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LABORATORY MEASUREMENTS OF SOME ION-MOLECULE REACTIONS RELATED TO THE FORMATION OF HCN IN DENSE INTERSTELLAR CLOUDS

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ABSTRACT

Recent models have attributed the formation of HCN in dense, interstellar clouds to dissociative recombination of H_2CN^+ ions formed by the reaction of C^+ ions with NH_3. We have studied this reaction in the laboratory at 297° K and found the rate constant to be $(2.3 \pm 0.2) \times 10^{-9}$ cm³ s⁻¹. However, only about 5 percent of the reaction produced H_2CN^+ while the remaining 95 percent produced NH_3^+ by charge transfer. We also found that the reaction of NH_3^+ with H_2, postulated in the model as the only source of NH_3, has a rate constant equal to $(4 \pm 2) \times 10^{-13}$ cm³ s⁻¹.

Subject headings: atomic and molecular processes — molecules, interstellar

Ion-molecule reactions have recently gained favor in explaining the genesis of polyatomic molecules in dense interstellar clouds for several reasons. Exoergic ion-molecule reactions generally have rate constants several orders of magnitude greater than those involving only neutral species and can, therefore, be effective processes at the low pressures of interstellar space. They generally do not involve activation barriers which could not be overcome at the low temperatures of these clouds. In fact, the rate constants of many ion-molecule reactions have been found to increase with decreasing temperature. Although a number of the reactions postulated in the models have been studied in the laboratory, many have not. We wish to report here recent laboratory observations on some ion-molecule reactions related to the formation of HCN.

Herbst and Klemperer (1973) (hereafter referred to as HK) have proposed that HCN is formed by the ion-molecule reaction

$$C^+ + NH_3 \rightarrow CNH_2^+ + H\,, \qquad (1)$$

followed by dissociative recombination:

$$CNH_2^+ + e^- \rightarrow CNH + H\,. \qquad (2)$$

Watson (1974) has also suggested this mechanism for HCN/CNH synthesis. We have investigated reaction (1) using a flowing afterglow system described elsewhere (Bohme *et al.* 1973) in which the reactants are believed to be in thermal equilibrium at 297° K. The reaction of C^+ with NH_3 was found to be rapid, with a rate constant of $(2.3 \pm 0.2) \times 10^{-9}$ cm³ s⁻¹. However, reaction (1) was only a minor channel (~5%) with the major channel (~95%) being charge transfer:

$$C^+ + NH_3 \rightarrow NH_3^+ + C\,. \qquad (3)$$

No evidence was found for the occurrence of other exoergic channels such as

$$C^+ + NH_3 \rightarrow HCN^+ + H_2$$
$$\rightarrow HCN + H_2^+$$
$$\rightarrow CH_3^+ + N$$
$$\rightarrow CH_2^+ + NH$$
$$\rightarrow CN + H_3^+\,,$$

all of which require considerable molecular rearrangement. The effective rate constant for reaction (1) is, therefore, $k_1 \simeq 0.12 \times 10^{-9}$ cm³ s⁻¹ compared with the value of 2×10^{-9} cm³ s⁻¹ used by HK in their model. It is possible, of course, that the branching ratio for reactions (1) and (3) might reverse at interstellar cloud temperatures, but there is no *a priori* reason to suspect that it would.

We further found that the proton transfer reaction

$$CNH_2^+ + NH_3 \rightarrow NH_4^+ + CNH \qquad (4)$$

is rapid, with a rate constant $\geq 1.5 \times 10^{-9}$ cm³ s⁻¹. It is probably worth noting that both reactions (2) and (4) are more likely to produce the CNH rather than the HCN isomer. Pearson *et al.* (1973) concluded that even though CNH has an energy 0.6 eV higher than HCN, there is an activation energy preventing the isomerization. They find consistency between their calculations of the molecular properties of CNH and the galactic emission lines of Snyder and Buhl (1971*a*, *b*).

It is unlikely that reaction (4) would compete successfully against reaction (2) in converting CNH_2^+ to CNH since, according to the HK model, the densities of NH_3 and electrons are comparable while the rate constant for reaction (2) is probably two orders of magnitude greater than for reaction (4).

The only mechanism suggested by HK for the production of NH_3, the precursor to HCN in reaction (1), is

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H\,, \qquad (5)$$

followed again by dissociative recombination:

$$NH_4^+ + e^- \rightarrow NH_3 + H\,. \qquad (6)$$

HK adopted a value of 1×10^{-13} cm³ s⁻¹ for k_5 based on the upper limit of 5×10^{-13} cm³ s⁻¹ placed on this rate constant by Ferguson (1973). We have also studied this reaction and find the rate constant $k_5 = (4 \pm 2) \times 10^{-13}$ cm^3 s^{-1}. It does not appear to be sufficiently larger than the value adopted by HK to compensate for the fact that the observed value of k_1 is more than an order of magnitude smaller than that used in the model.

Other mechanisms have been proposed (Harteck and Reeves 1973; Herbst 1974; Watson 1974) for the synthesis of HCN, viz.,

$$CH_3^+ + N \rightarrow HCN^+ + H_2 ,$$

$$HCN^+ + H \rightarrow HCN + H^+ ,$$

$$HCN^+ + H_2 \rightarrow H_2CN^+ + H ,$$

$$H_2CN^+ + e \rightarrow HCN + H ,$$

and

$$CH_3^+ + C \rightarrow C_2H_2^+ + H ,$$

$$C_2H_2^+ + N \rightarrow HCN + CH^+ .$$

However, these mechanisms have not been evaluated theoretically, nor have the reactions been studied in the laboratory.

Oppenheimer and Dalgarno (1974) have recently pointed out that charge transfer with metal atoms may play an important role in interstellar clouds. HCN and NH_3 might be produced by such charge transfer from HCN^+ and NH_3^+, respectively, both of which can be formed by well-established ion-molecule reactions.

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