EXPERIMENTAL MEASUREMENTS OF ION-MOLECULE REACTIONS

F.C. Fehsenfeld
NOAA/ERL, Aeronomy Laboratory, Boulder, Colorado 80303

ABSTRACT

The applicability of ion-molecule reaction rate constants measured at room temperature to simulation of interstellar cloud chemistry is discussed. Three-body association-rate constants of C^+ and NH_3^+ have been measured between 100 K and 300 K. These results give information about the same associations by radiative processes. Possible implications for interstellar molecule production by radiative association and free radical reaction are discussed.

Observations of interstellar clouds made during the past ten years have revealed a variety of complicated molecules (Townes, 1977). It is now generally accepted that positive ion-neutral reactions play an important role in the synthesis of many of these molecules (Black and Dalgarno, 1973; Herbst and Klemperer, 1973; Watson, 1974; Prasad and Huntress, 1979a). Thus far, several hundred positive ion-molecule reactions of astrochemical interest have been measured (Huntress, 1977; Albritton, 1978; Sieck, 1979). Most studies have been carried out at 300 K, a temperature almost an order of magnitude above the temperature characteristic of dense clouds. However, evidence indicates that rate constants for reactions which occur in a large fraction ($\gtrsim \cdot 1$) of the ion-neutral collisions have little if any energy dependence. This encompasses a large majority of the exothermic reactions studied. Although exceptional at low energy, there are also slow exothermic ion-molecule reactions with rate constant less than 10% of the ion-neutral collision rate constant. The reaction

$$S^+ + O_2 \rightarrow SO^+ + O \tag{1}$$
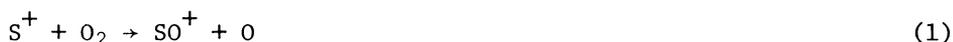
is an example (Dotan, et al., 1979). Reaction (1) has a rate constant, $k_1 = 1.6 \times 10^{-11}$ $cm^3 s^{-1}$ at 300 K and is inversely proportional to energy for center-of-mass kinetic energy less than 0.15 eV, a behavior characteristic of many slow reactions at low energy that is attributed to the increasing lifetime of the ion-neutral collision complex with

decreasing energy. For this reason, at interstellar cloud temperatures reaction (1) is expected to have a rate constant several times that at 300 K. Another very slow reaction at low energy is

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H. \tag{2}$$

The rate constant for this reaction is linear in an Arrhenius plot with $k_2 = 1.7 \times 10^{-11} \exp(-0.09/kT)$ (Fehsenfeld et al., 1975) with $k_2 = 10^{-13}$ cm^{3}s^{-1} at 100 K.

Ion-molecule radiative association in interstellar clouds is potentially a powerful mechanism by which atoms and simple molecules can be combined to form more complex molecules. Theory and indirect experimental evidence suggest these reactions are important. The present understanding of the mechanism is exemplified by the reaction

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu. \tag{3}$$

Reaction (3) was first proposed by Black and Dalgarno (1973). The rate constant for the reaction has been calculated by Herbst (1976, 77, 79). The reaction begins with the collision of C^+ with H_2 to form an excited complex, CH_2^{+*}, which is unstable against predissociation into the original C^+ and H_2 reactants. The lifetime of the collision complex is determined by the energy which the C^+ and H_2 carry into the complex, the disposition of this energy into the internal modes of the CH_2^{+*}, and the bond dissociation energy of the CH_2^+ states which are formed. The CH_2^{+*} is composed of two electronic states of the molecular ion, the $^2A_1$ and $^2B_1$ states in C_{2v} symmetry. The states are assumed to be completely mixed. The complex is stabilized by the allowed radiative transition from the $^2B_1$ state to the $^2A_1$ state. In the calculation the rate constant for the formation of the excited complex and the lifetime of the complex against predissociation are estimated from the measured rate constant for the analogous three body association (Herbst, 1979)

$$C^+ + H_2 + He \rightarrow CH_2^+ + He. \tag{4}$$

The data for this reaction are fit by the expression $k_4 = 5.1 \times 10^{-30} (300/T)^{1.3}$. From this data several conclusions concerning reaction (3) are drawn. The three body association rate increases smoothly down to the lowest temperature which implies that there are no energy barriers preventing the formation of CH_2^{+*}. At a pressure of 1.3 torr and temperature of 100 K, the effective binary rate constant for the reaction is 4×10^{-12} cm^{3}s^{-1} and shows no indication of saturation which implies a large fraction of the C^+ collision with H_2 yields CH_2^{+*}. Finally the rate constant of the three body association at 100 K is 2×10^{-29} cm^{6}s^{-1} which implies that the lifetime of CH_2^{+*} is $\gtrsim 10^{-10}$s. These results lend support for the radiative association mechanism.

Another radiative association reaction

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu \tag{5}$$

is suggested as a key reaction in the formation of CH_4 and ultimately C_2H_2 and C_2H_4 (Prasad and Huntress, 1979b). The analogous three body association

$$CH_3^+ + H_2 + He \rightarrow CH_5^+ + He \qquad (6)$$

is fast. Smith and Adams (1979) find $k_6 = 6.3 \times 10^{-27} cm^6 s^{-1}$ at 110 K. This supports the assumption that reaction (5) is fast. Prasad and Huntress (1979b) have also suggested that the radiative association

$$NH_3^+ + H_2 \rightarrow NH_5^+ + h\nu \qquad (7)$$
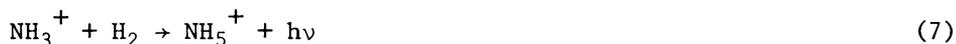
can overcome the bottleneck in the formation of NH_3 caused by the slow rate constants for reaction (2). In this case the analogous three body association

$$NH_3^+ + H_2 + He \rightarrow NH_4^+ + H + He \qquad (8)$$

$$\rightarrow NH_5^+ + He$$
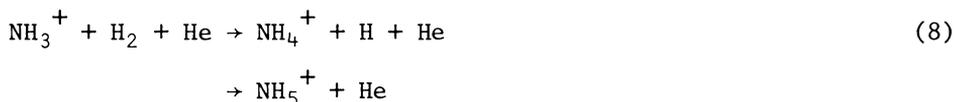
is immeasurably slow, $k_8 < 3 \times 10^{-30} cm^6 s^{-1}$, in the variable temperature flowing afterglow apparatus at 100 K and indicates that reaction (7) is also slow.

It seems reasonable to use measured three body association rates at 100 K and the energetics of the association reaction to indicate a crude upper bound on the radiative association rate constant (Herbst, 1979). The limits indicate that radiative association will play an important role in simple molecule ($n \lesssim 20$) building. The largest uncertainty in these estimates is the transition probability for radiative stabilization of the ion-neutral association complex. In the discussion of radiative association, it should be noted that although the radiative association reactions have not been directly observed for molecules of astrophysical interest, the direct attachment of substituted benzenes to Li^+ has been observed at 300 K at low pressure in the ICR and attributed to radiative association (Woodin and Beauchamp, 1978).

Another challenge presented by the interstellar medium is the relatively large concentration of atomic and molecular free radicals. At low cloud temperatures these neutral radicals can be expected to react rapidly with other neutral radicals as well as ions. Experimental difficulty in dealing with these extremely reactive species has limited measurements. Atomic hydrogen reactions have been measured in both ICR (Karpas, et al., 1979) and flowing afterglow reactors (Fehsenfeld and Ferguson, 1971). The study of Karpas et al.(1979) indicates that H_2^+, CO^+, N_2^+ and HCN^+ react with atomic hydrogen while hydrocarbon ions of the type CH_n^+ and $C_2H_n^+$, n = 2, 3 and 4, do not. Atomic oxygen and atomic nitrogen reactions have been studied at 300 K in flowing afterglow and selected ion flow tube reactions (Fehsenfeld and Ferguson, 1972; Fehsenfeld, 1976; Viggiano et al., 1979). Rate constants have been determined for the reactions of H^+, D^+, H_3^+, CH^+, CH_3^+, CH_5^+, C_2^+, C_2H^+,

$C_2H_2^+$, and CO^+ with atomic oxygen and CH^+, CH_2^+, CH_3^+, H_2O^+, C_2^+, $C_2H_2^+$, and O_2^+ with atomic nitrogen. The rate constants obtained for the N and O reactions are generally a substantial fraction of the collision limiting rate constant and characteristically produce C-N and C-O bonded products. The O and N reactions are important steps in the synthesis of molecules observed in interstellar clouds.

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DISCUSSION FOLLOWING FEHSENFELD

Glassgold: Two long standing questions concerning gas-phase ion molecules have been (a) the reaction of H_3^+ with atomic nitrogen, and (b) charge exchange of molecular ions with neutral metal atoms. Could you comment on the status of measurements of these reactions.
    Fehsenfeld: We have not measured the H_3^+ reaction with atomic nitrogen. Charge exchanges between molecular ions and neutral metal

atoms are generally rapid. I would expect them to be rapid at inter-
stellar cloud temperatures.

Langer: Can the reaction $H_3^+ + N \rightarrow NH_2^+ + H$ take place rapidly? I
believe Huntress has indicated that it may be slow.

Fehsenfeld: We have not studied this reaction, so I do not know.

Huntress: We have made some attempts to measure the rate constant
and product distribution for the reaction of H_3^+ ions with N atoms.
Preliminary data indicates that the reaction may proceed at a rate on
the order of a few times $10^{-10} cm^3/s$, and that the product may indeed be
NH_2^+. The present state of the experiment is uncertain, however. The
NH^+ ion cannot be produced from this reaction since this channel is
endothermic.

Bar-Nun: Could you give us your estimate of the certainty of these
complex reaction schemes. The recent findings of strong lightning
activity by the Voyageur and Pioneer - Venus space probes has demonstrated
the failure of chemical modelling of the atmospheres of Venus and Jupiter.

Fehsenfeld: The only estimate of the certainty of a chemical model
is its ability to explain the observations. It is too early to make such
a judgement concerning the current models of the gas-phase chemistry of
the interstellar clouds.

Allamandola: You notice that the rate constant as the temperature
drops from room temperature is higher than that which you would get from
an extrapolation of your data. The effect is due to the lower kinetic
energy the reacting partners must dissipate, and you suggest that this
results in a longer lived transition state which ultimately relaxes into
reactants. Do you see a rate constant decrease as you get to much lower
temperature due to the dominance of activation energy and the fact that
the kinetic energy is lower than the required activation energy?

Fehsenfeld: We have not observed the effect you describe on the
ion reactions we have studied, but our measurements do not extend below
100 K.

Allamandola: In our experiment we store atoms, for example oxygen,
in solid argon. We find that a very slight rise in temperature (½ K is
enough) is sufficient to cause chemiluminescence from O_2, but when the
temperature has again dropped the reaction is completely stopped. We
believe the effect is due to atoms which are neighbouring, but unable
to react because there is insufficient energy to provide the activation
energy. The mild warming provides the required energy. The reactions
then take place freely until 50-60 K, at which temperature atom mobility
is so great that all atoms have apparently encountered a partner or left
the system via the gas-phase.

Herbst: Not all polyatomic ion-molecule association reactions will
be rapid at T≤50 K. The reasons for this assertion are (1) activation
barriers to tightly-held complexes, and (2) the need for significant
(>1 eV) bond energies of cluster ions.

Thaddeus: It seems to me obvious that there are pitfalls associated
with symmetry if you try to deduce two body radiative association rates
from three body rates. You clearly cannot say anything about
$H+H \nrightarrow H_2 + h\nu$ from $H+H+He \rightarrow H_2 + He$.

Fehsenfeld: I agree. The correspondence between three body asso-
ciation and the analogous radiative association, at present, is useful

only in establishing an upper limit on the radiative association.

    Field: There is some reasonably good experimental evidence to suggest that interaction of *neutral* radicals with H-atoms (e.g. H+OH, H+NH$_2$, H+CH etc.) may involve radiative association proceeding at a significant rate. Such interactions occur on strongly attractive potential energy surfaces (with no energy barriers) and may well be dominated by resonant scattering phenomena.

    P. Smith: There are several discrepancies between observations and the predictions of models of chlorine species in diffuse clouds. Black and myself, in a poster paper presented at this symposium, have suggested that these discrepancies can be explained if the reaction $Cl^+ + H_2 \rightarrow HCl^+ + H$ is slow at cloud temperatures. Such a slow rate could be due to the presence of a modest energy barrier in the reaction, which is exothermic by only 0.22 eV. You have stated that the rates for rapid reactions tend to be independent of temperature. Do you have any comment on our conjecture?

    Fehsenfeld: There may certainly be exceptions to the generalization that the rate constants of fast reactions are independent of energy. Your suggestion is very interesting.