J. Am. Chem. Soc. 1988, 110, 5286-5290

Structural Isomers of C_2N^+: A Selected-Ion Flow Tube Study

J. S. Knight,[†] S. A. H. Petrie,[†] C. G. Freeman,*[,†] M. J. McEwan,*[,†] A. D. McLean,[‡] and D. J. DeFrees[§]

Contribution from the Department of Chemistry, University of Canterbury, Christchurch, New Zealand, IBM Research Center, 650 Harry Road, San Jose, California 95120, and Molecular Research Institute, 701 Welch Road, Suite 213, Palo Alto, California 94304.

Received November 10, 1987

Abstract: Reactivities of the structural isomers CCN^+ and CNC^+ were examined in a selected-ion flow tube at 300 ± 5 K. The less reactive CNC^+ isomer was identified as the product of the reactions of $C^+ + HCN$ and $C^+ + C_2N_2$; in these reactions only CNC^+ can be produced because of energy constraints. Rate coefficients and branching ratios are reported for the reactions of each isomer with H_2, CH_4, NH_3, H_2O, C_2H_2, HCN, N_2, O_2, N_2O, and CO_2. Ab initio calculations are presented for CCN^+ and CNC^+; a saddle point for the reaction $CCN^+ \rightarrow CNC^+$ is calculated to be 195 kJ mol^{-1} above CNC^+. The results provide evidence that the more reactive CCN^+ isomer is unlikely to be present in measurable densities in interstellar clouds.

Interest in the species C_2N^+ has arisen from its predicted presence in dense interstellar clouds.[1] Laboratory measurements have established that C_2N^+ can be formed from species known to be present in molecular clouds. These production processes are[2-5] given in eq 1 and 2 where the rate coefficients for these

$$C^+ + HCN \rightarrow C_2N^+ + H \tag{1}$$

$$He^+ + HC_3N \rightarrow C_2N^+ + CH + He \tag{2}$$

reactions are 3.0×10^{-9} and 2.8×10^{-9} cm^3 s^{-1}, respectively. Two laboratory investigations of the ion chemistry of C_2N^+ have been undertaken within the past 10 years but without regard to the isomeric form of C_2N^+.[6,7] Recently, several theoretical and experimental investigations on isomeric structures of C_2N^+ have appeared, which have prompted a reinvestigation of C_2N^+ ion chemistry. Haese and Woods[1] reported ab initio calculations on the molecular structures CNC^+ and CCN^+ and computed an energy difference between the two isomers of 205 kJ mol^{-1}. They also suggested that only the lower energy CNC^+ isomer is formed in reaction 1. Yoshimine and Kraemer[8] also carried out ab initio calculations using a large sp Slater basis set augmented with two sets of d polarization functions to compute an energy difference between CCN^+ and CNC^+ of 117 kJ mol^{-1} at the CISD + Q level (configuration interaction with all single and double substitutions and the quadruples contribution estimated by the Davidson method[9]). Kraemer, Bunker, and Yoshimine[10] used a Gaussian triple-ζ polarized basis set at the CISD + Q level of theory to compute an isomer difference of 117 kJ mol^{-1}. A calculation has also been reported of the barrier to isomerization being 272 kJ mol^{-1} above CCN^+.[11] Harland and McIntosh,[12] using the technique of "monochromatic" electron impact on the compounds C_2N_2 and CH_3NC, measured an energy difference of 106 ± 16 kJ mol^{-1} between the two isomeric forms of C_2N^+. The enthalpies of formation derived for each isomer were 1726 ± 12 kJ mol^{-1} ($\Delta H_f[CCN^+]$) and 1620 ± 11 kJ mol^{-1} ($\Delta H_f[CNC^+]$).[12] We note that the experimental thermodynamic data indicate that reaction 1 has sufficient energy to form only the lower energy CNC^+ isomer, where it is exothermic by 100 ± 11 kJ mol^{-1}. Daniel et al.[13] in a recent crossed ion beam–molecular beam study of reaction 1, at relative collision energies between 0.62 and 1.75 eV, also found evidence from the kinetic energy release that CNC^+ was the only product of the reaction.

In their discussion on the implications to astrochemistry of the two isomeric forms of C_2N^+, Haese and Woods[1] suggested that each isomer might exhibit a very different reactivity. Kraemer et al.[10] on the basis of their calculated dipole moment for CCN^+ suggested that CCN^+ might react with molecular hydrogen. The differences in reactivity of the two isomers are investigated in this study. Either CNC^+ or a mixture of CNC^+ and CCN^+ was produced in the flow tube, and hence the reactivity toward various added neutral gases was deduced.

We have also undertaken an ab initio molecular orbital study of the C_2N^+ system and of reactions 1 and 2. This provides a clear picture of the energetics of the CCN^+/CNC^+ isomerization relative to the energies of the reactants in eq 1 and 2.

Experimental Section

The measurements were performed at room temperature (300 ± 5 K) with a selected-ion flow tube (SIFT) that has been described previously.[5] In the reactions detailed in this study, the C_2N^+ ion was generated in several different ways: by electron impact on C_2N_2, CH_3CN, and HC_3N or as the product of the ion–molecule reactions $C^+ + HCN$ and $C^+ + C_2N_2$. Because of uncertainties introduced by the iterative procedure used to fit a double exponential to the curved semilogarithmic plots of m/z 38 ion signal versus neutral reactant flow, we estimate that rate coefficients in the present work are reliable to ±40%.

Reactant gases used in this study were generally of Analar grade and were vacuum distilled prior to use. Cyanogen, C_2N_2, was vacuum distilled from Matheson reagent grade; HCN was prepared by the action of phosphoric acid on KCN and was vacuum distilled after drying. Cyanoacetylene, HC_3N, was prepared by ammonolysis of methyl propiolate followed by dehydration.[14]

Theoretical Results

Ab initio molecular orbital theory was used to determine the enthalpies of reaction, $\Delta H(0\ K)$, for reactions 1 and 2 as well as $\Delta H(0\ K)$ and the potential energy barrier for the isomerization $CNC^+ \rightarrow CCN^+$. The geometries of all species were optimized at the HF/6-31G(d) level of theory; the basis set is split-valence with heavy-atom polarization.[15] The resultant geometrical parameters are given in Table I. This same level of theory was used to compute the harmonic vibrational frequencies and zeropoint vibrational energies; the frequencies and the zeropoint energy were scaled by 0.89 and are given in Table I.[16] More accurate the-

---

[†] University of Canterbury.
[‡] IBM Research Center.
[§] Molecular Research Institute.

[1] Haese, N. N.; Woods, R. C. *Astrophys. J.* **1981**, *246*, L51.

[2] Anicich, V. G.; Huntress, W. T.; Futrell, J. H. *Chem. Phys. Lett.* **1976**, *40*, 233.

[3] Liddy, J. P.; Freeman, C. G.; McEwan, M. J. *Mon. Not. R. Astron. Soc.* **1977**, *180*, 683.

[4] Schiff, H. I.; Bohme, D. K. *Astrophys. J.* **1979**, *232*, 740.

[5] Knight, J. S.; Freeman, C. G.; McEwan, M. J.; Adams, N. G.; Smith, D. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 317.

[6] Schiff, H. I.; Mackay, G. I.; Vlachos, G. D.; Bohme, D. K. In *Proceedings of the IAU Symposium on Interstellar Molecules*; Andrews, B., Ed.; Reidel: Dordrecht, The Netherlands, 1981; No. 87, p 307.

[7] McEwan, M. J.; Anicich, V. G.; Huntress, W. T.; Kemper, P. R.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *50*, 179.

[8] Yoshimine, M.; Kraemer, W. P. *Chem. Phys. Lett.* **1982**, *90*, 145.

[9] Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 5195.

[10] Kraemer, W. P.; Bunker, P. R.; Yoshimine, M. *J. Mol. Spectrosc.* **1984**, *107*, 191.

[11] Hopkinson, A., York University, unpublished data quoted in ref 1.

[12] Harland, P. W.; McIntosh, B. J. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 29.

[13] Daniel, R. G.; Keim, E. R.; Farrar, J. M. *Astrophys. J.* **1986**, *303*, 439.

[14] Moreu, C.; Bongrand, J. C. *Justus Liebigs Ann. Chem.* **1920**, *14*, 47.

[15] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

0002-7863/88/1510-5286$01.50/0 © 1988 American Chemical Society

Table I. Ab Initio Molecular Orbital Theory Results[a]

molecule	point group	HF/6-31G(d) geometry[b]	scaled HF/6-31G(d) vibrational frequencies, cm^{-1}			zero point energy, kJ mol^{-1}	MP4/6-311++G(df,pd)//6-31G(d), hartree
H	K_h						-0.499 98
C^+	K_h						-37.361 07
CN	$C_{\infty v}$	$r(CN) = 1.162$	1764 (σ)			10.5	-92.524 34
HCN	$C_{\infty v}$	$r(CN) = 1.133$ $r(CH) = 1.059$	3275 (σ)	2170 (σ)	791 (π)	41.8	-93.254 47
HNC	$C_{\infty v}$	$r(CN) = 1.154$ $r(CH) = 0.985$	3644 (σ)	2055 (σ)	481 (π)	39.7	-93.231 29
CNC^+	$D_{\infty h}$	$r(CN) = 1.227$	1294 (σ_g)	1963 (σ_u)	183 (π)	21.8	-130.143 53
CCN^+	$C_{\infty v}$	$r(CN) = 1.149$ $r(CC) = 1.383$	2257 (σ)	1077 (σ)	207 (π)	22.2	-130.110 34
SP[c]	C_s	$r(C_1N) = 1.174$ $r(CC) = 1.499$ $r(C_2N) = 1.507$ $\angle(C_2C_1N) = 67.4$	1989 (a′)	1004 (a′)	860*i* (a′)	18.0	-130.067 67
C_2N_2	$D_{\infty h}$	$r(CN) = 1.134$ $r(CC) = 1.397$	2437 (σ_g) 544 (π_g)	825 (σ_g) 248 (π_u)	2263 (σ_u)	42.7	-185.312 14[d]

[a] Many of these results have been published before; they are presented here for completeness. [b] Bond lengths in angstroms; angles in degrees. [c] Saddle point for the reaction $CCN^+ \rightarrow CNC^+$. [d] Computed using the approximation $E\{MP4/6\text{-}311{+}{+}G(df,pd)\} = E\{MP4/6\text{-}31G(d,p)\} + E\{MP2/6\text{-}311{+}{+}G(df,pd)\} - E\{MP2/6\text{-}31G(d,p)\}$. Using this approximation for the other molecules gives energies that are 7.3 ± 0.8 kJ mol^{-1} higher than the energies computed precisely except for C^+ and CNC^+ where the energy is 0.4 kJ mol^{-1} lower. This energy is used with energies computed using the approximation to generate the relative energies shown in the figure. These are -37.361 19 for C^+, -92.521 67 for CN, and -130.143 67 for CNC^+.

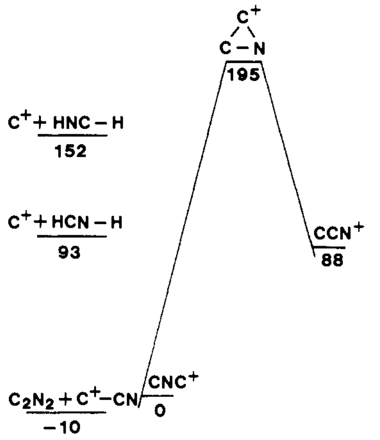

Figure 1. Energies on the C_2N^+ potential energy surface relative to CNC^+ in kilojoules per mole. These were computed at the MP4/6-311++G(df,pd)//6-31G level of theory and include scaled HF/6-31G zero point vibrational energies.

oretical values of the rotation–vibration levels for CCN^+ and CNC^+ have been reported by Kraemer, Bunker, and Yoshimine.[10] Accurate total energies were computed (using the HF/6-31G(d) geometries) with the MP4/6-311 ++ G(df,pd) theoretical model. This is fourth-order Møller–Plesset perturbation theory[17] including single, double, triple, and quadruple substitutions with the triple-split basis set augmented with a set of d and f polarization functions on heavy atoms and a set of p and d polarization functions on the hydrogens.[18] Relative energies computed at this level of theory can be expected to be accurate to roughly ±25 kJ mol^{-1}.[19]

The results of these calculations are presented in Table I. We note that a saddle point for the isomerization exists for a C_2N^+ species of triangular geometry that is 195 kJ mol^{-1} higher in energy than CNC^+ as shown in Figure 1. The difference calculated between the zero point energies of CCN^+ and CNC^+ was 88 kJ mol^{-1}, which agrees within the combined uncertainties with the recent experimental determination.[12] The previous best theoretical value of 117 kJ mol^{-1} differs primarily because it omits the important effect of triple substitutions; the different geometries used also contribute to the difference, to a lesser extent, as does the absence of f functions in the earlier calculation. Further, the calculations suggest that reaction 1 is exothermic to CNC^+

$$C^+ + HCN \rightarrow CNC^+ + H \qquad (1)$$

production by 93 kJ mol^{-1} and marginally exothermic to production of CCN^+ by 5 kJ mol^{-1}. However, the uncertainty in the calculation is greater than the calculated exothermicity of 5 kJ mol^{-1}. Furthermore, there is insufficient energy to cross the saddle point; a necessary requirement for CCN^+ production if the initial isomer formed is CNC^+. Similarly, the production of CNC^+ in reaction 3 is endothermic by 10 kJ mol^{-1} (which also is less than

$$C^+ + C_2N_2 \rightarrow CNC^+ + CN \qquad (3)$$

the uncertainty of the calculation) whereas CCN^+ production is endothermic by 98 kJ mol^{-1}. These predictions are in good agreement with the experimental results. We conclude from the results of these calculations and the experimental data that only the CNC^+ isomer can be produced in reactions 1 and 3.

Results and Discussion

As noted in the Experimental Section, C_2N^+ at *m/z* 38 was produced either by electron impact on C_2N_2, CH_3CN, or HC_3N in the ion source or by ion–molecule reaction within the flow tube. When C_2N^+ was generated by electron impact (typically 25 eV) on C_2N_2, CH_3CN, or HC_3N, then two C_2N^+ species of different reactivity were produced. These two different species, which are assumed to be the two structural isomers, were distinguished by their reactions with CH_4 added at the downstream inlet of the reaction tube. Although both isomers of C_2N^+ underwent a reaction with CH_4, the rate coefficient for reaction of each form was very different, and marked curvature in the semilogarithmic plot of the ion signal at *m/z* 38 against CH_4 flow was observed (Figure 2). We have analyzed the curved semilogarithmic decay in the ion signal using the technique described earlier[20] and have determined rate coefficients for each isomer and also the relative amounts of the two isomeric forms present. The isomer exhibiting the slower rate of reaction ($k = 4 \times 10^{-12}$ cm^3 s^{-1}) was identified

---

(16) (a) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F., Jr.; Hehre, W. J. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1981**, *15*, 269. (b) DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

(17) (a) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1978**, *14*, 91. (b) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(18) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(19) DeFrees, D. J.; McLean, A. D. *J. Comput. Chem.* **1986**, *7*, 321, and references therein.

(20) Knight, J. S.; Freeman, C. G.; McEwan, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1404.

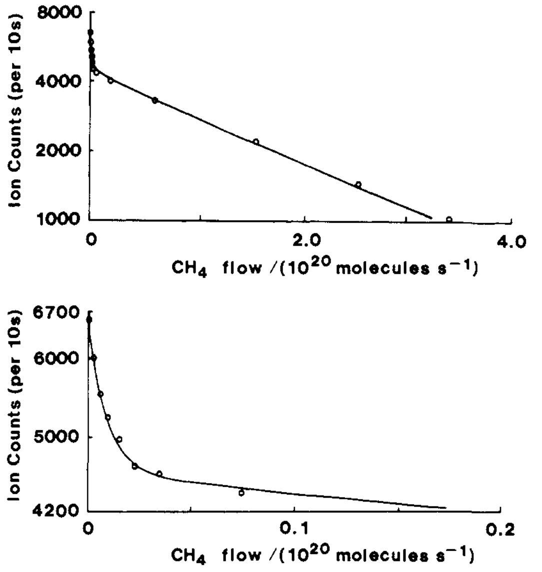

Figure 2. Data for the reaction of $C_2N^+ + CH_4$. Semilogarithmic plots of the ion count rate at *m/z* 38 against CH_4 flow. The C_2N^+ was generated by electron impact on C_2N_2. The points are experimental, and the curve is fitted to a double-exponential decay by least squares. The upper plot shows the complete set of experimental data and the fitted decay curve, while the lower plot shows in magnified form the initial decay due to CCN^+.

Table II. Percentage of Isomeric Forms of C_2N^+ Produced *Either* (a) in the Reaction of $C^+ + C_2N_2$, Where C^+ Was Formed by Electron Impact on the Source Gas Listed, *Or* (b) from Electron Impact Directly on the Stated Source Gas[a]

source gas	% CCN^+	% CNC^+
(a) In the Reaction of $C^+ + C_2N_2$		
CH_4	11	89
He/CO[b]	8	92
CO	11	89
CO_2	11	89
CCl_4	12	88
(b) From Electron Impact on Source Gas		
C_2N_2	20	80
CH_3CN	22	78
HC_3N	18	82

[a] In each case CH_4 was used as the diagnostic reactant to distinguish between CCN^+ and CNC^+. [b] The He/CO ratio was 30/1.

as CNC^+, as the same rate coefficient for reaction with CH_4 was found when C_2N^+ was formed in the flow tube from injected C^+ via reactions 1 and 3. As noted earlier, on energy grounds only CNC^+ should be formed in the reactions of C^+ with HCN and C_2N_2. Although each of these reactions produced a predominant form of C_2N^+ that behaved in a fashion identical with that of the less reactive form of C_2N^+ obtained from electron impact on C_2N_2, an unexpected result was that a small proportion of the more reactive CCN^+ form (~10%) was also generated via reactions 1 and 3 for all sources of C^+ tried. This reactive form decayed with the same rate coefficient ($k = 7 \times 10^{-10}$ cm^3 s^{-1}) as the reactive CCN^+ isomer produced by electron impact on C_2N_2, CH_3CN, and HC_3N. The relative amounts of CNC^+ and CCN^+ found in all the different sources of C_2N^+ used are shown in Table II.

As there is insufficient energy in reactions 1 and 3 to produce CCN^+ from the reaction of ground-state C^+ (^2P) ions, we therefore assume that a small proportion of the C^+ at *m/z* 12 formed in the ion source by electron impact was a metastable species, $(C^+)^*$. A prime candidate for this metastable species is C^+ (^4P), whose presence has been predicted by Tichy et al.[21] in C^+ produced in a manner similar to that in this study, viz. electron impact on CO.

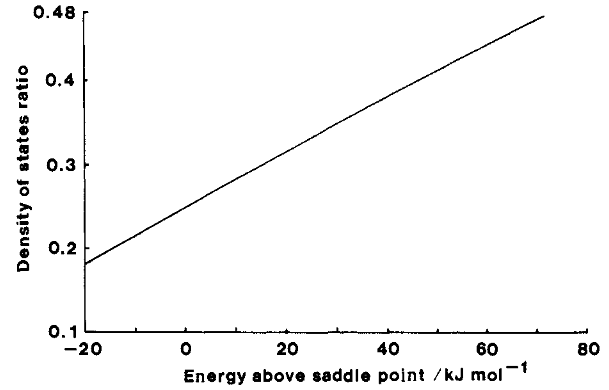

Figure 3. Calculated equilibrium coefficient between CCN^+ and CNC^+ shown as a function of energy above the saddle point. The curve shown is derived from the energies given in Figure 1.

The ~10% CCN^+ observed in the C_2N^+ signal formed from reactions 1 and 3 may not necessarily correspond to an equivalent fraction of $(C^+)^*$ injected into the flow tube. Instead, when C_2N^+ is produced in reaction 4, there is sufficient energy (≲565 kJ mol^{-1})

$$(C^+)^* + C_2N_2 \rightarrow CNC^+ + CN \qquad (4)$$

in $(CNC^+)^*$ to cross over the barrier to the CCN^+ form. If such a crossing occurs, then the ratio of CCN^+ to CNC^+ observed in the products of reactions 1 and 3 may be an indicator of the density of states ratio of CCN^+/CNC^+ rather than the fraction of $(C^+)^*$ in the C^+ ion signal.

Using the ab initio quantum chemical results presented in the preceding section, we have calculated the equilibrium coefficient, $K(E)$, for CCN^+/CNC^+ at energy E for the situation where isomerization across the barrier is fast compared to relaxation. Under these conditions

$$K(E) = N^{vr}{}_{CCN^+}/N^{vr}{}_{CNC^+}$$

where N^{vr} is the vibration–rotation density of states at energy E for each of the ions, respectively. We have used the Whitten–Rabinovitch analytical form[22] to estimate the densities of states and express values for $K(E)$ as a function of energy as shown in Figure 3. At the calculated barrier height energy of 195 kJ mol^{-1} above CNC^+, the equilibrium coefficient $K(E) = 0.25$. If isomerization is fast compared to relaxation, then the ratio of CCN^+/CNC^+ should be the density of states ratio at the barrier height. Reaction 4 may, however, produce $(C_2N^+)^*$ with internal energy considerably above that of the saddle-point energy and in a region where the density of states ratio is weighted in favor of CCN^+ (Figure 3). As the collision complex relaxes, the rate of isomerization decreases. Under flow tube conditions the time between collisions is typically 1.5×10^{-7} s, and the situation may be reached where collisional stabilization competes with isomerization. A weighting of CCN^+ could then be achieved that is larger than the barrier height ratio of 1:4. We conclude therefore that, for most sources of C^+ we examined, ≲20% of C^+ was in the metastable $(C^+)^*$ form and that it was the $(C^+)^*$ that gave rise to the small amount of CCN^+ observed in the products of reactions 1 and 3.

When electron impact (typically ~25 eV) on C_2N_2, CH_3CN, or HC_3N in the ion source region was used to generate the C_2N^+ injected into the flow tube, higher ratios of CCN^+ in the *m/z* 38 signal were observed (see Table II). These ratios were all very close to the value of CCN^+/CNC^+ calculated from the relative density of states at the saddle point. Typical pressures in the source region were 7×10^{-5} Torr, and thus the longer time between collisions allows ratios close to the density of state ratio at the saddle-point energy to be achieved. These calculations also favor

---

(21) Tichy, M.; Rakshit, A. B.; Lister, D. G.; Twiddy, N. D.; Adams, N. G.; Smith, D. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 239.

(22) Forst, W. In *Theory of Unimolecular Reactions*; Academic: New York, 1973.

(23) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

(24) Bohme, D. K.; Wlodek, S.; Raksit, A. B.; Schiff, H. I.; Mackay, G. I.; Keskinen, K. J. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 123.

Table III. Rate Coefficients k (10^{-9} cm^3 s^{-1}) and Product Distributions of C_2N^+ Isomers with the Given Neutral Reactant

						$-\Delta H$, kJ mol^{-1}	
reactant	products[a]	branching ratio	k(CCN$^+$)	k(CNC$^+$)	k_c[b]	CCN$^+$[c]	CNC$^+$[d]
H_2	$H_2CN^+ + C$[e]	0.90	0.90	<0.0001	1.53	62	
	$H_2C_2N^+$[e]	0.10				~512	
CH_4	$C_2H_3^+ + HCN$	0.60	0.70	0.004	1.12	399	293
	$H_2CN^+ + C_2H_2$	0.10				477	371
	$H_2C_3N^+ + H_2$	0.30				512	406
NH_3	$H_2CN^+ + HCN$	1.0	1.9	1.9	2.29	598	492
H_2O	$HCO^+ + HCN$	0.92	1.63	0.07	2.55	525	419
	$H_2CN^+ + CO$	0.08				648	542
C_2H_2	$C_3H^+ + HCN$	0.92	1.6	0.7	1.10	225	119
	$H_2CN^+ + C_3$	0.08				186	80
HCN	$HC_3N_2^+$	1.0	0.42[f]	0.42[f]	3.48		
N_2			<0.0001	<0.0001			
O_2	$C_2NO^+ + O$[e]	>0.97	~0.4	<0.0001	0.70		
	$O_2^+ + C_2N$[e]	<0.03					
N_2O	$C_2NO^+ + N_2$ or $CN_3^+ + CO$	0.73	1.0	0.40	0.93	518	412
	$NO^+ + C_2N_2$	0.22					
	$N_2O^+ + C_2N$	0.05					
CO_2	$C_2NO^+ + CO$[e]	1.0	1.1	<0.0001	0.83		

[a] The product distributions shown were obtained from a mixture of CCN$^+$ and CNC$^+$ isomers in the ratio CCN$^+$/CNC$^+$ ≈ 0.25. The isomeric mixture was obtained from electron impact on C_2N_2. [b] Collision rate coefficient obtained from ref 23. [c] Enthalpies based on ΔH_f[CCN$^+$] = 1726 kJ mol^{-1}. [d] Enthalpies based on ΔH_f[CNC$^+$] = 1620 kJ mol^{-1}. [e] Products refer to the reaction with CCN$^+$ only. [f] Pseudobimolecular rate coefficient at a reaction tube pressure of 0.30 Torr.

CNC$^+$ as being the major isomer in the low-pressure ICR study of McEwan et al.[7] and not CCN$^+$ as was assumed.

Reaction Chemistry. The reactions studied are summarized in Table III and include rate coefficients for each of CCN$^+$ and CNC$^+$. In most cases the branching ratios we report refer to the products produced from a 1:4 mixture of CCN$^+$/CNC$^+$ obtained by electron impact on dicyanogen. We have recently received a preprint of work by Bohme et al.[24] who also report a study of ion–molecule reactions of CCN$^+$ and CNC$^+$. In their study they used deactivation of the more reactive CCN$^+$ isomer by molecular oxygen as the means of isolating the CNC$^+$ isomer in the flow tube. In general, the results reported here are in reasonable agreement with their work.

CH_4. Three products of the reaction were observed: $C_2H_3^+$ (0.60), $H_2C_3N^+$ (0.30), and H_2CN^+ (0.10). These products can all be formed via exothermic pathways from either CCN$^+$ or CNC$^+$. The much slower rate of reaction of CNC$^+$ is probably indicative of a substantial barrier to product formation. A typical semilogarithmic decay curve for the isomeric mixture of C_2N^+ is shown in Figure 2 from which rate coefficients and the relative amounts of each isomer have been obtained.

NH_3 and HCN. A *linear* semilogarithmic decay was observed in the reactions of NH_3 and HCN, indicating that CCN$^+$ and CNC$^+$ are indistinguishable in their reactivities toward these reactants. In the case of NH_3 the major product of reaction was H_2CN^+, and the rate coefficient of 1.9×10^{-9} cm^3 s^{-1} was close to the collision rate. With HCN the only product observed was the association adduct $HC_3N_2^+$. No evidence was found for a reaction between C_2N^+ and HCN in the much lower pressure ICR study ($k \leq 3 \times 10^{-11}$ cm^3 s^{-1}),[7] which indicates that collisional stabilization in the flow tube was the mechanism responsible for deactivation of the $(HC_3N_2^+)^*$ complex. The rate coefficient found in this study ($k = 4.2 \times 10^{-10}$ cm^3 s^{-1}) is similar to that reported in our earlier flowing afterglow study of this reaction in which the product was not identified.[25]

H_2O. The major product of the reaction of C_2N^+ with H_2O was HCO^+ (92%), and a minor channel (8%) yielded H_2CN^+. The channel yielding HC_2N^+ was reported to be 25% in the ICR study.[7] Again the marked difference in rate coefficient for the CNC$^+$ isomer ($k = 7 \times 10^{-11}$ cm^3 s^{-1}) compared to that for the CCN$^+$ isomer ($k = 1.6 \times 10^{-9}$ cm^3 s^{-1}) is suggestive of a substantial barrier to the product channels resulting from CNC$^+$. The rate coefficient reported in the ICR study of this reaction $k = 3.4 \times 10^{-10}$ cm^3 s^{-1} was intermediate in value between the rate coefficients reported for the two isomers in this study.

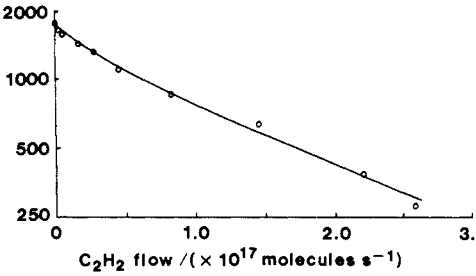

Figure 4. Data for the reaction of C_2N^+ with C_2H_2. Semilogarithmic plot of the ion count rate at m/z 38 against C_2H_2 flow. The C_2N^+ was generated by electron impact on C_2N_2. The points are experimental, and the curve is fitted to a double-exponential decay by least squares.

C_2H_2. In the reaction with C_2H_2 the semilogarithmic plot of the C_2N^+ signal versus C_2H_2 flow gave slight but reproducible curvature (see Figure 4). Analysis of this curve yielded the expected ratio of CCN$^+$/CNC$^+$ and indicated only a small difference in reactivity between CCN$^+$ ($k = 1.6 \times 10^{-9}$ cm^3 s^{-1}) and CNC$^+$ ($k = 7 \times 10^{-10}$ cm^3 s^{-1}). The major product was C_3H^+ (92%), which was also observed as the major product in the ICR study[7] and in an earlier SIFT study by Schiff and Bohme.[4] One other minor product H_2CN^+ (8%) was also observed. Rate coefficients in the earlier studies, and in the recent study by Bohme et al.[24] (in which a single decay component was assumed), lie in between the results of this work.

N_2O. Both isomers showed reactivity with N_2O, and, as for C_2H_2, reproducible curvature in the semilogarithmic plot of C_2N^+ signal against N_2O flow indicated a small difference in reactivity between CCN$^+$ ($k = 1.0 \times 10^{-9}$ cm^3 s^{-1}) and CNC$^+$ ($k = 4.0 \times 10^{-10}$ cm^3 s^{-1}). Two major product channels for the reaction were observed: $C_2NO^+ + N_2$ (or alternatively $CN_3^+ + CO$) at 73% and $NO^+ + C_2N_2$ at 22%. Again the rate coefficients we report straddle the (single) value of Bohme et al.[24] who interpreted their data in terms of identical reactivity for each isomer.

---

(25) Freeman, C. G.; Harland, P. W.; Liddy, J. P.; McEwan, M. J. *Aust. J. Chem.* **1978**, *31*, 963.

O_2 and CO_2. For each of these neutral species only the higher energy isomer, CCN^+, was found to react (as was observed by Bohme et al.[24]), with the major product in each case being C_2NO^+. If $OCCN^+$ is the most stable structure of C_2NO^+,[26] then considerable rearrangement will be required to produce it from CNC^+ even though the reaction channel leading to this product is probably exothermic for both O_2 and CO_2. The absence of any observed reactivity with CO_2 in the earlier ICR study is also suggestive that CNC^+ was the major isomer present in that study, as we have discussed above on the basis of the density of states calculations.

Conclusions

In their initial paper exploring possible differences in the reactivity of CCN^+ and CNC^+, Haese and Woods[1] suggested that the reactivities of the two isomers might be substantially different and that any differences could have important implications for the astrochemical environment. Kraemer et al.[10] also suggested the possibility of CCN^+ undergoing reaction with H_2, with CNC^+ being unreactive. We have demonstrated experimentally that, in several reactions, viz. those with H_2, CH_4, H_2O, O_2, and CO_2, there is indeed a large difference in reactivity, with the CCN^+ isomer being the more reactive in all cases. However, with the reactant neutrals NH_3, C_2H_2, HCN, and N_2O, the difference in reactivity between CCN^+ and CNC^+ is small or not detectable.

The most significant of these reactions to the interstellar medium is the reaction with hydrogen. We have observed experimentally that reaction 1 can produce *only* CNC^+ (if only ground-state C^+ is present) and that CCN^+ reacts rapidly with hydrogen. This ensures that CNC^+ is the only isomer of C_2N^+ likely to be present in appreciable amounts in dense interstellar clouds. As CNC^+ is unreactive with the major constituents of these clouds, its reactions with minor constituents need to be considered. We should also point out that our ab initio calculations show the reaction of C^+ with HNC (reaction 5), which is also

$$C^+ + HNC \rightarrow CCN^+ + H \qquad (5)$$

present in measurable densities, is exothermic to CCN^+ formation by ~65 kJ mol^{-1}. Assuming that CCN^+ is indeed a significant product in reaction 5, the ensuing reaction of CCN^+ with H_2 to produce H_2CN^+ + C (reaction 6) has sufficient energy to form

$$CCN^+ + H_2 \xrightarrow{0.90} H_2CN^+ + C \qquad (6)$$

$$\xrightarrow{0.10} H_2C_2N^+$$

only the $HCNH^+$ isomer of H_2CN^+. Subsequent dissociative recombination should therefore re-form HCN and HNC (eq 7);

$$H_2CN^+ + e^- \rightarrow HCN \textit{ or } HNC + H \qquad (7)$$

hence, reaction 5, if it occurs, only serves to recycle HNC. Thus, in spite of the undoubted presence of C_2N^+ in the interstellar medium, we would not expect the ion to be accessible to radioastronomical observation as the major isomeric form, CNC^+, is nonpolar.

Further, even though CNC^+ has a relatively large heat of formation (ΔH_f = 1620 kJ mol^{-1}), it does not react as rapidly as one might expect with species such as CH_4, H_2O, O_2, and CO_2 even when exothermic channels are available. If these reactions proceed at substantially less than the collision rate because of barriers in the exit channels, then the rate coefficients should decrease markedly at low temperatures. One avenue that may also present an important loss process for CNC^+ at low temperatures and pressures is the replacement of collisional stabilization of the association adduct of CNC^+ + HCN by the alternative mechanism of radiative stabilization.

Acknowledgment. We thank the New Zealand Universities Grants Committee and the New Zealand Lotteries Distribution Board for financial support and S. C. Smith for helpful discussions. D.J.D. thanks NASA for its support via Grant NAG 2-16. We also thank D. K. Bohme and coauthors for a preprint of their recent paper.[24]

Registry No. CNC^+, 78271-45-1; CCN^+, 76619-90-4; C_2N_2, 460-19-5; CH_3CN, 75-05-8; HC_3N, 1070-71-9; C^+, 14067-05-1; H_2, 1333-74-0; CH_4, 74-82-8; NH_3, 7664-41-7; H_2O, 7732-18-5; C_2H_2, 74-86-2; HCN, 74-90-8; N_2, 7727-37-9; O_2, 7782-44-7; N_2O, 10024-97-2; CO_2, 124-38-9.

---

[26] Lien, M. H.; Hopkinson, A. C., York University, unpublished results of ab initio calculations quoted in ref 24.

Reaction of Ground-State Aluminum Atoms with Propene: Electron Paramagnetic Resonance Spectroscopic Evidence for a π-Allylmetal Hydride[1]

M. Histed,[2] J. A. Howard,* H. Morris,[2] and B. Mile*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9. *Received December 3, 1987. Revised Manuscript Received March 7, 1988*

Abstract: Reaction of ground-state Al atoms (^2P) with propene on solid inert hydrocarbon surfaces at 77 K gives, in addition to allyl- and a dimethyl-substituted aluminocyclopentane, π-allylaluminum hydride. The magnetic parameters of this species are a_{Al} = 336 G, a_H(Al–H) = 57.4 G, a_H(2-endo) = 13.45 G, a_H(1) = 5.2 G, and g = 2.0023. This is the first direct electron spin resonance spectroscopic evidence for a π-allylmetal hydride, intermediates that are believed to be involved in the isomerization of alkenes.

We have previously shown by electron paramagnetic resonance spectroscopy (EPR) that Al atoms react with ethylene on a solid inert hydrocarbon surface at 77 K in a rotating cryostat to give aluminocyclopentane[3] and aluminum monoethylene.[4-6] The formation of an aluminocyclopentane substantiates Skell and McGlinchey's suggestion[7] that reaction of Al atoms with propene involves the intermediacy of an aluminocyclopentane. A related aluminocyclopentene is also formed by cheleotropic addition of

---

[1] Issued as NRCC No. 28991.

[2] Present address: Department of Chemistry and Biochemistry, Liverpool Polytechnic, Byrom St., Liverpool, England.

[3] Chenier, J. H. B.; Howard, J. A.; Mile, B. *J. Am. Chem. Soc.* **1987**, *109*, 4109–4110.

[4] Howard, J. A.; Mile, B.; Tse, J. S.; Morris, H. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3701–3707.

[5] Kasai, P. H.; McLeod, D., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 5609–5611.

[6] Kasai, P. H. *J. Am. Chem. Soc.* **1982**, *104*, 1165–1172.

[7] Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 195–199.

0002-7863/88/1510-5290$01.50/0 Published 1988 by the American Chemical Society