

Gas-phase reactions of some positive ions with atomic and molecular nitrogen

Graham B. I. Scott, David A. Fairley, Colin G. Freeman, and Murray J. McEwan^{a)}

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Vincent G. Anicich

Jet Propulsion Laboratory, 4800 Oak Grove Dr, Pasadena, California 91109

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The reactions of the cations CN^+ , HCN^+ , HCNH^+ , HC_3N^+ , HC_3NH^+ , H_3^+ , H_2O^+ , H_3O^+ , N_2^+ , CO^+ , HCO^+ , O_2^+ , CO_2^+ , HCO_2^+ , and C_2H_2^+ with atomic and molecular nitrogen have been characterized using a selected ion flow tube (SIFT) operating at room temperature. Rate coefficient and branching ratio data are reported for all ion-neutral reactions studied. Constraints arising from spin conservation considerations are found to be unimportant in cation-*N* atom processes. © 1998 American Institute of Physics. [S0021-9606(98)01044-7]

INTRODUCTION

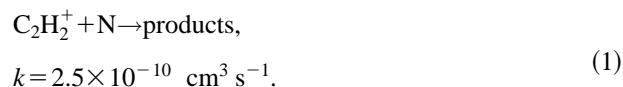
Laboratory investigations of the reactions of ions with atoms are much less common than those with molecules mainly because of difficulties in producing the atoms and monitoring their concentration. Flow tube techniques have proven to be particularly suited to the study of ion-atom reactions because of the titration methods most often used in monitoring the atom concentrations. It has been possible to overcome most of the difficulties associated with the production and monitoring of N atom densities and several ion-N atom reactions have been characterized.¹⁻⁵ Reactions with N atoms have relevance to the chemistry occurring in interstellar clouds, particularly diffuse clouds, which have larger atom-to-molecule ratios than dense clouds. N atom reactions are also pertinent to the chemistry occurring in the ionospheres of planetary bodies containing N_2 such as Earth and Titan. Indeed research relating to the aeronomy of the Earth's ionosphere provided the impetus for much of the early work in this field.

In this present study we report the results of a laboratory investigation into N atom reactions with a series of nitrile cations (R-CN^+) and other cations most of which contain an O atom. Because of the method utilized to monitor the N atom densities, it was necessary to measure reaction rate coefficients and product distributions for each ion with N_2 . These data have been reported as well.

EXPERIMENT

All the measurements reported here were made using the selected ion flow tube (SIFT) at the University of Canterbury operating at room temperature (300 ± 5) K, as has been described elsewhere.⁶ Nitrogen atoms were generated by subjecting pure N_2 to a microwave discharge, although a few experiments were conducted using 5%, 10%, and 50% mixtures of N_2 in He.

The N atoms were generated in a side arm similar in principle to the design used by Goldan *et al.*¹ and Viggiano *et al.*,⁴ except that two different side arms were used in this investigation. The first side arm was used to make relative measurements of the N atom density within the flow tube. These relative number densities were established using the reaction between $\text{C}_2\text{H}_2^+ + \text{N}$ as a reference reaction, viz



This particular reaction was chosen as it had earlier been studied in two different laboratories and each laboratory reported a rate coefficient of $k = 2.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.³⁻⁵

The second side arm (Fig. 1) enabled absolute measurements of the N atom concentration to be made. The microwave discharge cavity was located ~ 80 mm above the elbow in the quartz tubing section of the side arm. NO was introduced through an inlet consisting of a series of small holes facing into the N_2 flow. A three-coil helical section was added downstream from the NO inlet which in turn was coupled to a 71 mm i.d. length of pyrex tubing. The purpose of these two additions was to allow the N+NO titration reaction to proceed to completion, i.e.



Metastable species [$\text{N}_2(v > 0)$ and $\text{N}(^2D$ and $^2P)$] were removed from the N/ N_2 stream by a glass wool plug situated immediately downstream from the discharge.¹ The atomic nitrogen ($\text{N}(^4S)$) number density in the flow tube was then found from the semilogarithmic plot of \log [indicator ion counts] versus NO flow shown in Fig. 2 for the indicator ion O_2^+ . The graph in Fig. 2 was obtained by mass selecting and injecting Ar^+ into the flow tube and then adding a steady flow of O_2 via the upstream neutral inlet. Ground state O_2^+ ions are produced in the ensuing reaction between $\text{Ar}^+ + \text{O}_2$. Measured flow rates of nitric oxide were subsequently introduced at a downstream inlet while monitoring the O_2^+ count

^{a)}Electronic mail: m.mcewan@chem.canterbury.ac.nz

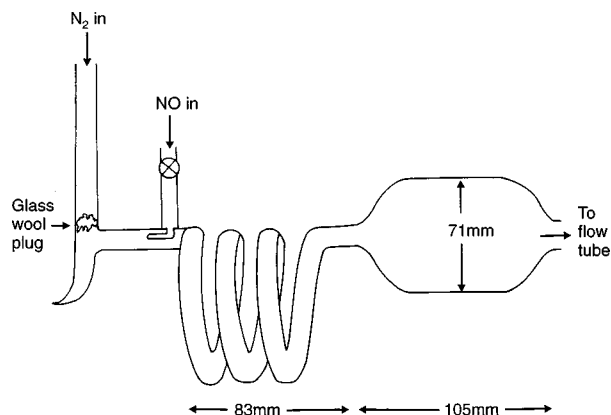


FIG. 1. Schematic diagram of the N atom probe used to determine absolute N atom densities.

rate. Atomic nitrogen was also generated at the same downstream inlet of the flow tube prior to the point of NO addition (see Fig. 1), by subjecting a monitored flow of N_2 to a microwave discharge. The resultant stream of the N/N_2 mixture contained typically 0.5%–1% of N atoms in N_2 . Nitric oxide was progressively added to the N_2/N flow, until a marked and abrupt decrease in O_2^+ signal was observed. The results were interpreted in the following way. As the flow of NO increases, more N becomes converted to O via reaction (2). There is no rapid reaction between O_2^+ and O so the O_2^+ signal increases slightly. When all the N atoms have been converted to O atoms (the so-called end point of the titration), NO enters the reaction tube and the reaction between O_2^+ and NO occurs. The transition to the steepest part of the curve in Fig. 2 corresponds to the onset of charge transfer reaction of $O_2^+ + NO$. The flow of NO corresponding to the point at which the sudden decrease in O_2^+ signal occurs represents the end point of the N+NO titration. At this point all the N atoms are converted to O atoms and the “original” (i.e., pre-NO titration) flux of N atoms equals the endpoint flow of NO. The sequence of steps depicted in Fig. 2 was then repeated for different N_2 flows and hence different N atom fluxes. The variation of N atom flux with N_2 flow is shown in Fig. 3 for a sequence of experiments performed

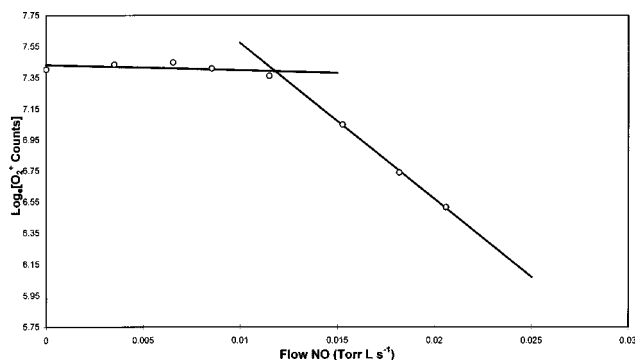


FIG. 2. A set of typical experimental data obtained from the NO titration using O_2^+ as the monitor ion. The horizontal line corresponds to the slow reaction between $O_2^+ + N$ and O atoms. The sloping line corresponds to the reaction between O_2^+ and NO. The intersection of the two lines corresponds to the end point of the titration.

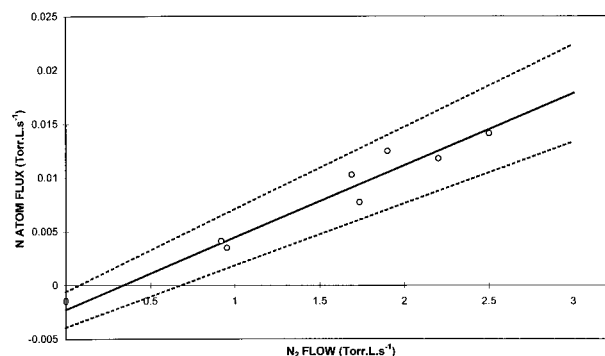


FIG. 3. A plot of N atom flux (monitored using the NO titration) against N_2 flow. These data were the results of a sequence of experiments carried out in a 4 h period. The dashed lines are the regression lines corresponding to ± 1 standard deviation.

within a 4 h period. Using the N atom number densities obtained in this way, the absolute rate coefficient for reaction (1) between $C_2H_2^+ + N$ was measured as $k = 2.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This value is in excellent agreement with the two previous measurements of this reaction.^{4,5}

A consequence of the difficulties associated with measuring atomic N fluxes is that the uncertainty in the rate coefficients we report for N atoms is $\pm 40\%$, whereas the uncertainty in the rate coefficients for stable neutral reactants is $\pm 15\%$.

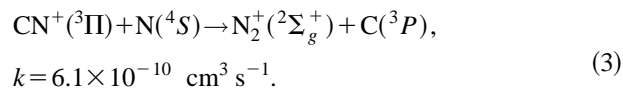
RESULTS AND DISCUSSION

The reactions of the different cations examined in this work with molecular and atomic nitrogen are summarized in Tables I and II, respectively.

Nitrile reactions. No previous reactions of nitrile cations with N atoms have been reported although the reactivity of both CN^+ and HCN^+ with N_2 has been detailed in an earlier study.

CN^+ . These ions were formed from C_2N_2 by electron impact. CN^+ undergoes a slow termolecular association with N_2 and the rate coefficient observed was in accord with earlier measurements^{7,8} except that the adduct CN^+N_2 was not reported in the earlier flow tube (SIFT) study.⁸

With $N(^4S)$ atoms, CN^+ undergoes a rapid spin-allowed reaction

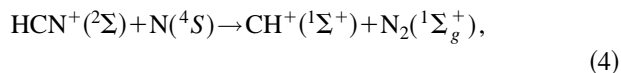


An interesting observation here is that the observed rate coefficient is significantly greater than the Langevin collision rate (k_L) weighted by the statistics of the spin allowed quartet channel; i.e., $k > (\frac{1}{2})k_L = 4.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Ferguson has noted the phenomenon of experimental rate coefficients in charge-transfer reactions that exceed the collision rate coefficient multiplied by the fractional statistical weight appropriate to the product ion and neutral.²⁷

HCN^+ , $HCNH^+$. Both of these ions were formed by electron impact on HCN in a high pressure source. Neither ion reacts with N_2 but HCN^+ undergoes a moderately fast reaction with N atoms, viz

TABLE I. Reactions of the given reactant ion with N₂.

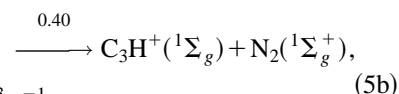
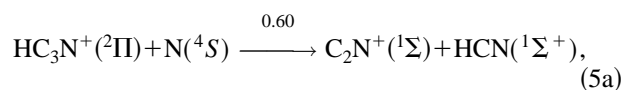
Reactant ion	Products	Branching ratio	k^a	k_{prev}^b	k_{coll}^c
CN ⁺	CN ⁺ N ₂		0.006 ^d	<0.1, ^e <0.043 ^f	8.4
HCN ⁺	NR		<0.005	<0.1 ^g	8.3
HCNH ⁺	NR		<0.005		8.2
HC ₃ N ⁺	NR		<0.005		7.2
HC ₃ NH ⁺	NR		<0.005		7.2
H ₃ ⁺	N ₂ H ⁺ +H ₂	1.0	16.3	18.5 ^h	18.7
H ₂ O ⁺	NR		<0.005	<0.1, ⁱ ~0.001 ^j	9.3
H ₃ O ⁺	NR		<0.005		9.2
N ₂ ⁺	N ₂ ⁺ N ₂	1.0	0.004 ^k	l	8.2
CO ⁺	CO ⁺ N ₂	1.0	0.005 ^m	n	8.2
HCO ⁺	NR		<0.005	<0.0004 ^o	8.2
O ₂ ⁺	NR		<0.006	p	8.0
CO ₂ ⁺	NR		<0.005		7.4
HCO ₂ ⁺	NR		<0.005	<0.0002 ^q	7.4
C ₂ H ₂ ⁺	NR		<0.005		8.4

^aObserved rate coefficient in units of 10⁻¹⁰ cm³ s⁻¹.^bPrevious determinations in units of 10⁻¹⁰ cm³ s⁻¹.^cLangevin rate coefficient in units of 10⁻¹⁰ cm³ s⁻¹.^dPseudobimolecular rate coefficient corresponding to a termolecular rate coefficient (M=He) of $k \sim 5 \times 10^{-29}$ cm⁶ s⁻¹.^eReference 7.^fReference 8.^gReference 9.^hReference 10.ⁱReference 11.^jA termolecular rate coefficient (M=He) of $k = 9 \times 10^{-30}$ cm⁶ s⁻¹ was reported in Ref. 12.^kPseudobimolecular rate coefficient corresponding to a termolecular rate coefficient (M=He) of $k \sim 3.5 \times 10^{-29}$ cm⁶ s⁻¹.^lQuite a number of measurements of the termolecular rate coefficient for this reaction have been reported: $k_3 = 1.8 \times 10^{-29}$ cm⁶ s⁻¹, Ref. 13; 1.9×10^{-29} cm⁶ s⁻¹, Ref. 14; 1.4×10^{-29} cm⁶ s⁻¹, Ref. 15; 1.8×10^{-29} cm⁶ s⁻¹, Ref. 16.^mPseudobimolecular rate coefficient corresponding to a termolecular rate coefficient (M=He) of $k \sim 3 \times 10^{-29}$ cm⁶ s⁻¹.ⁿA termolecular rate coefficient of $k = 2 \times 10^{-29}$ cm⁶ s⁻¹ was reported in Ref. 17.^oReference 18.^p $k < 1 \times 10^{-15}$ cm³ s⁻¹, Ref. 19; a termolecular rate coefficient of $k = 8 \times 10^{-31}$ cm⁶ s⁻¹ (M=He) was reported in Ref. 20.^qReference 21.

$$k = 2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.$$

Spin does not appear to be conserved in the reaction which is exothermic to ground-state products by 298 kJ mol⁻¹. The exothermicity is insufficient to access excited electronic states of different multiplicity.

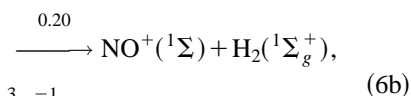
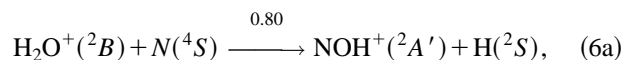
HC₃N⁺, HC₃NH⁺. Both of these ions were formed by electron impact on cyanoacetylene, HC₃N, in a high-pressure source and exhibited similar behavior to the previous case in that the only reaction observed was between HC₃N⁺+N, i.e.



$$k = 2.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.$$

As the products in both channels are singlets, spin is not conserved. The channel (5a) (60%) leading to C₂N⁺+HCN is less exothermic ($\Delta H = -95$ kJ mol⁻¹) than the 40% channel leading to C₃H⁺+N₂ ($\Delta H = -352$ kJ mol⁻¹). In each channel, there is only sufficient energy to form products in their ground electronic states.

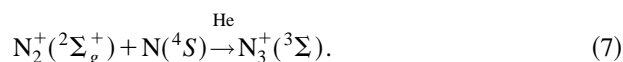
H₃⁺, H₂O⁺, H₃O⁺. The reaction between H₃⁺ and N has been discussed in detail elsewhere.²³ H₂O⁺ and H₃O⁺ were derived from electron impact on water vapor in a high-pressure source. Neither ion underwent reaction with N₂ and only H₂O⁺ exhibited a reaction with N atoms, viz



$$k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.$$

Again the most exothermic channel (NO⁺+H₂, $\Delta H = -463$ kJ mol⁻¹) has a smaller branching ratio (0.20) than does the less exothermic channel (NOH⁺+H, $\Delta H = -82$ kJ mol⁻¹). Both NOH⁺ and HNO⁺ isomers are energetically accessible. What is particularly interesting in this reaction is that one of the channels, NO⁺+H₂ [Eq. (6b)], is apparently spin forbidden while the other is spin allowed. The more exothermic spin forbidden channel has sufficient energy to only access products in the ground electronic states. The spin allowed pathway has a rate coefficient of $k = 0.80 \times 1.4 \times 10^{-10} = 1.1 \times 10^{-10}$ cm³ s⁻¹ which is $< (\frac{3}{8})k_L$ (the Langevin collision rate coefficient weighted by the statistical weight of the allowed triplet pathway). The one earlier measurement for this reaction by Viggiano *et al.*⁴ reported a rate coefficient $k = 1.9 \times 10^{-10}$ cm³ s⁻¹ which is within the experimental uncertainty of the present measurement. The earlier measurement noted the two product channels we observed for the reaction, but did not report a branching ratio.

N₂⁺. The association reaction between N₂⁺ and N₂ has been extensively investigated in many laboratories (see Table I). A slow association reaction was observed with N atoms, the pseudobimolecular rate coefficient being $k = 1.4 \times 10^{-11}$ cm³ s⁻¹.



Association reactions with atomic nitrogen are rare and even though spin is conserved, the observed rate coefficient is very much less than $(\frac{3}{8})k_L$ (the Langevin rate coefficient weighted by the statistical weight of the spin-allowed triplet

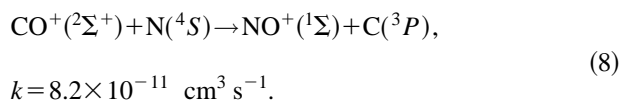
TABLE II. Reactions of the given reactant ion with N.

Reactant ion	Products	Branching ratio	k^a	k_{prev}^b	k_{coll}^c	$-\Delta H^{\circ d}/(\text{kJ mol}^{-1})$
CN ⁺	N ₂ ⁺ +C	1.0	6.1		8.1	47
HCN ⁺	CH ⁺ +N ₂	1.0	2.2		8.1	298
HCNH ⁺	NR		<0.25		8.0	
HC ₃ N ⁺	C ₂ N ⁺ +HCN	0.6				95
			2.4		7.4	
	C ₃ H ⁺ +N ₂	0.4				352
HC ₃ NH ⁺	NR		<0.25		7.4	
H ₃ ⁺	NR		<0.5 ^e		15.6	98
H ₂ O ⁺	NOH ⁺ +H	0.8				82 ^g
			1.4	1.9 ^f	8.7	
	NO ⁺ +H ₂	0.2				463
H ₃ O ⁺	NR		<0.25		8.6	
N ₂ ⁺	N ₃ ⁺	1.0	0.14 ^h	<0.1 ⁱ	8.0	
CO ⁺	NO ⁺ +C	1.0	0.82	<0.2 ^j	8.0	13
HCO ⁺	NR		<0.25		8.0	
O ₂ ⁺	NO ⁺ +O	1.0	1.0	1.2, ^k 1.8 ^l	7.8	404
CO ₂ ⁺	CO ⁺ +NO	1.0	3.4	<0.1 ^m	7.5	75
HCO ₂ ⁺	NR		<0.28		7.5	

^aObserved rate coefficient in units of 10⁻¹⁰ cm³ s⁻¹.^bPrevious determinations in units of 10⁻¹⁰ cm³ s⁻¹.^cLangevin rate coefficient in units of 10⁻¹⁰ cm³ s⁻¹.^dListed exothermicities from Ref. 22.^eThis reaction was reported elsewhere (Ref. 23) as 5×10⁻¹⁰ cm³ s⁻¹ (Ref. 23). However a recent reexamination of this reaction has found no reaction to occur (Ref. 30).^fReference 4.^gThe given enthalpy change is for the NOH⁺ isomer.^hPseudobimolecular rate coefficient corresponding to a termolecular rate coefficient $k \sim 1 \times 10^{-27}$ cm⁶ s⁻¹ (M=He).ⁱReference 24.^jReference 25.^kReference 2.^lReference 1.^mReference 26.

channel). The observed rate coefficient is in tolerable agreement with the value reported by Ferguson²⁴ as a limit to the charge-transfer reaction, bearing in mind the uncertainties of each experiment.

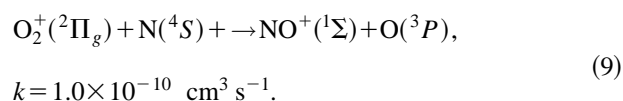
CO⁺, HCO⁺, O₂⁺, CO₂⁺, HCO₂⁺. Only CO⁺ underwent a reaction with N₂ with the product ion being the adduct, CO₂⁺N₂. We also observed a reaction between CO⁺ and N in disagreement with an earlier report on this reaction,²⁵ viz



Although spin is conserved, the rate coefficient observed is noticeably less than the Langevin rate coefficient weighted for the spin allowed triplet channel.

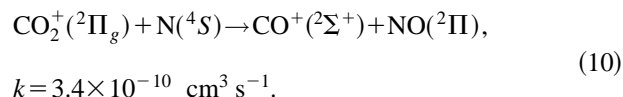
HCO⁺ was formed by electron impact on either dimethoxymethane or a 10% mixture of CO in H₂. No reaction was found with either N₂ or N.

O₂⁺ was formed by injecting Ar⁺ ions into the flow tube and adding O₂ at the first flow tube inlet to avoid the production of excited O₂⁺ metastables as discussed in the experimental section. O₂⁺ exhibits a moderately fast reaction with N in which spin is conserved, viz



Our observed rate coefficient is in agreement (within the experimental uncertainty) with the two previous measurements of $(1.8 \pm 0.2, -0.9) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ¹ and $(1.2 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ² for reaction (9).

CO₂⁺ was formed by electron impact on CO₂ and although unreactive with N₂, it did undergo a moderately fast reaction with N atoms, i.e.



Our result for this reaction is markedly different from the one previous measurement ($k < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) reported for this reaction.²⁶ We cannot explain this discrepancy as for almost all other reactions where overlap in the measurements occurred, we achieved good agreement for the reactions of N atoms. What is also unusual about reaction (10) is that even though spin is conserved, the rate coefficient slightly exceeds $(\frac{3}{8})k_L$, this being the spin weighted fraction of the allowed triplet channel.

No reactions were observed between HCO_2^+ and either N_2 or N atoms.

CONCLUDING REMARKS

The fact that ground-state atomic nitrogen is a quartet implies some interesting spin conservation constraints in the ion–N atom reactions. It is evident from the results, that spin conservation is not strongly adhered to in these reactions as was pointed out by Ferguson²⁷ who noted a number of apparent spin violations in charge-transfer reactions. Federer *et al.*⁵ in their study of ion–N atom reactions also concluded that the spin conservation constraint does not appear to be rigorous for reactions involving small positive ions. The measurements reported here certainly support their conclusions. For example, spin is not conserved in the nitrile cation–N atom reactions of HCN^+ and HC_3N^+ , yet both are relatively fast. Federer *et al.* proposed⁵ that during the ion–atom orbiting collisions that arise from the long-range electrostatic interactions, “curve crossings” take place such that there is a change in overall spin. Recently Phillips²⁸ proposed that violation of spin conservation is likely to be a common occurrence for reactions that satisfy three criteria: (1) the reaction rate is limited by the rate of capture over a long-range centrifugal barrier in an attractive potential; (2) product formation is the result of fast rearrangement of a bound collision complex, and (3) attractive short-range potentials exist for more than one spin state of the complex. The premise on which these criteria are based is that in situations where the success of a collision is determined by crossing a centrifugal barrier at long range, potential surfaces of differing multiplicity remain quasi-degenerate until the intermolecular separation is within the range when chemical effects become important. Most ion–atom reactions of the type examined in the present study satisfy these criteria.

There is no characteristic path found in the reactions of the listed cations with N atoms. Ion–atom interchange in which the N atom becomes part of the ion and it in turn releases an atom, or atom abstraction in which an atom is transferred from the ion to the N atom are the most common processes. Only one case of association was observed amongst the fifteen reactant ions studied and that was for N_2^+ . The fact that the association does occur at a reasonable rate means that in order for the $(\text{N}_3^+)^*$ complex to live long enough to be collision stabilized, the potential well to ground-state N_3^+ must lie some distance below the $\text{N}_2^+ + \text{N}$ entrance channel. The calculated well depth is 474 kJ mol^{-1} ²⁹ which is consistent with our observation.

The results for the nitrile cations are the first reported for reactions of these cations with N atoms. It is interesting to note that the most energetic of them (CN^+ , HCN^+ , HC_3N^+) all undergo rapid reactions. Again there is no common mechanistic path and the product channels most favored thermodynamically are the ones that occur. The exception is

the $\text{CN}^+ + \text{N}$ reaction. For this reaction there are two exothermic product channels possible ($\text{N}_2^+ + \text{C}$, $\Delta H = -47 \text{ kJ mol}^{-1}$ and $\text{C}^+ + \text{N}_2$, $\Delta H = -765 \text{ kJ mol}^{-1}$). Only the less exothermic channel ($\text{N}_2^+ + \text{C}$) was observed, implying that there is a substantial barrier to the $\text{C}^+ + \text{N}_2$ pathway on the CN_2^+ potential surface.

ACKNOWLEDGMENTS

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