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RATE OF THE REACTION $N_2H^+ + CO \rightarrow HCO^+ + N_2$ AND ITS SIGNIFICANCE FOR THE INTERSTELLAR CHEMISTRY OF N_2H^+

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ABSTRACT

The rate constant for the reaction $N_2H^+ + CO \rightarrow HCO^+ + N_2$ has been determined to be $(8.79 \pm 0.13) \times 10^{-10}$ cm^3 s^{-1} at 297 ± 2 K with an estimated accuracy of ±25 percent. The implications of this rate constant for the interstellar chemistry of N_2H^+ are discussed. Estimates are made for the frequencies of the first rotational transitions in $^{15}N^{14}NH^+$, $^{14}N^{15}NH^+$, and N_2D^+.

Subject headings: abundances — atomic and molecular processes — interstellar matter — molecules, interstellar — transition probabilities

I. INTRODUCTION

Recently, a new interstellar triplet of microwave lines was detected at 93.174 GHz in dense neutral clouds associated with H II regions (Turner 1974). The carrier of these lines has been tentatively identified as the polyatomic ion N_2H^+ (Green *et al.* 1974; Turner 1974). The identification is based on both the center of gravity of the newly discovered triplet and the hyperfine (quadrupolar) splittings among the three lines. The apparent observation of N_2H^+ in dense interstellar clouds is of importance to theories of interstellar molecule formation. Specifically, the observation provides confirmation of the theory that polyatomic ions are present in dense clouds and that, consequently, ion-molecule reactions must play a role in the chemistry of such clouds. In an earlier article (Herbst and Klemperer 1973, hereinafter referred to as HK), one of the present authors considered in some detail the formation and depletion of molecules in dense interstellar clouds via gas-phase ion-molecule reactions. The ion N_2H^+ was mentioned but, since our calculations indicated this ion to be of smaller abundance than several others, sufficient detail was not afforded this species. In addition, the rate of what was assumed to be the principal depletion reaction for N_2H^+,

$$N_2H^+ + CO \rightarrow HCO^+ + N_2 ,$$

had not been experimentally investigated. It is our intention here both to report an experimental determination of the rate constant for the above reaction and to reevaluate the HK calculations on N_2H^+.

II. MEASUREMENT OF THE RATE CONSTANT FOR THE REACTION $N_2H^+ + CO \rightarrow HCO^+ + N_2$

This reaction was studied at 297 ± 2 K with the flowing afterglow technique which has provided accurate rate data for a large number of proton-transfer (Burt *et al.* 1970; Bohme *et al.* 1973) and other ion-molecule reactions (Schiff *et al.* 1974). This particular reaction provides an interesting challenge for the technique since the reactant ion, N_2H^+, and the product ion, HCO^+, have mass-to-charge ratios which are identical, within the resolution of our mass spectrometer. Isotopic labeling of one of the reactants is an obvious but expensive solution to the problem. Instead, advantage was taken of the fact that CO has a higher proton affinity than N_2. A gas with an intermediate proton affinity can then be chosen to react specifically with N_2H^+ and, therefore, to differentiate between the reactant and product ions.

The experimental arrangement is shown schematically in Figure 1. H_2 is used as a carrier gas and to generate H_3^+ by electron impact. N_2 is added just downstream of the electron gun, in sufficient quantities to convert all the H_3^+ to N_2H^+ by the rapid reaction

$$H_3^+ + N_2 \rightarrow N_2H^+ + H_2 \qquad (1)$$

before the gas reaches the inlet through which the neutral reaction CO is added. The reaction of interest, *viz.*,

$$N_2H^+ + CO \rightarrow HCO^+ + N_2 , \qquad (2)$$

is allowed to occur between the CO and CO_2 inlets. CO_2 is added through an inlet located coaxially with, and 0.5 cm from, the sampling orifice.

The proton affinity of CO_2 is 0.57 eV higher than that for N_2, and N_2H^+ is rapidly converted to CO_2H^+ by the reaction

$$N_2H^+ + CO_2 \rightarrow CO_2H^+ + N_2 , \qquad (3)$$

which has a rate constant (Burt *et al.* 1970) of 9.2×10^{-10} cm^3 s^{-1}. Since the proton affinity of CO_2 is

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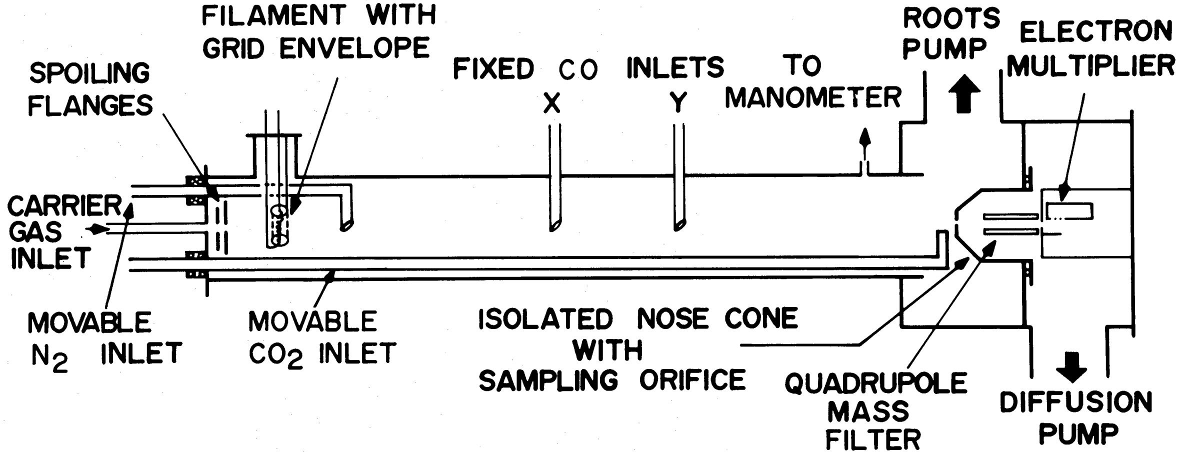

FIG. 1.—Schematic diagram of the flowing afterglow apparatus. The CO_2 inlet is positioned ~0.5 cm in front of the sampling orifice.

0.53 eV lower than that for CO, the reaction

$$HCO^+ + CO_2 \rightarrow CO_2H^+ + CO \qquad (4)$$

will not occur to a significant extent ($k_4 < 10^{-17}$ cm^3 s^{-1}). We have, in essence, converted the value of m/e of the reactant ion to 45 while leaving the value for the product ion at 29.

The results of a typical experiment are shown in Figure 2. Point A is the signal at $m/e = 29$ when the flows of CO and CO_2 are both zero and, therefore, is due only to N_2H^+ produced by reaction (1). Point B is the $m/e = 29$ signal with zero flow of CO but with a flow of CO_2 of 3.9×10^{18} molecules s^{-1}, and Point C is the corresponding signal at $m/e = 45$. Comparison of Points A and B shows that the N_2H^+ signal has been reduced by three orders of magnitude by reaction (3). The difference between C and A is due to mass discrimination of the instrument against the higher mass. The curves obtained at $m/e = 29$ and 45 when CO is added can then be ascribed to HCO^+ and CO_2H^+, respectively. The HCO^+ curves always reached plateau values which were within 10 percent of the initial N_2H^+ (cf. Point A). The impurity ion signal at mass 19, H_3O^+, remained constant with CO flow.

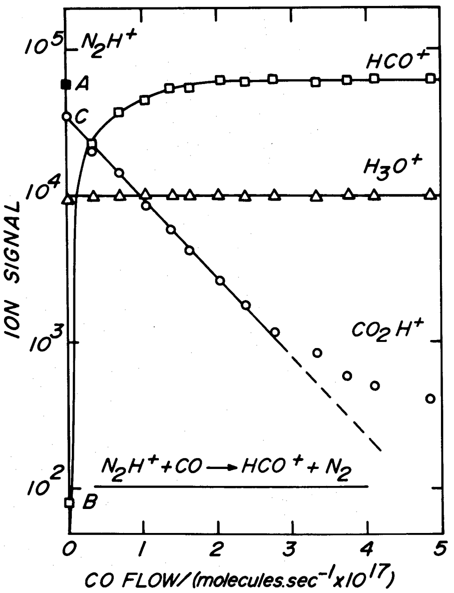

FIG. 2.—Plot of the variation of the ion signals as a function of CO flow. Point A is the initial N_2H^+ signal and Point B is the $m/e = 29$ signal with a CO_2 flow rate of 4.0×10^{18} molecules s^{-1}. The flow rate of N_2 is 3.9×10^{18} molecules s^{-1}. The CO in this experiment was added through inlet X (see Fig. 1), which gives an effective reaction length $L = 86$ cm. The pressure of $H_2 = 0.465$ torr, and the flow velocity $\bar{v} = 7.8 \times 10^3$ cm s^{-1}. The straight line drawn through the CO_2H^+ decay corresponds to a rate constant of $k = 8.78 \times 10^{-10}$ cm^3 s^{-1} for the reaction $N_2H^+ + CO \rightarrow HCO^+ + N_2$.

Since the CO_2H^+ curve mirrors the behavior of N_2H^+, it can be used to determine the rate constant for reaction (2) in the normal manner (Bohme *et al.* 1973). The logarithm of the CO_2H^+ signal was found to decrease linearly with CO flow over one to two decades, but showed some curvature at very high CO flows. A possible explanation for this curvature is the occurrence of reaction (4) to a small extent, due to the presence of some energetic HCO^+ ions produced by the electric field between the CO_2 inlet and the sampling orifice. Support for this explanation is provided by the observation that the amount of curvature increased with CO_2 pressure for a given N_2 flow. At any rate, the linear portions of these curves were considered adequate for obtaining reliable rate constants. No trends in the calculated rate constant were found over a considerable range in experimental parameters: the CO_2 flows were varied from 9.5×10^{17} to 6.9×10^{18} molecules s^{-1}, N_2 flows from 2.2 to 4.5×10^{18} molecules s^{-1}, total pressure from 0.333 to 0.643 torr, and the distance from the CO to CO_2 inlets from 55 to 80 cm. Seven experiments covering this range of parameters gave an average value of $k_2 = (8.79 \pm 0.13) \times 10^{-10}$ cm^3 s^{-1} with an estimated accuracy of ±25 percent. This experimental result is in

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excellent agreement with a value of 8.64×10^{-10} cm^3 s^{-1} calculated from the classical Langevin theory.

III. CALCULATED N_2H^+ DENSITIES

In the HK model, approximately 90 percent of the N_2H^+ production occurs via reaction (1):

$$N_2 + H_3^+ \rightarrow N_2H^+ + H_2 \,.$$

This reaction has a measured rate constant of $k_1 = 1.8 \times 10^{-9}$ cm^3 s^{-1} (Bohme *et al.* 1973). The remaining 10 percent of the N_2H^+ is produced via the reactions

$$N_2 + He^+ \rightarrow N_2^+ + He$$

$$N_2^+ + H_2 \rightarrow N_2H^+ + H \,.$$

The dominant mode for destruction of N_2H^+ is by reaction with carbon monoxide (reaction [2]):

$$N_2H^+ + CO \rightarrow HCO^+ + N_2 \,.$$

Prior to this work, the rate of this reaction, responsible for more than 90 percent of the N_2H^+ depletion rate, had not been reported in the literature. In the HK model, a rate constant $k_2 = 1.0 \times 10^{-9}$ cm^3 s^{-1} had been assumed based on the measured rate of the analogous N_2H^+–CO_2 reaction (Burt *et al.* 1970). The actual rate constant, reported in § II, has been determined to be $k_2 = 8.79 \times 10^{-10}$ cm^3 s^{-1}. This measurement clearly reinforces the HK calculation of N_2H^+ densities.

To understand the chemistry of N_2H^+, it is sufficient to consider reactions (1) and (2). In steady state, it is easily seen that

$$n_{N_2H^+} = \frac{k_1 n_{N_2} n_{H_3^+}}{k_2 n_{CO}} \,. \qquad (5)$$

Division by n_{H_2}, the molecular hydrogen density, yields

$$\frac{n_{N_2H^+}}{n_{H_2}} = \frac{k_1 n_{N_2} n_{H_3^+}}{k_2 n_{H_2} n_{CO}} \,. \qquad (6)$$

To estimate N_2H^+ densities, one need only know n_{N_2}, n_{CO}, and $n_{H_3^+}$.

HK found that the abundances of some molecular species were dependent on the assumed carbon-to-oxygen cosmic abundance ratio. Calculations were undertaken using two values for the C/O ratios—a "low O" value and a "high O" value. For HCN, the two C/O ratios led to calculated abundances differing by up to two orders of magnitude. Fortunately, the situation is quite different for N_2H^+. Utilizing HK values for the CO, N_2, and H_3^+ densities as a function of total gas density, we have recalculated N_2H^+ densities (expression [5]), and N_2H^+/H_2 density ratios (expression [6]), for several gas densities of interest using both the "low O" value (C/O = 0.85) and the high "high O" value (C/O = 0.55). The results are listed in Table 1. It is seen that the carbon-oxygen cosmic abundance ratio has virtually no effect on the calculated parameters.

One of the possible sources of error in the HK model is the assumption that virtually all carbon is tied up in the form of carbon monoxide. It is reasonable that a sizable percentage of the carbon is, instead, in the form of carbon dioxide, CO_2. The CO–CO_2 fractionation does not affect the calculated N_2H^+ abundances because the reaction (3),

$$N_2H^+ + CO_2 \rightarrow CO_2H^+ + N_2 \,,$$

has a rate constant $k_3 = 9.2 \times 10^{-10}$ cm^3 s^{-1} (Burt *et al.* 1970), and thus N_2H^+ will be destroyed at the same rate regardless of the relative abundances of CO and CO_2.

IV. COMPARISON WITH OBSERVATION

Turner (1974) has estimated that, if the carrier of U93.174 is N_2H^+, typical column densities of this species in the observed dense clouds near H II regions range from 2–7 $\times 10^{13}$ cm^{-2}. Turner (1974) has also estimated that $N_2H^+/H_2 \approx 3 \times 10^{-11}$ with an uncertainty of plus or minus one order of magnitude. A glance at Table 1 reveals our predicted N_2H^+/H_2 density ratio to be in best agreement with observation at a density of 3×10^4 cm^{-3}. There is clearly a large uncertainty in this number.

Theory indicates that the N_2H^+ density should be independent of total gas density in the range $10^4 \leq n \leq 3 \times 10^5$ cm^{-3}. At higher densities, cosmic ray-induced ionization should be less efficient and the N_2H^+ density should be lower. We thus expect N_2H^+ signals to be weak in the central cores of dense clouds (unless another source of ionization is present). Preliminary evidence for Orion A (Snyder 1975) is in agreement with this expectation.

TABLE 1

N_2H^+ ABUNDANCES

	"Low" O Abundance (C/O = 0.85)		"High" O Abundance (C/O = 0.55)	
n_{H_2} (cm^{-3})	N_2H^+ (cm^{-3})	N_2H^+/H_2	N_2H^+ (cm^{-3})	N_2H^+/H_2
1×10^4............	8×10^{-7}	8×10^{-11}	1×10^{-6}	1×10^{-10}
3×10^4............	8×10^{-7}	3×10^{-11}	7×10^{-7}	2×10^{-11}
1×10^5............	7×10^{-7}	7×10^{-12}	1×10^{-6}	1×10^{-11}
3×10^5............	8×10^{-7}	3×10^{-12}	7×10^{-7}	2×10^{-12}

V. DISCUSSION

An absolute identification of U93.174 as N_2H^+ coupled with the ubiquity of this ion in dense clouds associated with H II regions would indicate strongly that, at the least, ion-molecule formation schemes must be included in any general treatment of interstellar molecule chemistry. The case for N_2H^+ is a strong one because both the frequency of the triplet and the triplet splitting itself are pieces of evidence in favor of the identification. However, one piece of evidence—observation of a different N_2H^+ isotope—is missing. Wilson *et al.* (1972) estimate that the $^{15}N/^{14}N$ abundance ratio in interstellar HCN approximates its terrestrial value (0.0037). If this is true for N_2H^+, then the maximum column density to be expected for $^{15}N^{14}NH^+$ or $^{14}N^{15}H^+$ is $\sim 2\text{–}3 \times 10^{11}\ \mathrm{cm}^{-2}$ and observation of either of these isotopes appears to be a remote possibility. The observation of $^{15}N^{14}NH^+$ is marginally the more likely because this species will not have its rotational transitions split noticeably by hyperfine interactions. The reasons for this assertion are that ^{15}N has no quadrupole moment and the quadruple coupling constant of the inner nitrogen is too small to cause observable splittings (Green *et al.* 1974).

Assuming a range of H–N bond distances from 1.02–1.06 Å (Green *et al.* 1974), we obtain a value of 90,260 ± 50 MHz for the first rotational transition of $^{15}N^{14}NH^+$ (Herbst and Klemperer 1974). Similarly, we obtain frequencies of 91,210 ± 50 MHz and 77,000 ± 500 MHz for the centers of gravity of the first rotational transitions of $^{14}N^{15}NH^+$ and N_2D^+, respectively. These reported frequencies are obtained via primitive calculations of the type that provided an estimate for the $J = 1 \leftarrow 0$ transition of $H^{13}CO^+$ that was within 50 MHz of the observed value (Herbst and Klemperer 1974; Snyder 1975).

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