

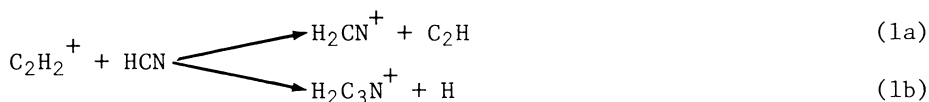
AN ICR STUDY OF ION-MOLECULE REACTIONS IN THE C₂H₂/HCN SYSTEM

M. J. McEwan, V. G. Anicich and W. T. Huntress, Jr.,
Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena,
CA 91103

ABSTRACT: Rate constants obtained by the ICR technique are reported for reaction (1), C₂H₂⁺ + HCN and reaction (2) HCN⁺ + C₂H₂ such that k₁ = 3.6 × 10⁻¹⁰ and k₂ = 6.9 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, respectively. Differences between these results and other measurements of reaction (1) are discussed. The relevance of reaction (1) to the formation of HC₃N in interstellar clouds is also briefly assessed.

INTRODUCTION

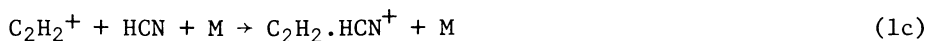
Three studies^{1,2,3} have recently been reported of the rate coefficient for reaction (1). Because of a considerable discrepancy in



the reported rate coefficient for this reaction, we decided to reinvestigate the system. In the first study by Huntress¹, the faster reverse charge transfer reaction was neglected. Reaction (2a) is a concurrent reaction in the HCN/C₂H₂ system.



Consequently, in the study of reaction (1), any C₂H₂⁺ reformed via reaction (2) has the effect of making the observed rate coefficient k₁ of reference 1 (5.3 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹) too small. Freeman et al² in a flowing afterglow study of reaction (1) reported a much larger value, k₁ = 7.1 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, but this result is now known to be too large due to interference from the Penning ionization reaction of HCN with He^{*4}. Schiff and Bohme³ have also reported a selected-ion-flow-tube (SIFT) study of reaction (1) and noted an additional major channel from the three body process (1c), which they estimated accounted for 90% of all products observed in their system.



EXPERIMENTAL

The JPL ICR mass spectrometer was used to obtain product distributions and rate constants as described elsewhere⁵. In order to produce C_2H_2^+ with a negligible fraction of vibrationally excited ions, the median energy of the ionizing electrons was kept below 12.5eV⁵. Because of the large energy spread in the electron beam, small amounts of HCN^+ were also formed even at these energies, and these were ejected during the ion formation pulse to prevent contamination of the C_2H_2^+ decay from the charge transfer reaction (2a). In the measurement of the rate coefficient k_2 , an electron energy of 15eV was used and corrections to the observed HCN^+ ($m/e=27$) decays were made for the natural ¹³C abundance of C_2H_2^+ which also occurs at $m/e = 27$.

RESULTS AND DISCUSSION

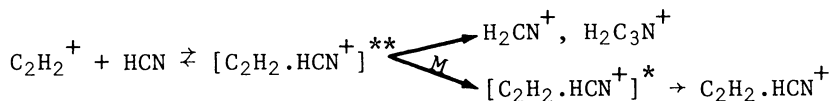
The rate coefficients and product distributions are shown in Table 1.

TABLE 1

<u>Reaction</u>	<u>Rate Coefficient</u> ($10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	<u>Reaction Number in Text</u>
$\text{C}_2\text{H}_2^+ + \text{HCN} \begin{cases} \xrightarrow{.66} \text{H}_2\text{CN}^+ + \text{C}_2\text{H} \\ \xrightarrow{.34} \text{H}_2\text{C}_3\text{N}^+ + \text{H} \end{cases}$	} 3.6 ± 1.4	(1a)
		(1b)
$\text{HCN}^+ + \text{C}_2\text{H}_2 \begin{cases} \xrightarrow{.6} \text{C}_2\text{H}_2^+ + \text{HCN} \\ \xrightarrow{.2} \text{H}_2\text{CN}^+ \text{ or } \text{C}_2\text{H}_3^+ \\ \quad \quad \quad (+ \text{neutral products}) \\ \xrightarrow{.2} \text{H}_2\text{C}_3\text{N}^+ + \text{H} \end{cases}$	} 6.9 ± 1.3	(2a)
		(2b)
		(2c)

Uncertainties shown in the rate coefficient represent the standard deviations of the measurements. We could not distinguish between C_2H_3^+ and H_2CN^+ in the products of reaction (2) as their masses coincide with other product ions in the system. Both ions have exothermic pathways leading to their formation. The rate coefficient reported by Schiff and Bohme³ of $3.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (1) is close to our measured value, but they estimate 90% of the reaction in their system proceeds by a three body pathway. A bimolecular rate

for $k_1(a+b) \sim 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is thus implied which is much less than our reported value $k_1(a+b) = 3.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These results may be reconciled if the $[\text{C}_2\text{H}_2.\text{HCN}^+]^{**}$ complex can be deactivated at the expense of the bimolecular process.



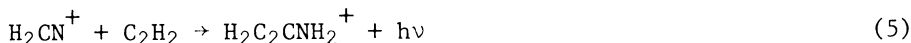
Reaction (1b) followed by dissociative recombination (3), has been proposed as a source of HC₃N in interstellar clouds.^{1,2}



Recent calculations⁶ show that this mechanism can reproduce the observed amount of HC₃N in Sgr B2 given a particular scenario for the cloud thermal history, and that the cloud is not in chemical steady-state (equilibrium). Under conditions of chemical equilibrium, reaction (1b) followed by (3) cannot account for the observed abundance of HC₃N in Sgr B2. Schiff and Bohme³ have proposed addition reactions of the type



which lead not only to HC₃N but also to successive members of the cyanopolyacetylene series. However, recent laboratory experiments show proton transfer, not addition, to be the favored process in these reactions.⁷ If the chemical steady state prevails in dense clouds such as Sgr B2, then an additional source is required for the cyanopolyacetylene series. Radiative association reactions of the type (5)⁸ or (6)³ have been proposed.



Laboratory experiments^{3,9} show that both reactions exhibit collision-stabilized association products at room temperature. Steady-state calculations⁸ indicate that reaction (5) is likely to be the stronger source in dense clouds.

ACKNOWLEDGEMENTS

This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National

Aeronautics and Space Administration. M.J.M. is grateful for the award of a N.R.C. Senior Research Associateship.

REFERENCES

1. Huntress, W. T.: 1976, Ap. J. Suppl. 33, p. 495.
2. Freeman, C. G., Harland, P. W., and McEwan, M. J.: 1978, Astrophys. Letters 19, p. 133.
3. Schiff, H. I., and Bohme, D. K.: 1979, Ap. J. in press.
4. Freeman, C. G., Harland, P. W., and McEwan, M. J.: 1979, private communication.
5. Kim, J. K., Anicich, V. G., and Huntress, W. T.: 1977, J. Phys. Chem. 81, p. 1798.
6. Prasad, S. S., and Huntress, W. T.: 1979, Ap. J. in press.
7. Freeman, C. G., Harland, P. W., and McEwan, M. J.: 1978, Proc. Mon. Not. Roy. Astron. Soc. 187, p. 441.
8. Mitchell, G. F., Huntress, W. T., and Prasad, S. S.: 1979, Ap. J. 233, p. 102.
9. Freeman, C. G., Harland, P. W., Huntress, W. T., and McEwan, M. J.: 1979, unpublished work.

DISCUSSION FOLLOWING McEWAN

Field: What is the kinetic energy of the ions in the I.C.R. experiments? It may influence your derived rate coefficients.

McEwan: The kinetic energy of the ions is small, although it is probably slightly higher than thermal. In most ion-molecule reactions the small amounts of kinetic energy above thermal do not influence the observed rate coefficients. Under typical cell conditions, an ion will experience five to 20 collisions with polyatomic neutrals. Energies <0.1 eV are suggested by a comparison of ICR data to data from other techniques for reactions where kinetic energy does affect the rate.

Glassgold: The abundance of HC₃N implied by the production mechanism $C_2H_2^+ + HCN \rightarrow H_2C_3N^+ + H$ should be very sensitive to the electron abundance. In making your estimate, did you use the low electron fractions $\sim 10^{-8}$ determined for dense clouds?

McEwan: According to the time-dependent model of Prasad and Huntress, the reaction cited can be an important synthetic mechanism for cyanoacetylene if the cloud does not reach steady state. The reaction produces insufficient HC₃N to account for observations if steady state concentrations of C₂H₂⁺ and HCN are used to predict the HC₃N abundance. The fractional electron abundances used in the model ranged between 10⁻⁷ and 10⁻⁸.

D. Smith: It has been shown that C₂H₂⁺ has a significant population in v=1 even at 300 K (Buttrill et al). Could you comment on the possible effects of such excitation on your measured association rate for the C₂H₂⁺+HCN reaction?

McEwan: Previous experiments with C₂H₂⁺ generated under similar conditions of electron impact (ref. 5 above) have shown that vibrational

excitation of C₂H₂⁺, although small, is nevertheless present. In the majority of reactions of C₂H₂⁺ studied by ICR in the trapped ion mode, good agreement in rate coefficient determinations has generally been observed when compared with other techniques. We would not expect the v=1 level to affect this C₂H₂⁺+HCN rate, as k for this association (ref 3) is too small for the association channel to be observed at the pressures we were using.

Winnewisser: Did you check the analogous reaction in cyanoacetylene and acetylene i.e. HC₃N+C₂H₂⁺? I expect this reaction to be slow. In our discharge experiments we observe a large amount of polymer formation. Do you observe the same phenomenon at the lower pressures you work at?

McEwan: To answer the first question, we did look at the reaction C₂H₂⁺+HC₃N, and found no evidence for addition having occurred (see refs. 2 and 7). We do not observe any polymer in our system. We have observed large quantities of polymer in reaction studies of neutral molecules containing the -CN group that have been subjected to a micro-wave discharge.

Herbst: The reaction C₂H₃⁺+CN should be investigated for formation of HC₃N.

McEwan: Ion reactions with radicals present more experimental difficulties than conventional ion-molecule reactions. However attempts will shortly be made to measure a series of CN-radical reactions, including the one you have mentioned.

Shiff: Careful search with our system failed to reveal the channel HCN⁺+C₂H₂ → C₃H₂N⁺+H, which suggests that reactions of this type do not present an attractive route to the cyanoacetylenes. On the other hand, we have recently observed that proton transfer is a minor channel in the case of C₂H₂⁺+HCN. One should therefore be cautious about rejecting reactions of C₂H₂⁺ with the cyanoacetylenes to form the next higher member, in spite of observations by McEwan et al. that they proceed exclusively by proton transfer.

McEwan: The reactions of HCN⁺ are not significant for interstellar synthesis because of its rapid reaction with H₂ to produce H₂CN⁺. The radiative association of H₂CN⁺ with C₂H₂ may be relevant for synthesis of cyanoacetylene.