ON THE FORMATION OF INTERSTELLAR LINEAR MOLECULES

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ABSTRACT

A possible mechanism for the formation of interstellar linear molecules is studied experimentally by means of synthesis apparatus. C_2 and CN radicals are abundantly formed from plasmas containing C, N and H atoms. The C_2 and CN radicals survive electron bombardment. They collide with each other and recombine to form linear molecules.

INTRODUCTION

It has been shown that unsaturated bonds survive the bombardment of excited electrons (Sakata et al., 1978). Especially prominent among unsaturated interstellar molecules are molecules which have linear-chained structure and conjugated triple bonds. Cyanoacetylene (HC_3N) (Turner, 1971), cyanobutadiyne (HC_5N) (Avery et al., 1976), cyanohexatriyne (HC_7N) (Kroto et al., 1978) and cyanooctatetrayne (HC_9N) (Broten et al., 1978) have been discovered in interstellar space. It is important to clarify how these molecules are formed.

APPARATUS AND EXPERIMENTAL DETAILS

Figure 1 shows a schematic diagram of our apparatus. The apparatus is composed of three parts: a plasma generator at the right of the diagram, high-vacuum reaction chambers near the center, and at the left a product detector that employs a quadrupole mass-spectrometer. Initial gases containing C, N, O and H atoms are introduced from a source gas reservoir. The gases are heated and decomposed into ions and radicals by electron bombardment using microwave power generated by a magnetron. The high energy gases are injected into the vacuum chamber. In these injected gases ions and radicals recombine to form new molecules. Two types of experiments have been performed: one detects directly the products from the plasmas and the other detects trapped molecules on a cooled copper block at a temperature of 25K.

B. H. Andrew (ed.), Interstellar Molecules, 325–329.

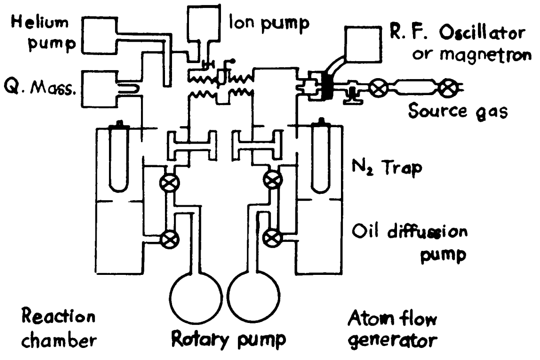


Fig. 1 Molecular Formation Apparatus

RESULTS

When bombarded, both a mixture of CH_4 and NH_3 and a gas of CH_3NH_2, all of which are single-bond molecules, were converted to gas mixtures of N_2, HCN, and C_2H_2, which have triple bonds. A similar pattern of time dependence was observed in both cases. Accordingly it was supposed that there is at some point a stage where the gases in the discharge tube are decomposed into monoatomic or diatomic ions and radicals.

From a gas mixture of methane and hydrogen, acetylene is abundantly formed at the time of discharge. When a mixture of CH_4, NH_3 and H_2 is bombarded, HCN, C_2H_2 and N_2 are produced. HCN and C_2H_2 are increasingly formed as the time of the discharge is increased. When four kinds of gas mixtures containing C, N, O and H atoms in the ratio 1:1:1:10, $C_2H_2+O_2+N_2+9H_2$, $2CH_4+O_2+N_2+6H_2$, $CO+NH_3+7/2H_2$ and $CH_4+NO+3H_2$, are bombarded, the products are as follows: from the gas mixture containing acetylene, CO, N_2, HCN and C_2H_2 are formed, and from the three gas mixtures without acetylene, CO, N_2 and HCN are formed. These results indicate that C_2 radicals survive oxidation. As a consequence of these experiments we think that C_2 and CN radicals are very stable in a radiation field.

Figure 2 and Tables 1 and 2 show the products derived from the bombardment of a gas mixture of C_2H_2, NH_3 and H_2 (2:1:2). They were trapped on a copper block cooled by a helium pump to 20K, and then gradually evaporated. Two types of products are seen: linear molecules such as $H(C{\equiv}C)_nH$ and $H(C{\equiv}C)_n{\cdot}CN$, and ring molecules such as cyclopentadiene, pyrrole, benzene, toluene, indole, indene and naphthalene.

Figure 3 shows typical patterns of the formation of linear molecules and ring molecules. M/e 74 and 75 indicate the linear molecules HC_6H and HC_5N, and m/e 78 indicates benzene (C_6H_6), a ring molecule. Linear molecules and ring molecules behave oppositely. At the beginning of the discharge ring molecules are formed, but with time they form less abundantly. On the other hand linear molecules are formed increasingly with time.

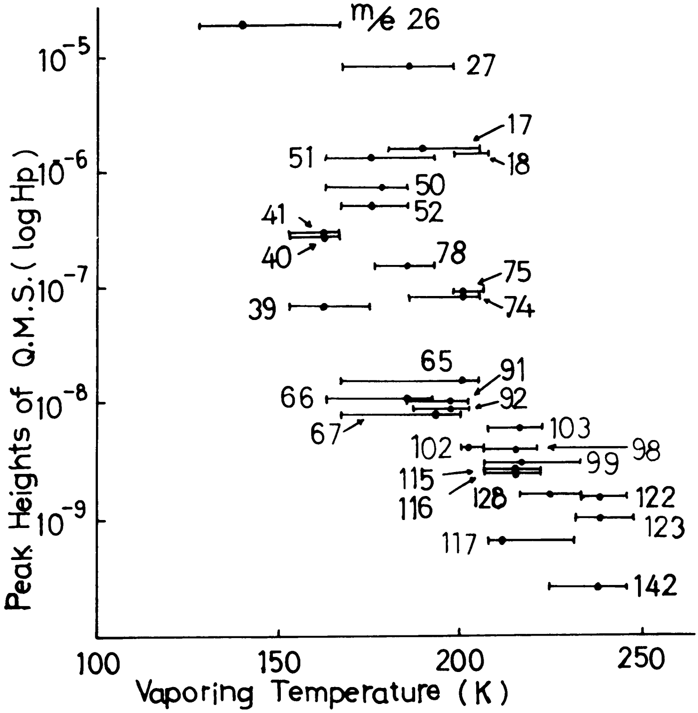


Fig. 2 Discharge products from the gas mixture of C_2H_2, NH_3 and H_2 (2:1:2)

Table 1 Produced molecules which are composed of C and H

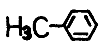
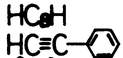
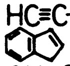
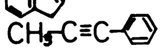
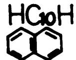
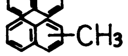
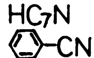
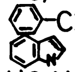
m/e		m/e	
16	CH_4	91,92	
26	C_2H_2	98	HC_8H
40	$H_2C{=}C{=}CH_2$	102	
40	$HC{\equiv}C{-}CH_3$	116	
50	HC_4H	116	
66		122	$HC_{10}H$
72	HC_6H	128	
78		142	

Table 2 Produced molecules which are composed of C, N and H

m/e		m/e	
17	NH_3	67	
27	HCN	75	HC_5N
28	N_2	99	HC_7N
41	$H_3C{-}CN$	103	
51	HC_3N	117	
52	NC-CN	123	HC_9N
65	$H_3C{-}C{\equiv}C{-}CN$		

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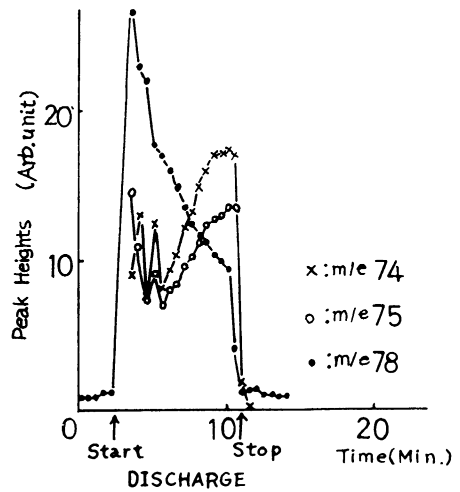

Fig. 3 Time variation of the mass-spectrum of the products from a gas mixture of C_2H_2, NH_3 and H_2 (2:1:2)

SUMMARY

A formation mechanism of interstellar linear molecules was investigated experimentally. The experiments were done with plasmas containing C, N, and H atoms. After condensation onto a cooled substrate, unsaturated organic molecules were abundantly formed. $-C{\equiv}C-$ and $-C{\equiv}N\cdot$ bonds are very strong and survive electron bombardment. $-C{\equiv}C-$ and $-C{\equiv}N$ radicals recombine each other to form $-C{\equiv}C-C{\equiv}C-$, $-C{\equiv}C-C{\equiv}N$, $-C{\equiv}C-C{\equiv}C-C{\equiv}C-$, and $-C{\equiv}C-C{\equiv}C-C{\equiv}N$ radicals. They form a series of cyanopolyyne molecules.

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DISCUSSION FOLLOWING SAKATA

Field: In a number of your experiments you consider the reactions of the products of a microwave discharge of mixtures containing H_2, for example. Many molecular species on emerging from microwave discharges will be vibrationally excited - indeed this is a standard method of forming H_2 (V=1). The chemistry which subsequently emerges may be strongly influenced by the presence of such vibrationally excited species, which are presumably not important in the interstellar medium.

Sakata: We have done our experiments supposing mainly highly excited conditions such as those found in the circumstellar clouds, in the shocked region in Orion, and so on.

Willner: Is there a simple physical reason for the formation of completely unsaturated molecules in preference to molecules having some degree of saturation?

Sakata: Saturated bonds which have one shared electron tend to be destroyed more easily by electron bombardment.

Feldman: Regarding the experimentally demonstrated production of ring molecules in microwave discharges, I wish to point out that Andrew and I have searched for pyrrole, pyridine, and benzonitrile at the peak HC_5N position in TMC 1 using the 46 m telescope at the Algonquin Radio Observatory. Our results are negative at the $T_A \sim 10$ mK level.

Allamandola: In what part of the interstellar medium do you think there takes place this process of the formation of diatomic molecules in a plasma, and their subsequent condensation into larger molecules?

Sakata: Diatomic molecules will be formed in such high energy fields as strong radiation and strong mutual collisions among atoms, molecules and radicals. Their subsequent condensation into larger molecules takes place under conditions milder than those in the field in which the diatomic molecules are formed. I think one might expect these processes in circumstellar atmospheres, in clouds irradiated by stars, and in shocked regions in interstellar clouds.