Gas Phase Reactions of Some Positive Ions with Atomic and Molecular Oxygen and Nitric Oxide at 300 K

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Rate coefficients and product ion distributions have been determined for the reactions of $HCNH^+$, HC_3N^+, $H_2C_3N^+$, H_2O^+, N_2^+, HCO^+, and HCO_2^+ with O atoms in a selected ion flow tube at 295 ± 5 K. Only two of these ions, HC_3N^+ and N_2^+, were found to react with atomic oxygen, and both ions exhibited multiple reaction channels. Reactions with O atoms may be relevant to synthetic processes occurring in some interstellar clouds. Because of the application of the N + NO titration to determine O atom concentrations, the rate coefficient and product distribution for the reaction of each ion with O_2 and NO was also measured.

1. Introduction

Relatively few reactions involving cations and atomic oxygen have been investigated,[1−3] despite more than thirty years having elapsed since the first measurement of an ion−O atom reaction was reported.[4] Indeed the paucity of reliable experimental measurements for cation−O atom reactions is a large and obvious gap in the database of ion−neutral reactions.

The principal reason for the lack of experimental data on cation−O atom reactions is that the experiments are quite difficult to perform. Atomic oxygen is not a trivial reagent to generate and monitor. Generally O atoms have been produced by forming atomic nitrogen in a microwave discharge of N_2 and then titrating the N atoms (∼1% of the N_2 flow) with measured flow rates of nitric oxide to form known fluxes of atomic oxygen, viz.[3,5]

$$N + NO \Rightarrow O + N_2 \qquad (1)$$

$$k = (3.4 \pm 1.0) \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

The first experimental study of a reaction between an ion and atomic oxygen was reported by Ferguson and colleagues in 1965.[4] These workers measured a rate constant and determined the product channels for the reaction between N_2^+ cations and O atoms, viz.[4]

$$N_2^+ + O \Rightarrow NO^+ + N \qquad (2a)$$

$$\Rightarrow O^+ + NO \qquad (2b)$$

$$k = (2.5 \pm 1.0) \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

The impetus for studying process 2 was the suggestion that it played an important role in the E and F1 regions of the earth's ionosphere.[4] Aeronomy therefore sparked the first efforts to characterize cation−O atom reactions.

Several studies of ion−O atom reactions have subsequently been reported,[6−11] again with aeronomy providing the principal motivating force for the investigations.

Fehsenfeld in 1976[12] and Viggiano et al. in 1980[13] undertook investigations of ion−O atom reactions with a different motivation: interstellar chemistry. These workers reported the reactions of several hydrocarbon ions with O atoms. The hydrocarbon ions they examined were found to react with O atoms via multiple channels including C^+ transfer, C atom transfer, CH transfer, CH^+ transfer, and other fragmentation pathways. Most recently Le Page et al.[14] examined the reactions of the prototypical polycyclic aromatic hydrocarbon (PAH) cations $C_{10}H_6^+$, $C_{10}H_7^+$, and $C_{10}H_8^+$ with O atoms. Of these, only the $C_{10}H_8^+$ species was found to react.

In the present work we extend the existing database by examining for the first time the reactions of atomic oxygen with nitrile cations, protonated nitriles, and protonated carbon oxides, as well as reporting a reexamination of the N_2^+ + O reaction.

As an adjunct to the primary task of establishing the rate coefficients and product distributions for the reactions of the selected cations with O atoms, experimental data are also obtained for the reactions of all cations studied with molecular oxygen and nitric oxide.

2. Experimental Section

The well-established NO titration procedure[13,15] was used to determine rate coefficients and product branching ratios for all of the O atom reactions reported in this paper.

Figure 1 of ref 16 shows a schematic diagram of the neutral probe used for this study. Essentially, the experimental methodology involved establishing a microwave discharge in pure (100%) nitrogen, thereby generating a small but sufficient flux of atomic nitrogen, (∼0.5% fractional dissociation was typical). Vibrationally excited N_2 molecules and metastable N atoms (^2D and ^2P) were removed from the neutral flow by a small glass wool plug located a short distance (∼5 cm) downstream of the discharge region.[3,15] Measured flow rates of nitric oxide were

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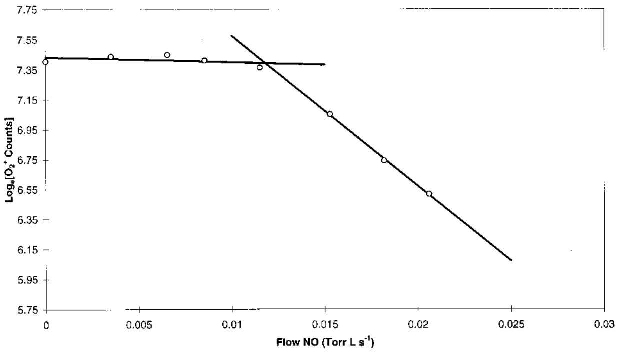

Figure 1. A set of typical data for the reaction of N_2^+ with N atoms, O atoms, and NO. The endpoint of the NO titration is clearly visible as the intersection of the two solid lines. The difference in the N_2^+ signal at zero NO flow indicates a very slow reaction between N_2^+ and N atoms.

admitted through a secondary reactant inlet protruding into the neutral flow immediately downstream of the probe's elbow; in this way known flow rates of atomic oxygen were formed via reaction 1. Sufficient flow time was available for the N + NO titration reaction to proceed to completion in the side tube.

The endpoint of the titration reaction, F_{endpoint}, was readily apparent for most systems as the intersection between two linear decays on a semilogarithmic plot of Ln[Cation$^+$] versus NO flow rate. Figure 1 illustrates this phenomenon for the NO titration of N_2^+. Additionally, for many reactions the endpoint of the titration reaction may be discerned by monitoring the appearance of product ion(s), provided they have been unequivocally identified as arising from the reaction of N or O atoms. Precisely at F_{endpoint}, the recorded NO flow was equal to the original flux of N atoms, (i.e., the atomic nitrogen flow before any NO had been introduced). Moreover, at the titration endpoint all of the N atoms were converted to O atoms. Determination of F_{endpoint} thus facilitated the calculation of N and O atom fluxes for any recorded NO flow. Simply put, any NO flow rate less than the F_{endpoint} was equal to the flow of O atoms, while the N atom flux for such a point was given by the difference between the original flux of N atoms and the flow of NO. This last statement is only approximately correct as atomic oxygen recombines (thereby forming O_2) more rapidly on surfaces than does atomic nitrogen. Oxygen atom recombination may cause the rate coefficient data reported in this study to be low by as much as ~20%.

The simultaneous presence of atomic nitrogen and oxygen precludes the determination of accurate product ratios except for systems in which the ionic products produced by the O atom reaction are unreactive with N atoms. This situation arises because as the O atom flux is extrapolated to zero flow, the N atom flux tends to its maximum value. This deleterious complicating feature of the NO titration procedure has not been previously discussed in the chemical literature but it may potentially skew product distribution data.

3. Results

Summaries of all of the results obtained in this work are presented in Tables 1, 2, and 3. Table 1 details the results obtained for the reactions between atomic oxygen and seven non-hydrocarbon cations. Tables 2 and 3 tabulate the data obtained for the reactions of these same ions with O_2 and NO, respectively.

All data were obtained at room temperature, 295 ± 5 K, and at flow tube pressures between 0.3 and 0.35 Torr. Owing to the inherent difficulties in accurately determining O atom fluxes, the rate coefficients for the reactions of the various cations with atomic oxygen are considered accurate to ±40%. In contrast, the appropriate error for the reactions of these same species with either NO or O_2 is ± 15%.

TABLE 1: Reaction Rate Coefficients and Product Distributions for the Reaction of the Specified Cations with Atomic Oxygen

reactant ion	products (branching ratio)	k_{obs}[a]	k_{prev}[b]	k_{coll}[c]	ΔH° (kJ mol^{-1})[d]
$HCNH^+$	no reaction	<0.25		6.6	
HC_3N^+	$C_3NO^+ + H$ (0.50)	4.1		6.0	
	$HC_2N^+ + CO$ (0.40)				−301.4
	HC_3NO^+ (0.10)				−651.1[e]
$H_2C_3N^+$	no reaction	<0.25		6.0	
H_2O^+	no reaction	<0.57		7.2	
N_2^+	$NO^+ + N$ (0.95)	1.4	1.4[f]	6.6	−295.3
	$O^+ + NO$ (0.05)		2.5[g]		−98.3
HCO^+	no reaction	<0.25		6.5	
HCO_2^+	no reaction	<0.25		6.1	

[a] Observed rate coefficient in units of 10^{-10} cm^3 s^{-1}. [b] Rate coefficients determined in other laboratories, in units of 10^{-10} cm^3 s^{-1}. [c] Langevin collision rate in units of 10^{-10} cm^3 s^{-1}. k_{coll} values were calculated according to the parameterized theory of Su and Chesnavich.[17] [d] The listed exothermicities are taken from Mallard.[18] [e] Thermochemistry for the NCCH=C=O$^+$ cation. [f] References 7, 9, and 19. [g] Reference 4.

TABLE 2: Reaction Rate Coefficients and Product Distributions for the Reaction of the Specified Cations with Molecular Oxygen

reactant ion	products (branching ratio)	k_{obs}[a]	k_{prev}[b]	k_{coll}[c]	ΔH° (kJ mol^{-1})[d]
$HCNH^+$	no reaction	<0.005		7.6	
HC_3N^+	$HCO^+ + CO +$ CN (0.55)	0.05	0.025[e]	6.6	−322.7[f]
	$HC_3N^+{\cdot}O_2$ (0.45)				
$H_2C_3N^+$	no reaction	<0.005		6.6	
H_2O^+	$O_2^+ + H_2O$ (1.0)	2.5	1.5[g], 4.3[h] 5.2[i], 3.3[j] 12.9[k], 2.0[l] 4.6[m]	8.6	−51.5
N_2^+	$O_2^+ + N_2$ (1.0)	0.51	0.98[n], 0.49[o] 0.51[p], 0.47[q] 0.457[r], 0.50[s] 0.90[t], 0.60[u] 0.65[v], 1.0[x] 1.1[y], 0.42[z]	7.6	−338.1
HCO^+	no reaction	<0.005	<0.5[A] <0.002[B]	7.5	
HCO_2^+	no reaction	<0.005		6.8	

[a] Observed rate coefficient in units of 10^{-10} cm^3 s^{-1}. [b] Rate coefficients determined in other laboratories, in units of 10^{-10} cm^3 s^{-1}. [c] Langevin collision rate in units of 10^{-10} cm^3 s^{-1}. k_{coll} values were calculated according to the parameterized theory of Su and Chesnavich.[17] [d] The listed exothermicities are taken from Mallard et al.[18] [e] Reference 20. [f] Thermochemistry based on the HCO^+ cation, (not HOC^+). [g] Reference 21. [h] Reference 22. [i] Reference 1. [j] Reference 23. [k] Reference 24. [l] Reference 25. [m] Reference 26. [n] Reference 27. [o] Reference 28. [p] References 29 and 30. [q] References 31, 32, 33, 34, and 35. [r] Reference 36. [s] Reference 37. [t] Reference 38. [u] Reference 39. [v] Reference 40. [x] References 15 and 40. [y] Reference 41. [z] Reference 42. [A] Reference 43. [B] Reference 44.

Previous measurements, where they exist, are listed in column 4 of each table.

4. Discussion of Results

(i) The nitrile and Protonated Nitrile Cations, ($HCNH^+$, HC_3N^+, and $H_2C_3N^+$), with O/O_2/NO. $HCNH^+$ was formed

TABLE 3: Reaction Rate Coefficients and Product Distributions for the Reaction of the Specified Cations with Nitric Oxide

reactant ion	products (branching ratio)	k_{obs}[a]	k_{prev}[b]	k_{coll}[c]	ΔH^o (kJ mol^{-1})[d]
$HCNH^+$	no reaction	<0.14		8.5	
HC_3N^+	$NO^+ + HC_3N$ (1.0)	1.8		7.4	−228.0
$H_2C_3N^+$	no reaction	<0.23		7.4	
H_2O^+	$NO^+ + H_2O$ (1.0)	3.6	4.4[e], 4.5[f] 5.9[g], 3.6[h] 11[i]	9.6	−323.4
N_2^+	$NO^+ + N_2$ (1.0)	3.6	3.0[j], 4.40[k] 4.8[l], 3.3[m] 5.0[n]	8.5	−610.0
HCO^+	no reaction	<0.005		8.4	
HCO_2^+	$HNO^+ + CO_2$ (1.0)	0.18	<1.0[0]	7.6	−2.4[p]

[a] Observed rate coefficient in units of 10^{-10} cm^3 s^{-1}. [b] Rate coefficients determined in other laboratories, in units of 10^{-10} cm^3 s^{-1}. [c] Langevin collision rate in units of 10^{-10} cm^3 s^{-1}. k_{coll} values were calculated according to the parameterized theory of Su and Chesnavich.[17] [d] The listed exothermicities are taken from Mallard et al.[18] [e] Reference 21. [f] References 23 and 45. [g] Reference 22. [h] Reference 13. [i] Reference 24. [j] Reference 46. [k] Reference 34. [l] Reference 38. [m] Reference 7 and 19. [n] Reference 15 and 40. [o] Reference 47. [p] Themochemistry based on the HNO^+ cation, (not NOH^+).

via electron impact on hydrogen cyanide, HCN, while HC_3N^+ and $H_2C_3N^+$ were both derived from cyanoacetylene, HC_3N. The protonated ions, $HCNH^+$ and $H_2C_3N^+$, are unreactive with all three neutral species considered in the current study, namely O atoms, O_2, and NO.

Atomic oxygen and HC_3N^+ react via a rapid three-channel process, viz.

$$HC_3N^+(^2\Pi) + O(^3P) \Rightarrow C_3NO^+ + H(^2S)\ (0.50) \qquad (3a)$$

$$\Rightarrow HC_2N^+(^2A) + CO(^1\Sigma^+)\ (0.40) \qquad (3b)$$

$$\Rightarrow NCCCHO^+(^2A'')\ (0.10) \qquad (3c)$$

$$k = 4.1 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

The ground electronic state of C_3NO^+ is unknown, and in view of its even number of electrons may well be a singlet. If so, then spin is conserved in all three channels and the observed rate coefficient for all channels is greater than 2/6 k_L. The two major channels, (3a and 3b), proceed via H−O exchange and C atom transfer from cation to neutral, respectively, within the $(HC_3N^+{\cdot}O)^*$ complex. Carbon monoxide, being a particularly stable neutral molecule, is generated in the 40% pathway, 3b. It is interesting to note from the observation of a 10% $NCCCHO^+$ channel that the lifetime of the association complex is sufficiently long for some stabilization to occur (i.e., within the time scale for stabilizing collisions with the bath gas which is ∼0.1 μs).

HC_3N^+ also undergoes a moderately rapid charge transfer reaction with nitric oxide, NO, and a slow two-channel reaction with molecular oxygen, i.e.

$$HC_3N^+ + O_2 \Rightarrow HCO^+ + CO + CN\ (0.55) \qquad (4a)$$

$$\Rightarrow HC_3N^+{\cdot}O_2\ (0.45) \qquad (4b)$$

$$k = 5.0 \times 10^{-12}\ \mathrm{cm^3\ s^{-1}}$$

The rate coefficient obtained from the present study is double that previously reported by Fox et al.; however, the product branching ratios obtained in the two measurements are in reasonable agreement.[20]

(ii) H_2O^+ with O/O_2/NO. The water cation appears unreactive with atomic oxygen, although presumably some O atom exchange occurs which is of course, not visible without isotopic labeling. H_2O^+ also participates in moderately rapid charge transfer reactions with both O_2 and NO.

(iii) N_2^+ with O/O_2/NO. The molecular nitrogen cation reaction is perhaps the best studied of all ion−O atom reactions. N_2^+ undergoes a moderately rapid two-channel reaction with atomic oxygen viz.

$$N_2^+(^2\Sigma_g^+) + O(^3P) \Rightarrow NO^+(^1\Sigma) + N(^4S)\ (0.95) \qquad (5a)$$

$$\Rightarrow O^+(^4S) + N_2(^1\Sigma^+_g)\ (0.05) \qquad (5b)$$

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

The rate coefficient and product distribution obtained from the current study are in excellent agreement with the two most recent prior investigations of this reaction carried out in the early 1970s.[7,9,19]

Spin is conserved in both the predominant channel, 5a, and the minor charge transfer pathway, 5b. Furthermore, the observed rate coefficient for both channels is < 4/6 k_L, this being the statistical weight of the spin allowed quartet channel.

The major channel, 5a, involves transfer of a N^+ fragment from the primary cation to the reactant neutral atom, thereby forming the stable NO^+ species and a nitrogen atom. The minor pathway, 5b, proceeds by simple charge transfer from cation to atom. Reaction 5b is one of the few molecular ion−atom charge transfer processes known.[1−3] There is some uncertainty in the literature as to the rate coefficient for reaction 5b.[48] McFarland et al.[9] quote a value for the rate coefficient of reaction 5b of $k_{5b} < 1 \times 10^{-11}$ cm^3 s^{-1}. Our value is $k_{5b} = 7 \times 10^{-12}$ cm^3 s^{-1} which is consistent with their measurement.

N_2^+ also undergoes charge transfer reactions with O_2 and NO; the results tabulated in the present work are in accordance with the evaluated data of Anicich for gas phase bimolecular ion−molecule reactions.[1]

(iv) HCO^+ and HCO_2^+ with O/O_2/NO. Both the HCO^+ and HCO_2^+ cations are unreactive with atomic and molecular oxygen. HCO^+ is also unreactive with NO; however, HCO_2^+ reacts with this neutral via a slow proton transfer reaction. This finding is in agreement with the sole previous measurement of the $HCO_2^+ + NO$ reaction by Roche and co-workers.[47]

5. Conclusions

An examination of the data in Table 1 indicates that few of the seven non-hydrocarbon species examined in the current study are reactive with O atoms. Specifically, $HCNH^+$, HCO^+, HCO_2^+, H_2O^+, and $H_2C_3N^+$are unreactive with atomic oxygen. The first three of the ions are observed interstellar species,[49] and interestingly this trio are also unreactive with H_2, N_2, N, and O,[1,2] (as also is $H_2C_3N^+$). It appears then that these cations are less reactive, particularly when located in an environment where the four neutrals cited above are among the most plentiful neutral species.[49,50] Only HC_3N^+ and N_2^+ undergo reactions with O but neither of these cations have been detected in the interstellar medium to date.[49] N_2^+ is unlikely to be detected because of its rapid reaction with H_2 but HC_3N^+ exhibits only very slow reaction with H_2,[1] indicating that a barrier may be present on the potential surface making the reaction with H_2 prohibitively slow at the temperatures of interstellar clouds.

Cyanoacetylene, (HCCCN), has, however, been detected in interstellar clouds.[49]

The two cations that were observed to react with atomic oxygen in the current study, HC_3N^+ and N_2^+, did so relatively rapidly, via multiple product channels. This finding suggests that the potential energy surfaces for the transition states may be complex. Moreover, in the case of the $HC_3N^+ + O$ reaction there is no clearly predominant product channel. Notwithstanding the observation of the minor (10%) adduct formation channel for the $HC_3N^+ + O$ reaction, the systems examined in the present work show little propensity to participate in termolecular association processes. In other words, the association complex formed in the ion−atom collision is short-lived ($\ll 0.11\ \mu s$) on the time scale of a flow tube experiment. This outcome is different from that observed for the reactions between various cations and either H or N atoms;[51,52] however, the reasons for the divergent behavior are unclear. Note also that the two viable cation−O atom reactions encountered in this work demonstrate a tendency to generate particularly stable neutral molecules such as CO and NO.

Three of the cations examined participate in reactions with O_2, namely HC_3N^+, H_2O^+, and N_2^+. These last two reactions proceed by charge transfer, generating O_2^+, which, while not yet detected in the interstellar medium,[49] is very likely to be present. These same cations, along with HCO_2^+, also react with NO mainly via moderately rapid charge transfer processes. A large body of data exists in the scientific literature for the reaction of positive ions with both O_2 and NO and the reactions reported here further enlarge this database.[1,2]

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References and Notes

(1) Anicich, V. G. *J. Phys. Chem. Ref. Data* **1993**, *22*, 1469.

(2) Ikezoe, Y.; Matsuoka, S.; Takebe, M.; Viggiano, A. *Gas-Phase Ion-Molecule Reaction Rate Constants Through 1986*; Maruzen: Tokyo, Japan, 1987.

(3) Sablier, M.; Rolando, C. *Mass Spectrom. Rev.* **1993**, *12*, 285.

(4) Ferguson, E. E.; Fehsenfeld, F. C.; Goldan, P. D.; Schmeltekopf, A. L.; Schiff, H. I. *Planet. Space Sci.* **1965**, *13*, 823.

(5) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling,* Evaluation Number 10, JPL Publication 92-20, JPL, CIT, Pasadena, California, 1992.

(6) Fehsenfeld, F. C. *Can. J. Chem.* **1969**, *47*, 1808.

(7) Fehsenfeld, F. C.; Dunkin, D. B.; Ferguson, E. E. *Planet. Space Sci.* **1970**, *18*, 1267.

(8) Fehsenfeld, F. C.; Fergusson, E. E. *J. Chem. Phys.* **1972**, *56*, 3066.

(9) McFarland, M.; Albritton, D. L.; Fehsenfeld, F. C.; Fergusson, E. E.; Schmeltekopf, A. L. *J. Geophys. Res.* **1974**, *79*, 2925.

(10) Fehsenfeld, F. C. *Planet. Space Sci.* **1977**, *25*, 195.

(11) Bohme, D. K.; Mackay, G. I.; Schiff, H. I. *J. Chem. Phys.* **1980**, *73*, 4976.

(12) Fehsenfeld, F. C. *Astrophys. J.* **1976**, *209*, 638.

(13) Viggiano, A. A.; Howorka, F.; Albritton, D. L.; Fehsenfeld, F. C.; Adams, N. D.; Smith, D. *Astrophys. J.* **1980**, *236*, 492.

(14) Le Page, V.; Keheyan, Y.; Bierbaum, V. M.; Snow, T. P. *J. Am. Chem. Soc.* **1997**, *119*, 8373.

(15) Goldan, P. D.; Schmeltekopf, A. L.; Fehsenfeld, F. C.; Schiff, H. I.; Ferguson, E. E. *J. Chem. Phys.* **1966**, *44*, 4095.

(16) Scott, G. B. I.; Fairley, D. A.; Freeman, C. G.; McEwan, M. J.; Anicich, V. G. *J. Chem. Phys.* **1998**, *109*, 9010.

(17) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *72*, 5183.

(18) Webbook, Mallard, W. G., Gen Ed.; NIST: Gaithersburg, MD, 1998.

(19) Fehsenfeld, F. C.; Fergusson, E. E. *Radio Sci.* **1972**, *7*, 113.

(20) Fox, A.; Raksit, A. B.; Dheandhanoo, S.; Bohme, D. K. *Can. J. Chem.* **1986**, *64*, 399.

(21) Shul, R. J.; Passarella, R.; DiFazio, L. T., Jr.; Keesee, R. G.; Castleman, A. W., Jr. *J. Phys. Chem.* **1988**, *92*, 4947.

(22) Jones, J. D. C.;, Birkinshaw, K.; Twiddy, N. D. *Chem. Phys. Lett.* **1981**, *77*, 484.

(23) Dotan, I.; Lindinger, W.; Rowe, B.; Fahey, D. W.; Fehsenfeld, F. C.; Albritton, D. L. *Chem. Phys. Lett.* **1980**, *72*, 67.

(24) Karpas, Z.; Huntress, W. T. *Chem. Phys. Lett.* **1978**, *59*, 87.

(25) Fehsenfeld, F. C.; Schmeltekopf, A. L.; Ferguson, E. E. *J. Chem. Phys.* **1967**, *46*, 2802.

(26) Rakshit, A. B.; Warneck, P. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1084.

(27) Schultz, R. H.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *95*, 121.

(28) Alge, E.; Lindinger, W. *J. Geophys. Res.* **1981**, *86*, 871.

(29) Adams, N. G.; Smith, D.; Paulson, J. F. *J. Chem. Phys.* **1980**, *72*, 288.

(30) Smith, D.; Adams, N. G.; Miller, T. M. *J. Chem. Phys.* **1978**, *69*, 308.

(31) Dunkin, D. B.; Fehsenfeld, F. C.; Schmeltekopf, A. L.; Ferguson, E. E. *J. Chem. Phys.* **1968**, *49*, 1365.

(32) Adams, N. G.; Smith, D. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *21*, 349.

(33) Adams, N. G.; Smith, D. *J. Phys. B* **1976**, *9*, 1439.

(34) Tichy, M.; Rakshit, A. B.; Lister, D. G.; Twiddy, N. D.; Adams, N. G.; Smith, D. *Int. J. Mass. Spectrom. Ion Phys.* **1979**, *29*, 231.

(35) Lindinger, W.; Fehsenfeld, F. C.; Schmeltekopf, A. L.; Ferguson, E. E. *J Geophys. Res.* **1974**, *79*, 4753.

(36) McFarland, M.; Albritton, D. L.; Fehsenfeld, F. C.; Ferguson, E. E.; Schmeltekopf, A. L. *J. Chem. Phys.* **1973**, *59*, 6620.

(37) Warnech, V. P. *Ber Bunsen-Ges. Phys. Chem.* **1972**, *76*, 413.

(38) Johnsen, R.; Brown, H. L.; Biondi, M. A. *J. Chem. Phys.* **1970**, *52*, 5080.

(39) Farragher, A. L. *Trans. Faraday Soc.* **1970**, *66*, 1411.

(40) Fehsenfeld, F. C.; Schmeltekopf, A. L.; Ferguson, E. E. *Planet. Space Sci.* **1965**, *13*, 219.

(41) Warneck, P. *J. Chem. Phys.* **1967**, *46*, 502.

(42) Dreyer, J. W.; Perner, D. *Chem. Phys. Lett.* **1971**, *12*, 299.

(43) Wagner-Redeker, W.; Kemper, P. R.; Jarrold, M. F.; Bowers, M. T. *J. Chem. Phys.* **1985**, *83*, 1121.

(44) Adams, N. G.; Smith, D.; Grief, D. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 405.

(45) Durup-Ferguson, M.; Bohringer, H.; Fehey, D. W.; Ferguson, E. E. *J. Chem. Phys.* **1983**, *79*, 265.

(46) Villinger, H.; Lukac, P.; Howarka, F.; Alge, E.; Ramler, H.; Lindinger, W. *Czech. J. Phys.* **1981**, *B31*, 832.

(47) Roche, A. E.; Sutton, M. M.; Bohme, D. K.; Schiff, H. I. *J. Chem. Phys.* **1971**, *55*, 5480.

(48) Ferguson, E. E. In *Chemical Kinetics*, *International* Review of Science, Physics and Chemistry; Ser 2., Vol. 9; Herschbach, D. R., Ed.; Butterworths: London, 1976; p 93.

(49) Millar, T. J.; Farquhar, P. R. A.; Willacy, K. *Astron. Astrophys. Suppl. Ser.* **1997**, *121*, 139.

(50) Lee, H.-H.; Bettens, R. P. A.; Herbst, E. *Astron. Astrophys. Suppl. Ser.* **1996**, *119*, 111.

(51) Scott, G. B. I.; Fairley, D. A.; Freeman, C. G.; McEwan, M. J.; Adams, N. G.; Babcock, L. M. *J. Phys. Chem. A* **1997**, *101*, 4973.

(52) Scott, G. B. I.; Fairley, D. A.; Freeman, C. G.; McEwan, M. J.; Anicich, V. G. *J. Phys. Chem. A* **1999**, *103*, 1073.