

CHEMIIONIZATION IN INTERSTELLAR CLOUDS

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ABSTRACT

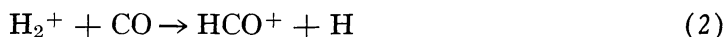
It is pointed out that the chemiionization reaction $\text{CH} + \text{O} \rightarrow \text{HCO}^+ + e$ is a source of positive ions and free electrons in interstellar clouds and that carbon monoxide is produced efficiently by the sequence of chemiionization and dissociative recombination.

Subject headings: interstellar matter — molecules, interstellar

Positive and negative ions may play an important role in the production of complex molecules in interstellar clouds. Even in the absence of a physical source of ionization, free electrons can be produced by the chemiionization mechanism of associative ionization



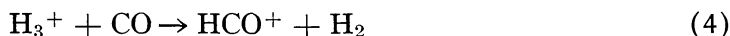
which at temperatures appropriate to interstellar clouds probably has a rate coefficient of about $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (MacGregor and Berry 1973) though the possibility that the coefficient is an order of magnitude higher cannot be excluded. The production of the triatomic molecular ion HCO^+ is of particular interest because Klemperer (1970) has suggested that HCO^+ may be the identity of the emitter X-ogen detected at 89.190 GHz (Buhl and Snyder 1970) toward several galactic radio sources. Klemperer (1970) noted as possible chemical origins the reactions



and



A further possibility is



(Herbst and Klemperer 1973). Since H_2^+ and CO^+ are rare constituents, reaction (4) is usually more efficient than reaction (2) or (3), but we shall argue that in many circumstances, the associative ionization process (1) is the dominant source of HCO^+ .

The production of H_3^+ requires an ionizing source of radiation such as cosmic rays or X-rays. We postulate an ionizing flux $\xi \text{ s}^{-1}$. In a dense cloud composed mostly of H_2 , a fraction 0.95 of the resulting ions are H_2^+ and the remaining fraction 0.05 are H^+ ions. The H_2^+ ions are rapidly converted to H_3^+ ions which then recombine dissociatively according to



if the electron density is sufficiently large. The efficiency of dissociative recombination

of diatomic molecules usually increases with decreasing temperature (cf. Bardsley and Biondi 1970), but a more nearly constant rate may be appropriate to complex polyatomic ions. We adopt for the rate coefficient of reaction (5) the value $3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ measured at 205° K by Leu, Biondi, and Johnsen (1973). Then in equilibrium

$$n(\text{H}_3^+) \sim 3 \times 10^6 \zeta n_{\text{H}_2} / n_e, \quad (7)$$

n_{H_2} being the density of molecular hydrogen. The electron density, n_e , is controlled at low temperatures by the slowly recombining H^+ ions which are largely removed by radiative recombination at a rate of about $10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Thus

$$n_e \sim n_{\text{H}^+} \sim 7 \times 10^4 (\zeta n_{\text{H}_2})^{1/2} \quad (8)$$

and

$$n(\text{H}_3^+) \sim 40 (\zeta n_{\text{H}_2})^{1/2}. \quad (9)$$

Because (5) can enhance the atomic hydrogen concentration to a value at which production of H^+ by direct ionization of H and by charge transfer from H_2^+ become significant, formula (9) overestimates the equilibrium abundance of H_3^+ at large values of ζ if n_e is determined by formula (8). However except at low temperatures H^+ is also removed by



and O^+ reacts with H_2 to form OH^+ :



Further reactions occur (Herbst and Klemperer 1972; Watson 1973), and n_e is controlled by reactions such as



and not radiative recombination to H . Thus n_e may be much reduced below (8). The abundance of H_3^+ is similarly controlled by reactions with heavy constituents such as CO and O . With a value of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for the rate coefficient of such ion-molecule reactions, $n(\text{H}_3^+) \sim 2 \times 10^{12} \zeta$.

The abundance of CO appears to be of the order of $10^{-5} n$ (cf. Rank, Townes, and Welch 1971; Penzias *et al.* 1971), so that with the adoption of the high rate coefficient of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for reaction (4), the rate of production of HCO^+ through reaction (4) is

$$p(\text{HCO}^+) = 4 \times 10^{-13} \zeta^{1/2} n_{\text{H}_2}^{3/2} \text{ cm}^3 \text{ s}^{-1} \quad (16)$$

if dissociative recombination dominates the H_3^+ destruction, and $2 \times 10^{-2} \zeta n_{\text{H}_2}$ if reactions with CO and O dominate.

If we accept the arguments of Bates and Spitzer (1951), McNally (1962), Solomon and Klemperer (1972), and Watson and Salpeter (1972) for the formation of CH , the ratio of the density of CH to that of H_2 in a dense cloud in which only a small fraction of the carbon is in molecular forms is of the order 6×10^{-9} . The rate of formation of HCO^+ by association ionization (1) is then about $3 \times 10^{-23} n_{\text{H}_2}^2 \text{ cm}^{-3}$

s^{-1} . Thus production of HCO^+ through reaction (1) is more efficient than through reaction (4) whenever $\xi/n_{\text{H}_2} < 1.5 \times 10^{-21}$. In dense clouds without internal ionization sources, ξ is presumably no larger than the value $10^{-17} s^{-1}$ appropriate to 100-MeV cosmic rays (Spitzer 1968) because neither low-energy cosmic rays nor X-rays can penetrate far into the cloud. It follows that in the interior of clouds with densities exceeding about $7 \times 10^3 \text{ cm}^{-3}$, associative ionization is the major source of HCO^+ . This conclusion depends critically on the assumed density of CH in dense clouds.

The observational evidence (cf. Frisch 1972) suggests that in diffuse clouds in which a significant fraction of the hydrogen content is in the form of atomic hydrogen, the ratio of the density of CH to that of C is about 10^{-4} . The rate of formation of HCO^+ is accordingly about $3 \times 10^{-22} n_{\text{H}}^2 \text{ cm}^{-3} s^{-1}$, n_{H} being the density of atomic hydrogen. In such clouds, none of the reactions (2), (3), or (4) occurs rapidly, and associative ionization appears to be the only significant source of HCO^+ .

The mean lifetime of HCO^+ is given by $5 \times 10^6/n_e s$, and the abundance is critically dependent on the presence of sources of ionization. In the case of the Orion cloud, the column density is about $2 \times 10^{23} \text{ cm}^{-2}$ (Rank *et al.* 1971) and reaction (1) may be not only the major source of HCO^+ but also the major source of free electrons. Then $n_e \simeq n(\text{HCO}^+)$. The ion is removed by dissociative recombination, the rate coefficient of which is $2 \times 10^{-7} \text{ cm}^3 s^{-1}$ at 300° K and $3 \times 10^{-7} \text{ cm}^3 s^{-1}$ at 205° K (Leu *et al.* 1973). The temperature dependence of the rate coefficient is uncertain at low temperatures, and we adopt the value measured at 205° K . Thus the equilibrium abundance of HCO^+ is about $10^{-8} n_{\text{H}_2} \text{ cm}^{-3}$ and the mean lifetime of HCO^+ is about $10^7 n_{\text{H}_2}^{-1}$ years. The predicted column density of HCO^+ is accordingly about $3 \times 10^{15} \text{ cm}^{-2}$ which is in harmony with the rough estimate of the abundance of X-ogen (Buhl and Snyder 1970).

In a diffuse cloud, ionization by starlight leads to an electron density of at least $6 \times 10^{-4} n_{\text{H}}$, and the equilibrium abundance of HCO^+ is not more than $10^{-12} n_{\text{H}}$. Thus the ion HCO^+ is probably detectable only in dense clouds into which the ionizing starlight radiation cannot penetrate.

The recombination path for the dissociative recombination of HCO^+ is almost certainly



and there is little prospect that dissociative recombination is a significant source of OH; the production of an HCO^+ ion results in the destruction of a CH molecule and the production of a CO molecule.

As a source of CO, the sequence of reactions (1) and (17) is probably more efficient in both diffuse and dense clouds than the direct reaction



advocated by Solomon and Klemperer (1972).

The associative ionization process (1) is favored over the chemical exchange process (18) statistically and also, apparently, by the shapes of the potential surfaces. Of the eight surfaces for the linear H-C-O configuration and the 12 for the bent configuration, only the $^2\Sigma^+$ state leads to reaction (18). The $^2\Sigma^+$, $^2\Sigma^-$, and $^2\Delta$ surfaces can all lead to reaction (1). At the low temperatures of interstellar clouds, the $^2\Sigma^-$ and perhaps the $^2\Delta$ seem to be the only states that are energetically accessible (MacGregor and Berry 1973). It is useful to note that because of reactions (1) and (17), the large abundances of CO predicted by Solomon and Klemperer will still occur even if reaction (18) is found to be slow.

Depending upon the degree of rotational and vibrational excitation of the product

molecules HCO^+ and CO , the heat source from the sequence of reactions (1) and (17) or from reaction (18) in a dense cloud may amount to $4 \times 10^{-34} n_{\text{H}_2}^2$ ergs $\text{cm}^{-3} \text{s}^{-1}$. In the sequence of (1) and (17), $8 \times 10^{-36} n_{\text{H}}^2$ ergs $\text{cm}^{-3} \text{s}^{-1}$ is carried by the electron emitted in the chemiionization process. The HCO^+ ion can also act as a cooling agent; the cross-section for the rotational excitation of HCO^+ is presumably much larger than that for the rotational excitation of CO .

The presence of HCO^+ leads to the formation of other complex ionic species. The ion H_3O^+ is formed by



and the ion NH_4^+ by



In the direction of Sagittarius B2, the column density of $\text{NH}_3 \geq 10^{17} \text{ cm}^{-2}$ and the total particle column density is $\geq 10^{22} \text{ cm}^{-2}$. The ion NH_4^+ is probably removed by dissociative recombination with a rate coefficient near $10^{-6} \text{ cm}^3 \text{ s}^{-1}$. In Sgr B2, the equilibrium abundance of NH_4^+ is probably comparable to that of HCO^+ .

The presence of HCO^+ may be critical to the formation of formaldehyde (Herbst and Klemperer 1973). The chemiionization source (1) may help to explain the wide distribution of formaldehyde in the Galaxy.

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