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$C_mH_n^+$ Reactions with Atomic and Molecular Nitrogen: An Experimental Study

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The reactions of a series of $C_mH_n^+$ ions ($m = 1-6$; $n = 0-6$) with atomic and molecular nitrogen have been investigated using a selected ion flow tube (SIFT) operating at room temperature. Rate coefficients and product distributions are reported for the reactions studied. The hydrocarbon cations examined in this work are largely unreactive with molecular nitrogen (association is found in just three cases), whereas multiple product channels are observed in reactions between $C_mH_n^+$ ions and N atoms. For $m < 3$, some N atom incorporation into the hydrocarbon ion occurs. For $m > 3$, the N atom is usually incorporated into the neutral leaving group (as HCN).

Introduction

Flow tube studies have proven particularly suited to the investigation of ion−atom reactions. It is possible to utilize the flexibility of the flow tube to overcome the joint difficulties of atom generation and atom detection. The early investigations of ion−N atom reactions were motivated by their relevance to terrestrial ionospheric chemistry.[1−5] Two subsequent studies[6,7] explored the possibility that ion−N atom chemistry might provide important steps in interstellar cloud synthesis. Viggiano et al.[6] examined several reactions between atomic nitrogen and simple hydrocarbon ions $C_mH_n^+$ ($m = 1$ or 2, $n = 1-5$) and found that CN or CN^+ is a common reaction product. Federer et al.[7] examined the reactions of several slightly larger hydrocarbon cations containing two, three, and four carbon atoms. The latter group concluded that the dominant mechanism was the exchange of N for H with consequent formation of a C−N bond and the concomitant rupture of a C−H bond. They also noted that spin conservation did not appear to be a strong selection rule. Recently, we examined the reactions of a series of nitrile ions and ions containing O atoms with atomic nitrogen and likewise noted their apparent insensitivity to spin conservation.[8]

We report here the result of a study of a more extensive range of $C_mH_n^+$ ions ($m = 1-6$; $n = 0-6$) with N atoms. This investigation was partly motivated by the need to explore whether N atoms can be easily accommodated into the hydrocarbon skeleton in interstellar clouds, but also by the need to examine reactions that are potentially relevant to Titan's ionosphere. Titan is the largest satellite of the planet Saturn. NASA presently has a mass spectrometer aboard the Cassini spacecraft which will reach Saturn in 2004. Nitrogen is the major component of Titan's atmosphere; hence elucidating the chemistry between N atoms and the various hydrocarbon ions present in the atmosphere of this satellite is a prerequisite to correctly interpreting the mass spectra returned by the Cassini spacecraft.

Experimental Section

The measurements were carried out at room temperature (295 ± 10) K, using the selected ion flow tube (SIFT) at the University of Canterbury, which has been described elsewhere.[9] The method of production and detection of atomic nitrogen was discussed in some detail in our earlier study.[8] The salient features of the method are that molecular nitrogen is subjected to a microwave discharge in a sidearm to the main flow tube, thereby creating approximately 0.5% to 1% N in N_2. Excited species also generated in the discharge are removed by a glass wool plug.[1] The absolute number density of N in N_2 is then found by progressively adding NO in the titration reaction[8]

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

Because of the difficulties in measuring the N atom concentrations using this technique, we estimate the uncertainties in the rate coefficients reported here as ±40% for the N atom reactions, compared with ±15% for stable neutral reactants. As only small amounts of N in N_2 were produced in the microwave discharge, it was also necessary to characterize the reactivity of each $C_mH_n^+$ cation with N_2. These data are reported as well.

Results and Discussion

Rate coefficient and product distribution data for the reactions of all $C_mH_n^+$ reactant species with both molecular and atomic nitrogen are summarized in Tables 1 and 2, respectively.

CH_3^+. The methyl cation was generated by electron impact on methyl bromide. The ion undergoes a slow association reaction with N_2 (probably forming an electrostatically bound cluster ion) and a moderately fast reaction with N atoms, viz.,

$$CH_3^+(^1A) + N(^4S) \xrightarrow{0.65} HCNH^+(^1\Sigma_g) + H(^2S) \qquad (2a)$$

$$\xrightarrow{0.35} HCN^+(^2\Sigma) + H_2(^1\Sigma_g^+) \qquad (2b)$$

$$k = 9.4 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

The ion product of reaction 2a, $HCNH^+$, may also have the

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TABLE 1: Reactions of the Given Reactant Ion with N_2

reactant ion	products	branching ratio	k^a	$k_{prev}{}^b$	$k_{coll}{}^c$
CH_3^+	$CH_3^+{\cdot}N_2$		0.005^d	0.006^e	9.9
C_2H^+	$C_2H^+{\cdot}N_2$	1.0	0.029^f		8.5
$c\text{-}C_6H_5^+$	$c\text{-}C_6H_5^+{\cdot}N_2$	1.0	0.091^g		6.8
h	NR		<0.005		

[a] Observed rate coefficient in units of 10^{-10} cm^3 s^{-1}. [b] Rate coefficients measured in other laboratories in units of 10^{-10} cm^3 s^{-1}. [c] Langevin capture rate in units of 10^{-10} cm^3 s^{-1}. [d] Pseudobimolecular rate coefficient at 0.36 Torr He. The rate coefficient shown corresponds to $k_3 \sim 4.3 \times 10^{-29}$ cm^6 s^{-1} (M = He). [e] A termolecular rate coefficient of $k_3 = 5.4 \times 10^{-29}$ cm^6 s^{-1} at 300 K was reported in refs 10 and 11. [f] Pseudobimolecular rate coefficient at 0.35 Torr He. The rate coefficient shown corresponds to $k_3 \sim 2.6 \times 10^{-28}$ cm^6 s^{-1} (M = He). [g] Pseudobimolecular rate coefficient at 0.32−0.36 Torr He. The rate coefficient shown corresponds to $k_3 \sim 8.0 \times 10^{-28}$ cm^6 s^{-1} (M = He). [h] No reaction ($k < 5 \times 10^{-13}$ cm^6 s^{-1}) was observed for $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$, C_3^+, C_3H^+, $C_3H_2^+$, ac-$C_3H_3^+$, c-$C_3H_3^+$, $C_3H_5^+$, $C_4H_2^+$, $C_4H_3^+$, $C_6H_2^+$, $C_6H_3^+$, ac-$C_6H_5^+$, and c-$C_6H_6^+$.

H_2NC^+ structure, as the reaction leading to the H_2NC^+ product ion is exothermic by ∼239 kJ mol^{-1}. Similarly, in reaction 2b, the ion product designated HCN^+ could also be HNC^+, as the reaction leading to its formation is exothermic by 160 kJ mol^{-1}. Our observed rate coefficient for reaction 2 is within the experimental uncertainty of two previous measurements of this reaction.[7,13] Neither of the earlier studies reported a product distribution, although the product ions we observed were recorded. Spin is not conserved in either product channel. The question of why many ion−atom reactions do not appear to conserve spin has been discussed previously by Ferguson[7,14] and other workers.[8]

C_2H^+. The C_2H^+ ion was formed by electron impact on a 10% mixture of C_2H_2 in helium and is found to undergo slow association with N_2. The C_2H^+/N reaction was not examined in this study and has been reported elsewhere.[6,7]

$C_2H_2^+$, being also formed by electron impact on C_2H_2, is unreactive with N_2 but exhibits a moderately fast reaction with N atoms.

$$C_2H_2^+(^2\Sigma) + N(^4S) \xrightarrow{0.60} HCCN^+(^2A) + H(^2S) \qquad (3a)$$

$$\xrightarrow{0.25} HCNH^+(^1\Sigma_g) + C(^3P) \qquad (3b)$$

$$\xrightarrow{0.10} C_2N^+(^1\Sigma) + H_2(^1\Sigma_g{}^+) \qquad (3c)$$

$$\xrightarrow{0.05} CH^+(^1\Sigma) + HCN(^1\Sigma^+) \qquad (3d)$$

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

Our measured value for the rate coefficient is in excellent agreement with the two earlier measurements of this reaction ($k = 2.5 \times 10^{-10}$ cm^3 s^{-1}).[6,7] The major product channel reported in all studies is the spin-allowed pathway resulting in H, N exchange [reaction 3a]. Federer et al.[7] noted that the rate coefficient for this channel of $k = 1.4 \times 10^{-10}$ cm^3 s^{-1} is less than the Langevin capture rate, k_L, multiplied by the statistical weight of the spin allowed triplet pathway (i.e., $k < (3/8)(0.6\ k_L)$). Channel 3b, the second most important channel, is also spin allowed but was not reported in the two earlier studies. This reaction pathway requires substantial rearrangement within the collision complex.

$C_2H_3^+$. This ion was produced by collisional dissociation of $C_2H_5^+$ (generated by electron impact on C_2H_5Br) during the injection process. A slow reaction with N atoms is found, viz.,

$$C_2H_3^+(^1A) + N(^4S) \xrightarrow{>0.90} HC_2N^+(^2A) + H_2(^1\Sigma_g{}^+) \qquad (4a)$$

$$\xrightarrow{<0.10} H_2C_2N^+(^1A_1) + H(^2S) \qquad (4b)$$

$$k = 2.2 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

The rate coefficient observed is 1 order of magnitude smaller than that reported by Federer et al. ($k = 2.2 \times 10^{-10}$ cm^3 s^{-1}),[7] who also apparently did not observe the minor channel (4b). In their study they produced $C_2H_3^+$ by electron impact on C_2H_6, but it seems unlikely that the different precursor used is responsible for this inconsistency. We discuss this discrepancy further in comments pertaining to the $C_3H_3^+$ cation. The reaction appears to violate spin conservation.

$C_2H_4^+$. This ion was made by electron impact on ethylene and undergoes a moderately fast reaction with N atoms, i.e.:

$$C_2H_4^+(^2A) + N(^4S) \rightarrow CH_2CNH^+(^2B_1) + H(^2S) \qquad (5)$$

$$k = 3.0 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

Spin is conserved in the reaction, and we note that the rate coefficient $k \sim (3/8)k_L$, which is the Langevin collision rate multiplied by the statistical weight of the spin-allowed H ↔ N pathway.

$C_2H_5^+$ was made by electron impact on C_2H_5Br and does not exhibit any reaction with N_2 or N.

$C_3H_n^+$. The ions C_3^+, C_3H^+, $C_3H_2^+$ and $C_3H_3^+$ were all generated from propyne, $HC{\equiv}CCH_3$, by electron impact.

C_3^+ is unreactive with N_2 yet undergoes an unusual but rapid reaction with N atoms, viz.,

$$C_3^+(^2B_2) + N(^4S) \rightarrow C_3N^+(^3\Sigma) \qquad (6)$$

$$k = 2.3 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

Spin is conserved in the reaction and the observed rate coefficient is close to the Langevin capture rate multiplied by the statistical weight of the spin-allowed triplet pathway (i.e., $(3/8)k_L$). The unusual feature of the C_3^+/N reaction is the very fast association channel, which is presumably termolecular, at flow tube conditions of 0.35 Torr helium. Generally, ion−atom association is uncommon due to the large amount of energy required to be accommodated among the various modes of the complex but it can occur even for reactant ions containing as few as 4−5 atoms, providing there is a stable association product ion. This association product is generally a covalently bound ion. In the present case, the rapid association observed is presumably a consequence of the deep well in the C_3N^+ potential energy surface corresponding to either $CCCN^+$ or $CNCC^+$. Assuming the N atom attacks the terminus of the C_3^+ cation, the resultant $CCCN^+$ product ion lies 638 kJ mol^{-1} below the C_3^+ + N entrance channel energy.[15] Alternatively, the association product is conceivably c-C_3N^+, as this species is quite stable, lying 542 kJ mol^{-1} below the reactant entrance channel.[15]

C_3H^+. Like C_3^+, C_3H^+ is unreactive with N_2 but undergoes a relatively fast reaction with N atoms, i.e.

$$C_3H^+(^1\Sigma_g) + N(^4S) \xrightarrow{0.90} C_3N^+(^3\Sigma) + H(^2S) \qquad (7a)$$

$$\xrightarrow{0.10} HC_3N^+(^2\Pi) \qquad (7b)$$

$$k = 2.7 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

TABLE 2: Reactions of the Given Reactant Ion with N

reactant ion	products	branching ratio	k[a]	k_{prev}[b]	k_{coll}[c]	$-\Delta H°/(kJ\ mol^{-1})$[d]
CH_3^+	$HCNH^+ + H$	0.65	0.94	0.67[e]	9.1	401
	$HCN^+ + H_2$	0.35				118
$C_2H_2^+$	$HC_2N^+ + H$	0.60				52
	$HCNH^+ + C$	0.25				139
			2.4	2.5[f]	8.1	
	$C_2N^+ + H_2$	0.10				85[g]
	$CH^+ + HCN$	0.05				43
$C_2H_3^+$	$HCCN^+ + H_2$	>0.90				54
			0.22	2.2[h]	8.1	
	$H_2CCN^+ + H$	<0.10				154
$C_2H_4^+$	$CH_2CNH^+ + H$	1.0	3.0		8.0	317[i]
$C_2H_5^+$	NR		<0.23		8.0	
C_3^+	C_3N^+	1.0	2.3[j]		7.7	542[k]
C_3H^+	$C_3N^+ + H$	0.9				594
			2.7[l]		7.7	
	HC_3N^+	0.1				383
$C_3H_2^+$	$C_2H_2^+ + CN$	0.85				90[m]
			0.44		7.7	
	$HCNH^+ + C_2$	0.15				76[m]
ac-$C_3H_3^+$	$HC_3N^+ + H_2$	1.0	0.58	1.3[n]	7.6	180
c-$C_3H_3^+$	NR		<0.25		7.6	
$C_3H_5^+$	NR		<0.25	1.25[n]	7.6	
$C_4H_2^+$	$C_3H^+ + HCN$	0.90				166
	$C_4HN^+ + H$	0.05	1.9		7.4	
	$HCNH^+ + C_3$	0.05				113
$C_4H_3^+$	NR		<0.25		7.4	
$C_6H_2^+$	$C_5H^+ + HCN$	1.0	1.9		7.1	
c-$C_6H_5^+$	$C_5H_4^+ + HCN$	1.0	0.37		7.1	147[o]
ac-$C_6H_5^+$	NR		<0.5		7.1	
$C_6H_6^+$	$C_5H_5^+ + HCN$	>0.95				259[p]
			1.4		7.1	
	$C_3H_3^+ + C_3H_3N$	<0.05				189[q]

[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 capture rate in units of 10^{-10} cm^3 s^{-1}. [d] The listed thermochemistry is from ref 12. [e] See refs 7 and 13. [f] See refs 6 and 7. [g] Thermochemistry is for the CCN^+ structure. [h] See ref 7. [i] Thermochemistry is for the CH_2CNH^+ structure. [j] The rate coefficient shown is for flow tube pressures between 0.36 Torr and 0.5 Torr. The termolecular rate coefficient for this association pathway is estimated as $k_3 \sim 2.0 \times 10^{-26}$ cm^6 s^{-1}. [k] Thermochemistry is for the c-C_3N^+ structure. [l] Pseudobimolecular rate coefficient. The rate coefficient corresponds to $k_3 \sim 2.4 \times 10^{-27}$ cm^6 s^{-1} (M = He). [m] Thermochemistry is for the $HC{\equiv}CCH^+$ reactant ion. [n] See ref 7. [o] Thermochemistry assuming the structure $H_2C{=}C{=}C{=}C{=}CH_2^+$. [p] Thermochemistry assumes the cyclopentadienyl cation structure. [q] Thermochemistry assumes the cyclopropenyl cation structure and acrylonitrile.

The major channel is the more exothermic bimolecular channel that occurs as the result of H and N interchange. The 10% association channel is similar to the $C_3^+ + N$ adduct formation process in that the association reaction in 0.35 Torr of helium is probably termolecular, corresponding to a rate coefficient $k_3 \sim 2.4 \times 10^{-27}$ cm^6 s^{-1} (M = He). Again the stability of the HC_3N^+ complex may be attributed to the deep potential well encountered by the interacting species as they proceed along the reaction coordinate. Assuming the adduct has the HC_3N^+ structure, this well has a depth of 594 kJ mol^{-1}.

$C_3H_2^+$. As this ion was produced from propyne by electron impact, a mixture of linear and cyclic isomers of $C_3H_2^+$ are likely to be formed.[16] From our previous studies we know that the linear isomer is present in a greater amount. No evidence was found for any difference in reactivity with N atoms between the isomeric structures, and the thermochemistry in Table 2 is evaluated on the basis that $C_3H_2^+$ is the linear isomer. A slow reaction with N atoms is observed, yielding two product channels, viz.,

$$C_3H_2^+(^2A') + N(^4S) \xrightarrow{0.85} C_2H_2^+(^2\Sigma) + CN(^2\Sigma^+) \tag{8a}$$

$$\xrightarrow{0.15} HCNH^+(^1\Sigma_g) + C_2(^3\Pi_u) \tag{8b}$$

$$k = 4.4 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

The major channel, (8a), is the more exothermic and is accessed via simple C atom transfer from the reactant cation, whereas the $HCNH^+ + C_2$ channel requires substantial rearrangement within the complex.

$C_3H_3^+$. Like $C_3H_2^+$, $C_3H_3^+$ can be present as cyclic or acyclic isomers. To distinguish between them, one of the isomers, c-$C_3H_3^+$, was formed via the reaction of $C_2H_4^+$ with C_2H_2, viz.,

$$C_2H_4^+ + C_2H_2 \rightarrow c\text{-}C_3H_3^+ + CH_3 \tag{9}$$

There is only sufficient energy available in reaction 9 to form the cyclic isomer, which is unreactive with both N atoms and N_2. Electron impact on propyne forms a mixture of the two isomers in the ratio ~60% c-$C_3H_3^+$, ~40% ac-$C_3H_3^+$ as determined by examining the subsequent reactivity of the (c, ac) $C_3H_3^+$ mixture with C_2H_2.[17] We found ac-$C_3H_3^+$ reacts slowly with N atoms, viz.,

$$ac\text{-}C_3H_3^+(^1A) + N(^4S) \rightarrow HC_3N^+(^2\Pi) + H_2(^1\Sigma_g^+) \tag{10}$$

$$k = 5.8 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

These data differ from the earlier observation of Federer et al.,[7] who reported a larger rate coefficient ($k = 1.3 \times 10^{-10}$ cm^3 s^{-1}) and a different reaction product ($HC_3NH^+ + H$). The value for k reported in the earlier study lies just outside the margin of error of the two experiments. It is not clear why these differences exist for the two reactions 4 and 10, when good agreement is found in other reactions common to both investigations. In each of the reactions 4 and 10, the precursor gases used to generate the ion were different but it is unlikely that this should prove to be significant. Perhaps more influential is that the earlier studies were carried out at energies estimated around 0.12 eV in a combined flow drift tube,[7] whereas the data in the present study were gathered at room temperature. We also note that recent calculations of the potential energy surface for c-$C_3H_3^+$ + N do not show a pathway to products from (^{4}S) N atoms but do for (^{2}D) N atoms.[18]

$C_3H_5^+$ ions were generated from secondary reactions following electron impact on ethylene in a high-pressure ion source. The $C_3H_5^+$ ions generated under these conditions are thought to exist as the allyl cation structure.[19] No reaction is observed with either N_2 or N atoms ($k < 2.5 \times 10^{-11}$ cm^3 s^{-1}), but the results for N are in conflict with the one earlier measurement reported. Federer et al.[7] noted two product channels, $C_2H_4^+$ + HCN and $H_3C_3N^+$ + H_2, having a combined rate coefficient $k = 1.25 \times 10^{-10}$ cm^3 s^{-1}. The situation is analogous to the difference in results between this work and Federer et al.[7] already noted for $C_3H_3^+$ and $C_2H_3^+$. In all three examples the thermal energy rate coefficients we report are smaller than the rate coefficients they report at ~0.12 eV in their flow drift tube. However, as we have noted earlier, the results for other N atom reactions common to both studies (e.g., CH_3^+, $C_2H_2^+$) give good agreement. One other possibility that should perhaps be considered in the present $C_3H_5^+$ case is the different $C_3H_5^+$ precursor molecules that were employed in the two studies, viz., C_2H_4 in this work and C_3H_7Br in the Federer et al. investigation. We have noted that the allyl $C_3H_5^+$ cation is obtained from C_2H_4, whereas it may be possible to generate the 2-propenyl structure from C_3H_7Br. Having said that, in most reactions we have not, however, found much difference in reactivity between the allyl $C_3H_5^+$ ion and the 2-propenyl $C_3H_5^+$ ion.[20]

$C_4H_2^+$, $C_4H_3^+$. Both of these ions were generated from acetylene by electron impact in a high-pressure ion source. Neither ion is reactive with N_2 and only $C_4H_2^+$ undergoes a reaction with N atoms, viz.,

$$C_4H_2^+(^2\Pi_g) + N(^4S) \xrightarrow{0.90} C_3H^+(^1\Sigma_g) + HCN(^1\Sigma^+) \qquad (11a)$$

$$\xrightarrow{0.05} HCNH^+(^1\Sigma_g) + C_3(^1\Sigma_g^+) \qquad (11b)$$

$$\xrightarrow{0.05} C_4HN^+ + H(^2S) \qquad (11c)$$

$$k = 1.9 \times 10^{-10}\ \text{cm}^3\ \text{s}^{-1}$$

The major channel (11a) is possibly the result of end attack by N followed by fragmentation. Spin is not conserved in reactions 11a and 11b. The spin state for C_4HN^+ is not known but is likely to be a doublet, making reaction 11c spin allowed.

$C_6H_2^+$ ions were generated from acetylene by electron impact in a high-pressure ion source. This ion is unreactive with N_2 but undergoes a moderately fast reaction with N atoms via a single channel, viz.,

$$C_6H_2^+(^2\Pi_u) + N(^4S) \rightarrow C_5H^+(^1\Sigma^+) + HCN(^1\Sigma^+) \qquad (12)$$

$$k = 1.9 \times 10^{-10}\ \text{cm}^3\ \text{s}^{-1}$$

This reaction does not conserve spin, and the observed product channel appears to be the most favored on energetic grounds.

$C_6H_5^+$ ions were prepared by electron impact on bromobenzene. The $C_6H_5^+$ ions generated in this way are a mixture of cyclic and acyclic isomers, based on their subsequent reactions with N_2 and C_2H_2.[21,22] About 70% are in the cyclic form with the remaining 30% being acyclic. The semilogarithmic decay of total $C_6H_5^+$ ion counts versus N_2 flow was fitted to a double exponential decay. From this decay, ac-$C_6H_5^+$ is found to be unreactive with N_2, whereas c-$C_6H_5^+$ engages in a slow reaction giving the adduct, $C_6H_5{\cdot}N_2^+$, as the sole product. The pseudobimolecular rate coefficient corresponds to a termolecular rate coefficient $k_3 \sim 8.0 \times 10^{-28}$ cm^6 s^{-1} (M = He), viz.,

$$\text{c-}C_6H_5^+ + N_2 \rightarrow \text{c-}C_6H_5{\cdot}N_2^+ \qquad (13)$$

$$k = 9.1 \times 10^{-12}\ \text{cm}^3\ \text{s}^{-1}\ \text{at 0.35 Torr He}$$

Similar behavior was also found for the reactions of the (c, ac)-$C_6H_5^+$ ions with atomic nitrogen in that only c-$C_6H_5^+$ participates in a reaction forming a single product ion, viz.,

$$\text{c-}C_6H_5^+(^1A_1) + N(^4S) \rightarrow C_5H_4^+ + HCN(^1\Sigma^+) \qquad (14)$$

$$k = 3.7 \times 10^{-11}\ \text{cm}^3\ \text{s}^{-1}$$

At least three stable isomers of $C_5H_4^+$ have been identified,[12] and all three are energetically accessible in reaction 14.

$C_6H_6^+$ ions were generated by electron impact on benzene vapor. These $C_6H_6^+$ ions are found to behave as a single isomeric form, c-$C_6H_6^+$. Although they are unreactive with N_2, a moderately fast reaction was found with atomic nitrogen, which proceeded via two pathways, viz.,

$$\text{c-}C_6H_6^+\ (^2E_{1g}) + N\ (^4S) \xrightarrow{0.95} C_5H_5^+\ (^3A'_2) + HCN\ (^1\Sigma^+) \qquad (15a)$$

$$\xrightarrow{0.05} C_3H_3^+\ (^1A) + CH_2CHCN(^1A') \qquad (15b)$$

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

Several isomers of $C_5H_5^+$ are accessible on energetic grounds, including the cyclopentadienyl cation, $HC{\equiv}CCHCH{\equiv}CH_2^+$ and the vinylcyclopropenyl cation.

Conclusions

The reaction chemistry investigated in this work and summarized in Table 1 for molecular nitrogen and Table 2 for atomic nitrogen exemplifies $C_mH_n^+$ ion chemistry in nitrogen. Molecular nitrogen is relatively unreactive to $C_mH_n^+$ ions because of the strong N≡N bond. Reactions with N_2 are therefore rare and when they are seen, they tend to occur via an association mechanism with a weak bond formed between the ion and N_2. These bonds are probably electrostatic in nature. That the bonds are weak is strongly indicated by the low termolecular association rate coefficients found.

In contrast, $C_mH_n^+$ reactions with atomic nitrogen are common with many exhibiting a multiplicity of reaction channels. The question of interest here is what happens to the N atom? Is it incorporated into the $C_mH_n^+$ ion or into the neutral fragment? A common reaction pathway for many hydrocarbon ions examined in this study involves the N atom becoming part of the neutral fragment leaving the $(C_mH_n^+{\cdot}N)^*$ complex, predominantly in the form of HCN. There are, however, a significant number of reactions of smaller hydrocarbon ions ($m \leq 3$) where the N atom is incorporated into the carbon skeleton of the ion itself, thereby converting the ion into a nitrile ion. In almost all cases, $C_mH_n^+$ ions having $m > 3$ yielded $C_{m'}H_{n'}^+$ ion products ($m' < m$, $n' < n$) and HCN.

One of the most interesting results obtained was the reaction of C_3^+ and N, where a rapid association reaction was observed, giving an extremely efficient mechanism for making C_3N^+. The fast termolecular rate coefficient of $k_3 \sim 2 \times 10^{-26}$ cm^6 s^{-1} is indicative of the formation of a strong $C_3^+{-}N$ covalent bond. It is interesting to speculate whether such reactions might be common for larger C_n^+ ions. Presumably, such a reaction might occur for C_5^+ but not for C_4^+ in view of the lower stability of the C_4N^+ ion compared to C_5N^+.

Finally, we acknowledge the characteristics observed by previous investigators of ion−N atom reactions,[7] in that spin constraints are relatively unimportant in controlling the reaction rate.

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