LABORATORY STUDIES OF INTERSTELLAR CARBON/NITROGEN ION CHEMISTRY

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ABSTRACT

Laboratory measurements are reported for ion-molecule reactions involving CN^+, HCN^+, C_2N^+ and HCN, and their implications for interstellar synthesis for C/N compounds are discussed. The reaction of C^+ with HCN was found not to constitute a major loss process for HCN, which is regenerated by reactions of C_2N^+ with NH_3, H_2O, CH_4, C_2H_2 and H_2S. These latter reactions lead to C addition rather than C-N bond formation. Rapid association reactions were observed for CH_3^+ and $C_2H_2^+$ with HCN. These suggest efficient radiative association reactions under interstellar conditions to form ions which may form larger C/N compounds upon neutralization.

INTRODUCTION

Ion-molecule reactions remain an attractive mechanism for the formation of large molecules observed in dense interstellar clouds. Studies of these reactions in our and other laboratories have shown them capable of synthesizing large 'straight-chain' hydrocarbons. In this paper we report the results of our studies involving HCN, HCN^+, CN^+, and C_2N^+.

The reaction channels observed and the rate constants found for these reactions are shown in Table 1. The reactions were studied using a modified form of the selected ion flow tube first developed by Adams and Smith (1976).

REACTIONS WITH HCN

The reactions of C^+ and C_2^+ with HCN proceed exclusively by condensation with H atom elimination, and with a rate constant close to the theoretical limit. In contrast, the reaction of C_2H^+ with HCN proceeds by two almost equal channels, proton transfer from C_2H^+, and H atom transfer from HCN. The combined rate constant is again close to the theoretical value. The somewhat slower reaction between $C_2H_2^+$ and HCN has three primary channels. In the presence of about 0.5 Torr of

B. H. Andrew (ed.), Interstellar Molecules, 307–310.

https://doi.org/10.1017/S0074180900072776 Published online by Cambridge University Press

He, 87% of the reactive collisions lead, by three-body association, to $C_2H_2^+.HCN$. This suggests a fast rate for radiative recombination under interstellar conditions. Neutralization of this cluster ion could well lead to the observed molecules cyanoacetylene and vinyl cyanide. About 8% of the reactive collisions goes by a two-body channel to produce $H_2C_3N^+$. Neutralization of this ion probably also leads to cyanoacetylene. The third (5%) channel leads to $HCNH^+$ which, upon neutralization, probably regenerates HCN.

The reaction of CH_3^+ with HCN proceeds exclusively by very rapid three-body association to form $CH_3^+.HCN$ in the presence of 0.5 Torr He. This again suggests an efficient radiative association reaction under interstellar conditions to form the same ion. Neutralization by electron recombination or proton transfer could give rise to the observed neutral molecule CH_3CN. For example we have found that the ion does indeed proton transfer, very rapidly, with NH_3 and $(CH_3)_2O$ to produce methyl cyanide.

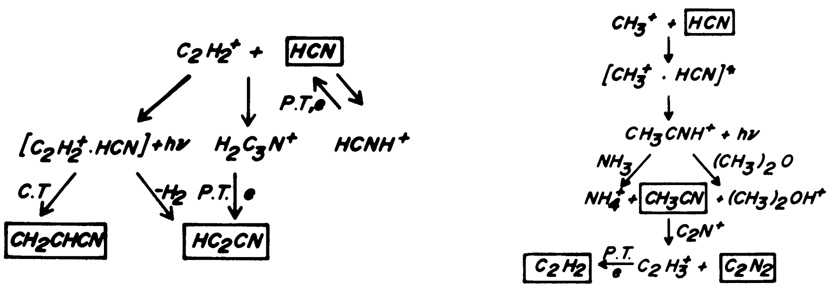

Fig. 1. Possible consequences of the reactions of HCN with $C_2H_2^+$ and CH_3^+. (P.T. ≡ proton transfer, e ≡ electron recombination, C.T. ≡ charge transfer)

HCN^+ AND CN^+ REACTIONS

HCN^+ reacts rapidly with C_2H_2 by three channels. The dominant channel produces HC_3N^+ which can lead to HC_3N by charge transfer. The channel producing $H_2C_3N^+$ was not observed, which appears to rule out this route to HC_3N by electron recombination. The other two channels, charge transfer and proton transfer, do not, of course, lead to C-N bond formation. Reactions of HCN^+ with CH_4 have two channels. The major channel (80%) produces H_2CN^+ and therefore, by recombination, HCN. The minor (20%) channel produces NH_2 and results in C-C bond formation which, upon neutralization, could yield C_2H_2. The reaction of CN^+ with CH_4 also has two channels. The major channel is H^- transfer, which produces HCN. The minor channel is H_2 transfer; recombination of the resulting H_2CN^+ ion probably also leads to HCN. It is of interest to note that there appears to be little kinetic isotope effect in the reactions of CN^+ with CD_4, whereas the rate constant for the reaction of HCN^+ with CH_4 is 1.7 times the rate constant with CD_4.

Table 1. Summary of measured rate constants (in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}) at 300 K. [a]

Reactions with HCN	
$C^+ + HCN \rightarrow C_2N^+ + H$	3.5
$C_2^+ + HCN \rightarrow C_3N^+ + H$	2.5
$C_2H^+ + HCN \rightarrow HCNH^+ + C_2$	2.5
$\rightarrow C_2H_2^+ + CN$	
$C_2H_2^+ + HCN \rightarrow C_2H_2^+.HCN$	0.38[b]
$\rightarrow H_2C_3N^+ + H$	
$\rightarrow HCNH^+ + C_2H$	
$CH_3^+ + HCN \rightarrow CH_3^+.HCN$	2.0[b]
$CH_3^+.HCN + NH_3 \rightarrow NH_4^+ + CH_3CN$	0.87
$CH_3^+.HCN + (CH_3)_2O \rightarrow (CH_3)_2\ OH^+ + CH_3CN$	$\gtrsim 1$
Reactions of CN^+ and HCN^+	
$CN^+ + CH_4 \rightarrow CH_3^+ + HCN$	0.97
$\rightarrow HCNH^+ + CH_2$	
$CN^+ + CD_4 \rightarrow CD_3^+ + DCN$	1.1
$\rightarrow DCND^+ + CH_2$	
$HCN^+ + CH_4 \rightarrow HCNH^+ + CH_3$	1.3
$\rightarrow C_2H_3^+ + NH_2$	
$HCN^+ + CD_4 \rightarrow HCND^+ + CD_3$	0.77
$\rightarrow C_2D_2H^+ + ND_2$	
$HCN^+ + C_2H_2 \rightarrow C_2H_2^+ + HCN$	1.9
$\rightarrow HC_3N^+ + H_2$	
$\rightarrow C_2H_3^+ + CN$	
$\not\rightarrow H_2C_3N^+ + H$	
Reactions of C_2N^+	
$C_2N^+ + H_2 \not\rightarrow$	$\leqslant 0.0001$
$C_2N^+ + NH_3 \rightarrow HCNH^+ + HCN$	1.8
$C_2N^+ + H_2O \rightarrow HCO^+ + HCN$	0.31
$C_2N^+ + CH_4 \rightarrow C_2H_3^+ + HCN$	0.0044
$H_2C_3N^+ + H_2$	
$C_2N^+ + C_2H_2 \rightarrow C_3H^+ + HCN$	0.89
$\rightarrow HCNH^+ + C_3$	
$C_2N^+ + H_2S \rightarrow HCS^+ + HCN$	1.2
$C_2N^+ + CH_3CN \rightarrow C_2H_3^+ + C_2N_2$	4.1

[a] The branching ratios which were determined are discussed in the text.

[b] At a helium pressure of ≃ 0.5 Torr.

https://doi.org/10.1017/S0074180900072776 Published online by Cambridge University Press

C_2N^+ REACTIONS

No reaction was observed to occur between C_2N^+ and H_2, which suggests that this may be an abundant interstellar ion. It does react with NH_3, H_2O and H_2S by a single channel which can be represented as:

$$C_2N^+ + H_yX \rightarrow H_{y-1}CX^+ + HCN$$

The reaction of C_2N^+ with C_2H_2 has the additional channel giving H_2CN^+ and C_3 as products. However, electron recombination would result in identical neutral products from both channels. The reaction of C_2N^+ with CH_4 is slow - less than 1% of the collision frequency. There are two channels, and a condensation channel giving $H_2C_3N^+$, which therefore could be a minor source of interstellar HC_3N.

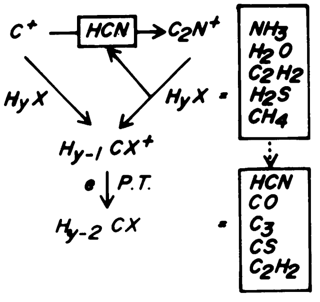

Fig. 2. C-X bond formation by reaction with C^+ and by C_2N^+ catalysis

There are two important generalizations from the above reactions with C_2N^+. First, they all produce HCN. Thus the reaction of C^+ with HCN to produce C_2N^+ does not constitute a major loss process for HCN since this ion regenerates HCN when it reacts with other major interstellar neutral molecules. Secondly, its reactions do not lead to C-N formation but rather to C addition to the neutral reactant. In fact the C_2N^+ reactions are equivalent to the counterpart reactions with C^+ ions. Thus the reaction of C^+ with HCN followed by C_2N^+ reaction with a neutral simply catalyses the direct reaction of C^+ with the neutral, albeit with a slower effective rate constant than the direct C^+ reaction.

In addition to the slow channel with CH_4, one other, possibly important exception was found to the above generalization, viz. the reaction of C_2N^+ with CH_3CN. This reaction is rapid and has an exclusive channel to form $C_2H_3^+$ and, most likely, the neutral C_2N_2.

REFERENCE

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