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Final Report: Ion Chemistry in Interstellar Space

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Abstract

The temperature dependence of the bimolecular reactions of Cl^+, HCl^+, CH^+, CH_2^+, N^+, Nh^+, and NH_2^+ reacting with H_2 have been investigated. For Cl^+ and HCl^+ rate constants have been determined over the temperature range of 150-400 °K. Preliminary data have been obtained for the other systems. The Cl^+/H_2 system shows a weak, but significant positive temperature dependence that could be important in interstellar modeling studies. The HCl^+/H_2 system shows a substantial negative temperature dependence with the rate constant approaching the collision rate at low temperatures. In a second study, the association reaction $CH_3^+ + HCN \rightarrow CH_3 \cdot HCN^+$ has been theoretically modeled using statistical phase space theory. Both radiative and collisional stabilization have been included. The results are compared with experiment with good agreement obtained over wide variatons in T and p. This system is potentially important in the mechanism of large molecule synthesis in interstellar space.

I. Introduction

It is well known that the environment in interstellar space is extreme - temperatures in the range of 10-100 °K and pressures of 10^{-9} torr and lower. Nonetheless about half of the mass of the universe exists in this frigid void in the form of interstellar "clouds" and increasingly complex molecules are being discovered at substantial concentrations. This report briefly summarizes the work that we've done in order to begin to understand the chemistry that occurs in this region of the universe. The report will be divided into two sections. The first of these will deal with the temperature dependence of simple ions reacting with H_2 and the second with the association reaction of CH_3^+ with HCN. Manuscripts are currently in preparation that will discuss the work in great detail. These will be forwarded to JPL when finished.

II. Temperature Dependence of Simple Bimolecular Ion-Molecule Reactions:

The most abundant molecule, by far, in the interstellar medium is H_2. Hence, it is of paramount importance that accurate rate constants be determined between various simple ions and this neutral over as wide a temperature range as possible - in particular low temperatures are especially important. We have initiated such a study for the ions CH^+, CH_2^+, N^+, NH^+, NH_2^+, Cl^+ and HCl^+ since these are relatively abundant ions in interstellar clouds. In this report only the ions Cl^+ and HCl^+ will be discussed in detail. The data on the remaining systems is still preliminary in nature.

We have studied the reactions

$$Cl^+ + H_2 \longrightarrow HCl^+ + H - 4\ \text{kcal/mole} \qquad (1)$$

$$HCl^+ + H_2 \longrightarrow H\ Cl^+ + \leq 0\ \text{kcal/mole} \qquad (2)$$

over the temperature range 150-400 °K using an Ion Cyclotron Resonance Spectrometer previously discribed in the literature.[1] The rate constant for (1) has a small but significant positive temperature dependence. If the Arrhenius form of the rate constant is assumed, Eqn (3),

$$k = Ae^{-E^{\ddagger}/RT} \qquad (3)$$

then a plot of ln k vs 1/T should yield a straight ling of slope-$E^{\ddagger}/R$. Such a plot is linear for reaction (1) yielding a barrier to reaction $E^{\ddagger}$ = 335 cal/mole. This is a small barrier yet can yield substantial variation in k with T. For example $k_{300} = 5.6 \times 10^{-10} cm^3/S$, $k_{100} = 1.8 \times 10^{-10}\ cm^3/s$ and $k_{20} - 2.1 \times 10^{-13} cm^3/s$. Hence, the rate constant is over 10^3 smaller at interstellar temperatures than at room temperature - the temperature of the only previously available measurement.[2]

Reaction (2), by contrast, has a substantial negative temperature dependence. For example, $k_{150} = 8.1 \times 10^{-10}\ cm^3/S$ and $k_{400} = 4.2 \times 10^{-10}\ cm^3/S$. Hence, this reaction will proceed at the collision limit at interstellar temperatures. The kind of behavior exhibited by reaction (2) suggests a tight transition state for which $E^{\ddagger} < E_0$ where E_0 is the threshold energy for the exit channel. Under these circumstances increasing the temperature (and thus the internal energy in the collision complex) will tend to drive the reaction towards reactants because entropy controls the reaction not energy.[3]

Finally, three sources of Cl^+ were used;

$$\left.\begin{matrix} CCl_4 \\ CCl_3H \\ CCl_2F_2 \end{matrix}\right\} + e^- \longrightarrow Cl^+ + 2e^- + \left\{\begin{matrix} CCl_3 \\ CCl_2H \\ CClF_2 \end{matrix}\right. \qquad (4)$$

In most cases CCl_2F_2 was used because of its low freezing point. No difference in k_1 was observed for any of the sources of Cl^+. In all cases HCl was used to generate HCl^+ in reaction (2)

II. $CH_3^+ + HCN \quad CH_3 \cdot HCN^+$

Recent experimental work[4] on the above reaction has suggested that both radiative and collisional stabilization compete. At low pressures radiative association dominates while at high pressures collisional stabilization is prevalent. The experimental data are consistent with the mechanism

$$CH_3^+ + HCN \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (CH_3 \cdot HCN^+)^* \tag{5a}$$

$$(CH_3^+ \cdot HCN)^* + M \xrightarrow{k_s} CH_3 \cdot HCN^+ + M \tag{5b}$$

$$(CH_3^+ \cdot HCN)^* \xrightarrow{k_r} CH_3 \cdot HCN^+ + h\nu \tag{5c}$$

Th experiments were performed over the pressure range $10^{-6} \leq p \leq 10^{-2}$ torr and temperature range $200 \geq T \leq 400$ °K. In order to confirm both the general form of mechanism (5) and to extend the results to interstellar values of p and T we have modeled the reaction using statistical phase space theory.[5] The details will be forwarded in the form of a manuscript that is currently being typed.[6] The important results are: i) reaction mechanism (5) has been substantial; ii) $k_r \sim 10^4$ sec^{-1}; iii) $k_b \sim 10^6$ sec^{-} and iv) the overall association rate is fast at interstellar values of p and T.

IV. References

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