^+$ has actually been observed with a mass spectrometer to be formed in a 3.5 : 1 mixture of cyanogen and xenon at a total pressure of 1 Torr (1). Its observation has provided support for this mechanism which has become known as the "cluster theory".

We report here laboratory measurements directed towards elucidating the nature and kinetics of the initial steps in the Xe^+-induced polymerization of C_2N_2. The reaction of Xe^+ with C_2N_2 is studied in complete "isolation" in helium carrier gas at room temperature. The primary ionic products are identified along with ionic products from ensuing secondary reactions. The results provide evidence for the direct formation of the adduct $Xe^+\cdot C_2N_2$ from Xe^+ and C_2N_2 but they also suggest that the simple charge transfer model may be entirely adequate to account for the Xe/C_2N_2 radiolysis results.

Experimental

The measurements were performed with the Selected-Ion Flow Tube (SIFT) apparatus in the Ion Chemistry Laboratory (4, 5). For the measurements reported here the instrument was fitted with an axial electron impact ionizer (Extranuclear, Model 041-3). Xe^+ and He^+ were derived from their parent gases at an electron energy of ca. 26 eV and an ion injection energy of ca. 13 V. Helium was used as the carrier gas in all experiments. The cyanogen was of a commercial grade (Matheson, 98.5% minimum by volume in the liquid phase). Separate measurements using H_3^+ as a chemical ionization reagent indicated a purity for the gas of more than 99%. All measurements were made at an ambient temperature of 296 ± 2 K.

Results and discussion

Figure 1 displays observations recorded with the addition of cyanogen into the reaction region of the SIFT apparatus in which the m/z 129 isotope of Xe^+ was established as the dominant ion. The loss curve for Xe^+ shows initial curvature followed by only a gradual decay. There is a sharp concomitant growth and decay in $C_2N_2^+$ and further reactions with C_2N_2 to form polymeric ions of the type $(C_2N_2)_x^+$. Also the cluster ion $Xe^+\cdot C_2N_2$ is observed to be formed as a product ion.

Overall the observations shown in Fig. 1 show a complicated behaviour. However, the behaviour may be understood if one recognizes the existence of the spin states of Xe^+ with configurations $^2P_{3/2}$ (lowest energy) and $^2P_{1/2}$ formed initially by electron impact, and if one allows for a possible difference in the reactivity of these two spin states (6). A difference in reactivity can be expected simply from a consideration of energetics. The recombination energies of $Xe^+(^2P_{3/2}) = 12.13$ eV and $Xe^+(^2P_{1/2}) = 13.44$ eV are such that charge transfer with C_2N_2, IE = 13.374 ± 0.008 eV (7), is endothermic for the $^2P_{3/2}$ state and slightly exothermic for the $^2P_{1/2}$ state.

The decay of Xe^+ shown in Fig. 1 contains contributions from both Xe^+ spin states and may be analysed in the manner described by Adams *et al.* for the analogous reactions of the spin states of Xe^+ with CH_4 (6). The decay in Xe^+ at small C_2N_2 additions may be attributed to reaction of the 1/2 spin state. The sharp rise in $C_2N_2^+$ at these additions indicates that this state reacts by charge transfer and Fig. 1 shows that $C_2N_2^+$ reacts further with C_2N_2 by addition to form $(C_2N_2)_2^+$ and then $(C_2N_2)_3^+$. Small amounts of $C_3N_3^+$ appear to be produced in a biomolecular reaction of $(C_2N_2)_2^+$ with C_2N_2. The much more gradual decay in Xe^+ at higher C_2N_2 additions may be attribut-

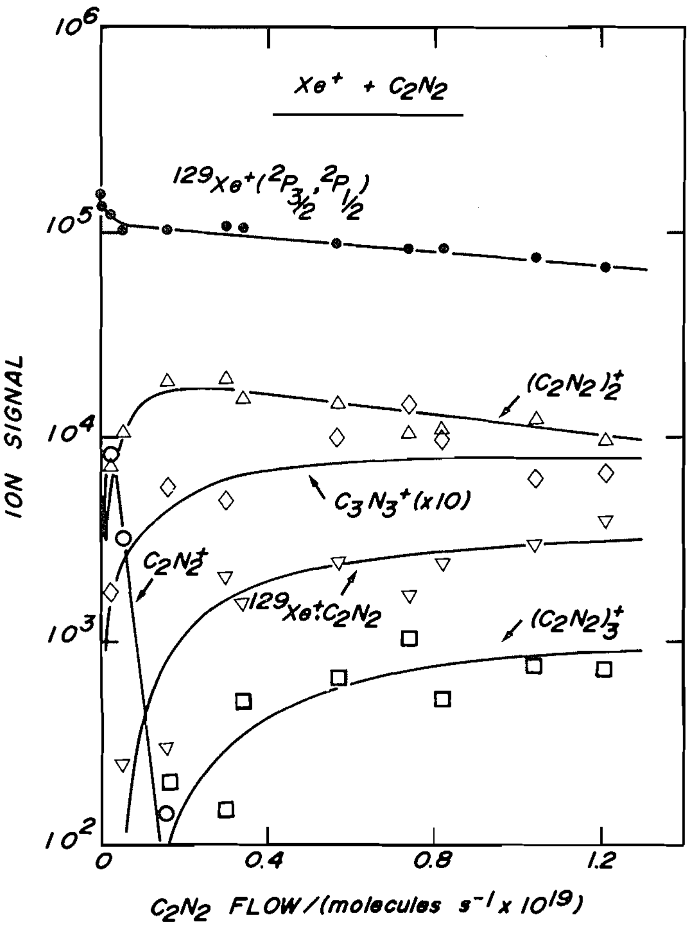

FIG. 1. The observed variation in ion signals for the addition of cyanogen into the reaction region where $^{129}Xe^+$ has been established by injection upstream into helium buffer gas. P = 0.296 Torr, $\bar{v} = 7.2 \times 10^3$ cm s^{-1}, L = 46 cm, T = 295 K. No correction has been made for mass discrimination in the mass spectrometer.

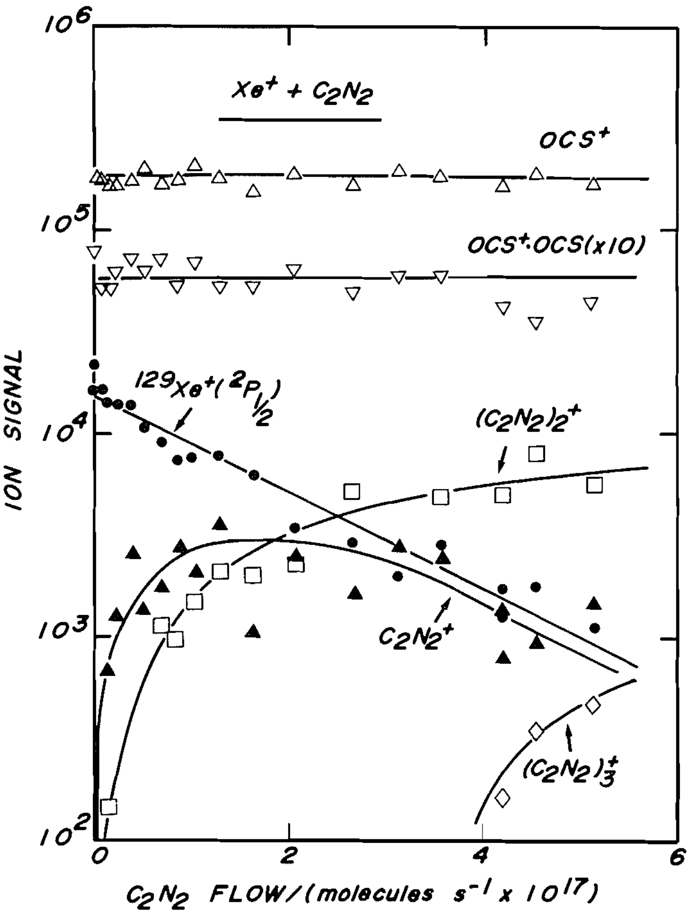

FIG. 2. The observed variation in ion signals for the addition of cyanogen into the reaction region where the 1/2 spin state of Xe^+ has been established by injection of Xe^+ and addition of 6×10^{17} molecules s^{-1} of OCS "filter gas" upstream into helium buffer gas. P = 0.298 Torr, $\bar{v} = 7.1 \times 10^3$ cm s^{-1}, L = 46 cm, T = 295 K. No correction has been made for mass discrimination in the mass spectrometer.

ed to the reaction of the 3/2 spin state and it is matched by the appearance of $Xe^+ \cdot C_2N_2$ due presumably to the thermolecular reaction [4]. The slope of this decay corresponds to an effective second-order rate constant of 4×10^{-12} cm^3 molecule^{-1} s^{-1}

$$[4] \quad Xe^+(^2P_{3/2}) + C_2N_2 + He \rightarrow Xe^+(^2P_{3/2}) \cdot C_2N_2 + He$$

at a helium density of 9.7×10^{15} atoms cm^{-3} or a third-order rate constant of 4×10^{-28} cm^6 molecule^{-2} s^{-1}. The $Xe^+(^2P_{3/2}) \cdot C_2N_2$ may add a second C_2N_2 molecule but there was no evidence for measurable amounts of $Xe^+ \cdot (C_2N_2)_2$ up to the largest flow of C_2N_2 indicated in Fig. 1. A bimolecular reaction between $Xe^+(^2P_{3/2}) \cdot C_2N_2$ and C_2N_2 is much less likely. Certainly charge transfer to produce $C_2N_2^+$ is endothermic. Also formation of $(C_2N_2)_2^+$ is exothermic only if the difference in the ionization energies of C_2N_2 and Xe (1.24 eV) is exceeded by the relative binding energies of $C_2N_2^+$ and Xe^+ (which are not known). However, the occurrence or non-occurrence of such a reaction cannot be resolved with the data in Fig. 1. The loss of $Xe^+(^2P_{3/2}) \cdot C_2N_2$ may be determined by its slow rate of formation and any $(C_2N_2)_2^+$ which might be produced is indistinguishable from the $(C_2N_2)_2^+$ produced concomitantly in large amounts from the reaction sequence initiated by the charge transfer reaction with the 1/2 spin state of Xe^+.

The 1/2 and 3/2 spin states are expected to be produced in the ion source in the ratio of 1 to 2 from statistical considerations (6). The initial reduction in the Xe^+ signal is about 25% which is sufficiently close to the statistical weight prediction (≈33%) that we may conclude that collisional quenching is not a significant loss process for the 1/2 spin state (6). This was corroborated with additional experiments in which OCS was added as a "filter gas" to study separately the reaction of the 1/2 spin state of Xe^+. Adams *et al.* (6) have shown that OCS reacts about 40 times more rapidly with the 3/2 spin state than with the 1/2 spin state. We have reproduced this result in our SIFT apparatus and added OCS upstream in a separate study of the reaction of Xe^+ with C_2N_2. Figure 2 shows observations made under these conditions. OCS^+ and $OCS^+ \cdot OCS$ are the primary and secondary products, respectively, of the charge transfer reaction of the 3/2 spin state of Xe^+ with OCS. With addition of C_2N_2 the remaining Xe^+, which is now predominantly in the 1/2 spin state, decays rapidly with a rate constant of 6.5×10^{-10} cm^3 molecule^{-1} s^{-1}. The primary charge transfer product, $C_2N_2^+$, appears and, as before, adds C_2N_2 in two sequential reactions. The Xe^+ decay is not strongly curved so that collisional quenching by C_2N_2 to form the much less reactive 3/2 spin state is not proceeding efficiently. Also $Xe^+ \cdot C_2N_2$ is observed *not* to be present in the product spectrum under these operating conditions from which we may conclude that the 1/2 spin state reacts predominantly by charge transfer.

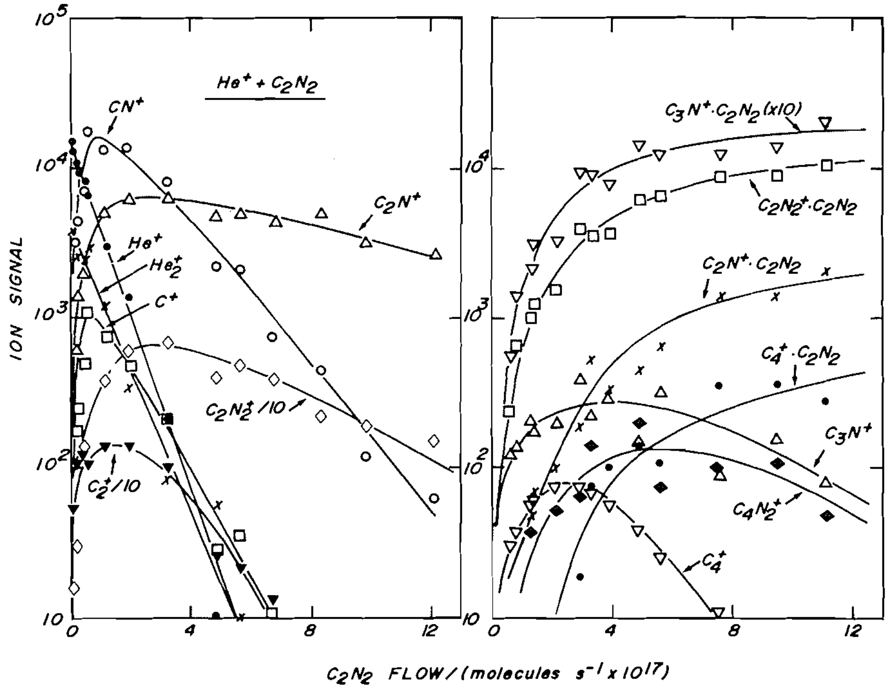

FIG. 3. The observed variation in ion signals for the addition of cyanogen into the reaction region where He^+ and He_2^+ have been established by injection of He^+ upstream into helium buffer gas. $P = 0.335$ Torr, $\bar{v} = 7.4 \times 10^3$ cm s^{-1}, $L = 46$ cm, $T = 297$ K. Left diagram: reactant ions and possible primary ions. Right diagram: secondary product ions.

To contrast the behaviour of Xe^+ towards C_2N_2 with that of another rare gas ion we have included in Fig. 3 results obtained for the reaction of He^+ which has a recombination energy of 24.6 eV which is well above the ionization energy of C_2N_2. Since helium was used as the buffer gas He_2^+ was established in the reaction region by reaction [5]. Both He^+ and He_2^+

[5] $He^+ + He + He \rightarrow He_2^+ + He$

appear to react rapidly with C_2N_2 primarily by dissociative charge transfer. The decay in the He^+ signal corresponds to a rate constant of 1.6×10^{-9} cm^3 molecule^{-1} s^{-1}. The decay in the He_2^+ is influenced in part by the depletion of the He^+ ion in the reaction region. The ions CN^+, C_2N^+, C_2^+, and C^+ were observed to be the principal primary product ions. There was no evidence for the formation of the cluster ion $He^+ \cdot C_2N_2$. The product analysis indicated that $C_2N_2^+$ was largely produced in a secondary reaction. In separate studies we have shown and characterized the occurrence of reactions [6] to [9] (8). All these reactions are seen to operate as secondary reactions in

[6] $CN^+ + C_2N_2 \rightarrow C_2N_2^+ + CN$
$\rightarrow C_3N^+ + N_2$
$\rightarrow C_2N^+ + CN_2$

[7] $C_2N^+ + C_2N_2 + He \rightarrow C_2N^+ \cdot C_2N_2 + He$

[8] $C_2^+ + C_2N_2 \rightarrow C_2N^+ + C_2N$
$\rightarrow C_3N^+ + CN$
$\rightarrow C_4^+ + N_2$

[9] $C^+ + C_2N_2 \rightarrow C_2N^+ + CN$

Fig. 3. Further C_2N_2 addition reactions establish $C_2N_2^+ \cdot C_2N_2$, $C_3N^+ \cdot C_2N_2$, $C_2N^+ \cdot C_2N_2$, and $C_4^+ \cdot C_2N_2$ already at relatively low flows of cyanogen.

The much larger variety of ion chemistry observed with He^+ in contrast to that observed with Xe^+ clearly is to be attributed to the much higher recombination energy of He^+. The high recombination energy results in charge transfer which is almost entirely dissociative so that fragment ions of $C_2N_2^+$ initiate the secondary ion chemistry. Dissociative charge transfer is endothermic with Xe^+ and the observed secondary ion chemistry appears to be initiated exclusively by $C_2N_2^+$.

Conclusions

(*1*) The two spin states of $Xe^+(^2P_{3/2}, {}^2P_{1/2})$ react differently with C_2N_2. The $^2P_{1/2}$ state which has a recombination energy *higher* than IE(C_2N_2) reacts predominantly by charge transfer while the $^2P_{3/2}$ state which has a recombination energy *lower* than IE(C_2N_2) reacts to form the adduct $Xe^+ \cdot C_2N_2$.

(*2*) The $C_2N_2^+$ charge transfer product of the reaction with $Xe^+(^2P_{1/2})$ reacts sequentially to add C_2N_2. The addition of two molecules of C_2N_2 was observed under the operating conditions adopted for the measurements reported here. The nature of the further reaction of $Xe^+ \cdot C_2N_2$ remains uncertain but we expect fast bimolecular reactions with C_2N_2 to be unlikely on thermodynamic grounds.

(*3*) If the two spin states of Xe^+ are produced in the ratio expected from statistical considerations, the ionization of Xe in a Xe/C_2N_2 mixture will result in rapid charge transfer with $Xe^+(^2P_{1/2})$ to produce $C_2N_2^+$ which quickly establishes polymeric ions of the type $(C_2N_2)_x^+$ in sequential addition reactions. Consequently the charge transfer mechanism will make a substantial contribution to the enhanced rate of polymerization of C_2N_2 observed in the radiolysis of such mixtures. Formation of the cluster ion $Xe^+ \cdot C_2N_2$ will also proceed initially but the $Xe^+ \cdot C_2N_2$ is not expected to react rapidly with C_2N_2 in a bimolecular fashion. Consequently the 3/2 spin state of Xe^+ is expected to have a relatively minor effect on cyanogen polymerization.

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