GAS PHASE SYNTHESIS OF AMINO-, CYANO- AND NITROSO-COMPOUNDS IN INTERSTELLAR CLOUDS

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ABSTRACT

From our laboratory data relating to several hundreds of ion-atom and ion-molecule reactions at thermal energies,we qualitatively describe probable chemical paths to the synthesis of amino-, cyano- and nitroso-compounds in interstellar clouds.

1. INTRODUCTION

-NH, -CN, -CO and to a lesser extent -NO groups are common in the observed interstellar molecules, and many attempts have been made during recent years to explain how these molecules are synthesised. Plausible qualitative and semi-quantitative ion-chemical models now exist based on known gas phase ion chemistry and intuitive guesses at likely reactions and their rate coefficients. However, the objective must be to establish the most important routes to the synthesis of the observed molecules by detailed chemical modelling. Before this can be satisfactorily achieved, more data is required on the composition and physical conditions within the gas clouds, as well as a great deal more laboratory data on the rate coefficients and products of ion-neutral and neutral-neutral reactions acquired at appropriately low temperatures.

Stimulated by the challenge presented to laboratory experimenters by the ion-chemical problems identified in the research papers on interstellar molecular synthesis, we conceived the Selected Ion Flow Tube (SIFT) technique (Adams and Smith, 1976) which we have developed and exploited during the last two years to determine the rate coefficients and product ion distributions of several hundreds of ion-neutral reactions. Most of the reactions studied have been selected because of their potential interest to interstellar chemistry. Thus, we have carried out detailed surveys of the reactions of the ion series CH_n^+(n = 0 to 4) (Smith and Adams, 1977a,b; Adams and Smith, 1977,1978), $C_2H_n^+$(n = 0 to 4) (Adams and Smith, 1977) H_nCO^+(n = 0 to 3) (Adams et al 1978), NH_n^+(n = 0 to 4) (Adams et al 1979a) and reactions of the

B. H. Andrew (ed.), Interstellar Molecules, 311–315.

ions N^+, N_2^+, O^+, O_2^+ and NO^+ (Smith et al 1978). In collaboration with the NOAA Group at Boulder, Colorado, we have also studied the reactions of several active ion species with nitrogen and oxygen atoms (Viggiano et al, 1979). The measurements have largely been carried out at 300 K but some of the ternary association reactions have been studied at temperatures as low as $\sim$100 K (Adams et al, 1979b).

2. DEDUCTIONS BASED ON SIFT DATA

2.1 Synthesis of Amino- and Cyano-Compounds in Interstellar Clouds.

The laboratory data reveals many ion-neutral routes to the formation of these compounds if it is accepted that N atoms and N^+ ions are present in the gas clouds. Thus the formation of ionized nitrogen hydrides will proceed as follows:

$$N^+ \xrightarrow{+H_2} NH^+ \xrightarrow{+H_2} NH_2^+ \xrightarrow{+H_2} NH_3^+ \qquad (1)$$

However, the binary reaction $NH_3^+ + H_2 \rightarrow NH_4^+$ does not proceed at a measurable rate at low temperatures and so NH_3^+ is likely to be a relatively long-lived species in the clouds. Our data however indicates the great propensity for NH_3^+ to abstract an hydrogen atom from almost any hydrogen-bearing molecule especially hydrocarbons, e.g. $NH_3^+ + CH_4 \rightarrow NH_4^+$, and so the synthesis of NH_3 is achieved following the electronic recombination, $NH_4^+ + e \rightarrow NH_2, NH_3$ although the branching ratio of the recombination is unknown. The synthesis of the hydrocarbons has been discussed previously by several authors and probably proceeds thus:

$$C^+ \xrightarrow{H_2} CH_2^+ \xrightarrow{H_2} CH_3^+ \qquad (2)$$

where the first stage of (2) is the much discussed radiative association reaction. Like NH_3^+, the binary reaction of CH_3^+ with H_2 is immeasurable at gas cloud temperatures, but following our detailed study of the three-body association reactions of CH_3^+ (see Smith and Adams in these Proceedings) we have suggested that the radiative association reaction $CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$, will proceed at an appreciable rate in molecular clouds after recombination generating CH_4 in relatively high abundance. Reactions of the ions CH_n^+ with CH_4 then generate higher hydrocarbons e.g.

$$C^+ + CH_4 \rightarrow C_2H_2^+, C_2H_3^+ \xrightarrow{e} C_2H, C_2H_2 \qquad (3)$$

The production of NH_3 and hydrocarbons are important steps in the synthesis of cyano-compounds, since from their reactions with the ions CH_n^+ and NH_n^+ respectively, -CN containing ions are inevitably generated. Examples are:

$$C^+ + NH_3 \rightarrow H_2CN^+, HCN^+; \quad CH_3^+ + NH_3 \rightarrow CH_2NH_2^+, CH_3NH_3^+ \qquad (4)$$

and

$$N^+ + CH_4 \rightarrow H_2CN^+, HCN^+ ; NH_2^+ + C_2H_4 \rightarrow H_4CN^+, H_5C_2N^+ \qquad (5)$$

which thus can lead to the generation of the observed species CN, HCN, CH_2NH and CH_3NH_2.

The above ion-molecule reactions are all very fast with rate coefficients near to the collisional limit. Positive ion-atom reactions are generally somewhat slower but nevertheless could play an important role in interstellar chemistry. Our recent study of the reactions of N atoms with several important interstellar ions (e.g.CH^+, CH_3^+, $C_2H_2^+$ etc.) has again demonstrated the effectiveness of production of -CN bearing compounds via ion-neutral reactions:

$$CH^+ + N \rightarrow CN^+, H^+ ; CH_3^+ + N \rightarrow H_2CN^+, HCN^+ \qquad (6)$$

The reaction $C_2H_2^+ + N \rightarrow HC_2N^+, C_2N^+, CH^+$ is interesting since it indicates how readily the N atoms are incorporated into the hydrocarbon ions generating other reactive ions. The C_2N^+ is unreactive with H_2 and so is available for reaction with more minor species. For example the reaction $C_2N^+ + H_2O$ generates the widely observed HCO^+ and HCN. So the more elementary N-atom reactions could probably contribute significantly to the synthesis of the observed cyano-compounds. Indeed most important could be the H_3^+ + N reaction which could compete with (1) as the most important first stage in NH_3 synthesis (although this has not been studied in the laboratory).

2.2 Synthesis of Nitroso-Compounds in Interstellar Clouds.

Our experiments have shown that few reactions between oxygen and nitrogen bearing ions and neutrals lead to the production of -NO bearing compounds and it is perhaps therefore not surprising that few such compounds have been detected in interstellar clouds. Thus whilst N^+ ions react with most observed oxygen bearing molecules as well as with O_2 (which must surely be present), the most common ion product bearing an NO bond is NO^+ and unless the NO^+ can charge transfer with a species of lower ionization energy (and few such species exist, metal atoms being notable exceptions), then the inevitable fate of the NO^+ ions is dissociative recombination with electrons producing N and O atoms. In contrast, the $C^+ + O_2$ reaction rapidly generates the widely observed CO as well as CO^+ which rapidly reacts with H_2 (unlike NO^+) producing the observed HCO^+. The latter ion does not react with N atoms (and indeed is unreactive with most molecules except those of high proton affinity like NH_3 and CH_3NH_2 to which it transfers a proton) and so is not a potential source of -NO containing compounds. We have, however, identified a few potentially important reactions which could lead to NO and HNO in interstellar clouds. For example, the reaction of NH^+ with CO_2 (which must surely be present) generates HNO^+ which on electronic recombination can lead to NO. Similarly the reaction

https://doi.org/10.1017/S0074180900072788 Published online by Cambridge University Press

$NH_2^+ + O_2 \rightarrow H_2NO^+$, HNO^+ can lead to both NO and HNO production, both of which have recently been detected in Sgr B2.

Nitrogen and oxygen atom reactions with positive ions are very likely to be sources of -NO bearing compounds, although unfortunately few such reactions have been studied in the laboratory. One such relevant reaction which we have studied, however, is $H_2O^+ + N \rightarrow HNO^+, NO^+$. The reactions of NH_2^+ and NH_3^+ with O atoms may be potential sources of HNO^+ and H_2NO^+.

3. CONCLUSIONS

Many ion-neutral reactions have been identified as sources of amino- and cyano-compounds. Clearly the most important reactions amongst those quoted above are those involving ions which do not react rapidly with H_2, such as C^+, CH_3^+, $C_2H_2^+$ and C_2N^+, but ions such as N^+, NH^+, NH_2^+, H_2O^+ which do react rapidly with H_2 cannot be ignored, since their reactions with relatively abundant neutrals such as CO, CH_4 (and presumably O_2 and CO_2) can clearly generate amino-, and cyano-compounds in their observed relatively small abundances. That nitroso-compounds are much less abundant in interstellar clouds is quite consistent with our laboratory observations of a very large number of ion-neutral reactions in which such products are relatively rare.

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DISCUSSION FOLLOWING ADAMS

Hollenbach: The impression I have from your remarks and those of Dr. Fehsenfeld is that the radiative-association rate-coefficient for C^+ with H_2 is about $10^{-14} cm^3 s^{-1}$ at low temperatures. What is the probable uncertainty in this coefficient?

https://doi.org/10.1017/S0074180900072788 Published online by Cambridge University Press

Adams: The greatest uncertainty lies in the value of the radiative lifetime for $(CH_2^+)^*$ formed in the C^++H_2 radiative-association reaction (see the papers by Herbst, and by Smith and Adams in these Proceedings).

Glassgold: Despite the excellent new results from laboratory measurements of reaction rates, I believe there remains a fundamental difficulty in explaining nitrogen-bearing molecules with gas-phase chemistry. The reason is that the progenitor ion N^+ you proposed has much too low an abundance in interstellar clouds. (It is presumed to arise from cosmic ray ionization of N; a similar problem arises if most of the nitrogen is in the form of N_2.)

Langer: Direct cosmic ray ionization of nitrogen is not important in initiating nitrogen chemistry. Reactions of N with carbon and oxygen radicals are dominant.

Adams: N^+ is rapidly produced by the reaction of N_2 with He^+, which is assumed to be formed by cosmic ray ionization of the abundant helium. So if most of the nitrogen in the clouds is in the form of N_2, then a ready source of N^+ is available. The reaction $He^++CO \rightarrow C^++O+He$ competes for the He^+, but even if $[CO]>>[N_2]$, sufficient N^+ would still be produced to explain the presence of the NH_3 via the sequence $N^++H_2 \rightarrow NH^++H_2 \rightarrow NH_2^++H_2 \rightarrow NH_3^++H_2 \rightarrow NH_4^++e \rightarrow NH_3$, especially since we have recently shown that the reaction of NH_3^+ with H_2 proceeds at a significant rate at low temperatures.

Langer: Could Dr. Fehsenfeld give a range of values for the radiative association rate of $C^++H_2 \rightarrow CH_2^++h\nu$?

Fehsenfeld: I would expect about $10^{-15}cm^3s^{-1}$ based on Herbst's calculations, perhaps one order of magnitude more or less.

Herbst: The calculated rate coefficient of the $C^++H_2 \rightarrow CH_2^++h\nu$ radiative association reaction could be made more precise by careful calculation of the radiative decay rate.

Winnewisser: You have shown that the fewer chemical pathways leading to N=O bearing molecules such as NO and HNO could be an explanation of their low interstellar abundance. Do you feel that this could also be a likely explanation for the conspicuous absence of larger NO bearing interstellar molecules, for example HNCO versus HCNO?

Adams: Yes. From our studies of many hundreds of ion-neutral reactions, the only reactions leading to HNCO are $NH_2^++COS \rightarrow H_2NCO^+$ ($+e \rightarrow$ HNCO?) and the association reaction $NH_2^++CO \rightarrow NH_2^+\cdot CO$ ($+e \rightarrow$ HNCO?), either or both of which may be responsible for the observed HNCO in interstellar clouds.