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# ICR studies of some hydrogen atom abstraction reactions: $X^+ + H_2 \rightarrow XH^+ + H$*

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Ion cyclotron resonance methods are used to identify and to measure the rate constants for the abstraction of a hydrogen atom from $H_2$ by $CH^+$, $CH_2^+$, $CH_4^+$, $N^+$, $NH^+$, $NH_2^+$, $NH_3^+$, $O^+$, $OH^+$, $H_2O^+$, $CO^+$, $N_2^+$, $C_2^+$, and $C_2H^+$ ions. Although in most cases hydrogen atom abstraction is the only available exothermic pathway for these reactions at thermal energies, the rate constants measured show that except for $O^+$, $CO^+$, and $N_2^+$, a large fraction of collisions between these ions and $H_2$ are not reactive. The rate constants measured range from a low of $(3\pm1)\times10^{-13}$ cm³/sec for the $NH_3^+$–$H_2$ reaction to $(1.73\pm0.04)\times10^{-9}$ cm³/sec for the $N_2^+$–$H_2$ reaction. These values compare to the Langevin value of about $1.5\times10^{-9}$ cm³/sec for collisions between these ions and $H_2$. An examination was also made for possible thermoneutral hydrogen atom exchange reactions for those ions which do not react with $H_2$ ($CH_5^+$, $CH_3^+$, $NH_4^+$, $H_3O^+$, $H_2S^+$, $H_3S^+$). The only exchange reaction observed was for collisions between $CD_3^+$ ions and $H_2$, for which a rate constant of $(5.1\pm0.5)\times10^{-10}$ cm³/sec was measured.

## I. INTRODUCTION

The reactions of ions in hydrogen are not only of fundamental interest, but are also important in present schemes for the synthesis of molecular species in dense interstellar clouds. For example, the loss processes involving the $CH^+$ ion in clouds containing large quantities of $H_2$ are important for determining the relative abundances of the CH and $CH^+$ species observed in these regions.[1,2] From the fundamental point of view, the abstraction of a hydrogen atom from $H_2$ by various ions represents a class of somewhat enigmatic reactions, since it appears that the occurrence of these reactions cannot be predicted on the basis of exothermicity.[3] Unlike other simple atom transfer processes in ion–molecule collisions (such as proton transfer), exothermic hydrogen atom abstraction does not always occur with every ion–molecule collision, even if the process is exothermic and is the only available reaction pathway. This is contrary to the prevailing conception that exothermic ion–molecule reactions have no activation energy and therefore should occur with nearly every collision. Only proton transfer reactions appear to occur at the maximum rate given by the collision frequency.

Abstraction reactions of ions in hydrogen have been previously examined,[3–11] but not without some experimental difficulties. Studies using conventional mass spectrometric techniques[6–11] generally involve ions with excess kinetic energy and suffer the difficulty that the reactant hydride ions are resynthesized in these mixtures by reaction of $H_2^+$ and $H_3^+$ ions with the neutral hydride additive. This latter problem can be especially acute for fragment ions with appearance potentials greater than the ionization potential of hydrogen, and in many cases prevents the identification of reactions and the measurement of rate constants. Measurements using the flowing afterglow technique[3,4] neatly avert this problem by separating the ion formation and hydrogen addition regions. The ion kinetic energy distribution in flowing afterglow experiments is thermal at 300 °K, but only approximate rate constants have been reported for several of the reactions studied in this work.

The ICR ion trapping technique used in this work[12] allows for the direct measurement of the decay of reactant ions with time, and has the advantage that thermal energy rate constants are easily and accurately obtained from simple kinetics. This technique is coupled in this work with continuous rf double resonance ejection of the $H_2^+$ ion formed by electron impact of $H_2$ in hydride–hydrogen gas mixtures. This capability for mass-selective ion ejection is unique to ICR methods and is required in this case in order to prevent the formation of ions by reactions of $H_2^+$ and $H_3^+$ ions with the hydride additive in these mixtures. The time dependence of the primary parent and fragment ions can then be followed without interference from secondary ion formation.

## II. EXPERIMENTAL

The ICR ion trapping technique used for measuring thermal energy rate constants has been previously described.[12,13] The decay of the primary ions with time yields the rate constant for the reaction with the neutral gas present. Figure 1 shows a semilogarithmic plot of the decay of the $CH^+$ and $CH_2^+$ ion signals in methane both with and without added hydrogen. The hydrogen was added through a second sample inlet, and the added hydrogen pressure was measured using the capacitance manometer–ion gauge procedure as previously described.[13] Without added hydrogen, the slope of the decay plots in Fig. 1, when divided by the methane neutral density, yield the rate constants for the reaction of $CH^+$ and $CH_2^+$ ions with $CH_4$. The difference in slope between these and the decay plots with added hydrogen, when divided by the added neutral hydrogen density, yield the rate constants for the reaction of $CH^+$ and $CH_2^+$ ions with $H_2$.

The rate constants for the reaction of $CH^+$, $CH_2^+$, $N^+$, $NH^+$, $NH_2^+$, $O^+$, $OH^+$, $N_2^+$, $C_2^+$, and $C_2H^+$ ions with hydrogen were determined using the procedure outlined above (Table I). These ions are not produced by $H_2^+$ or $H_3^+$ ions in the mixtures used, and the results obtained were unaffected by continuous rf ejection of the $H_2^+$ ions. However, without $H_2^+$ ion ejection the behavior of the

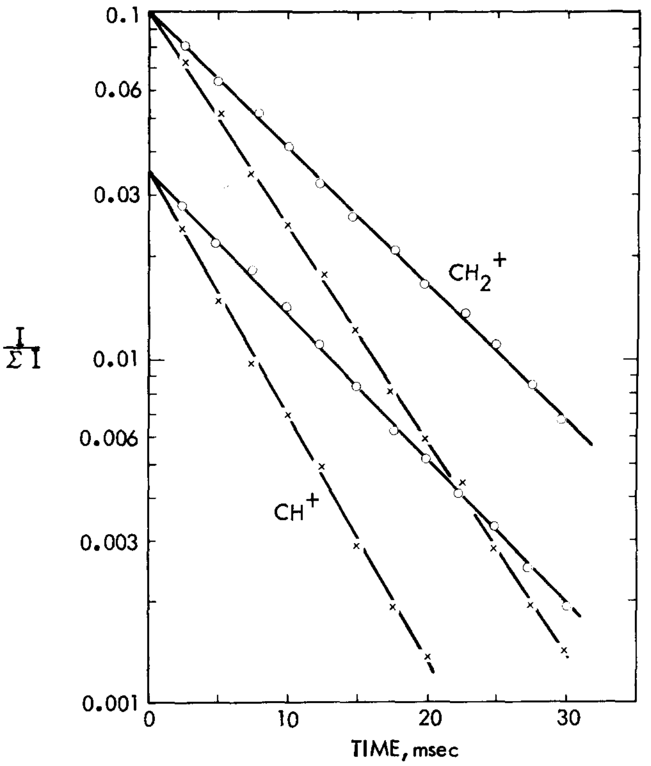

FIG. 1. Semilogarithmic plots of the decay of the $CH^+$ and $CH_2^+$ ion intensities with time in ion trapping experiments on (1) circles, methane alone, $CH_4$ pressure $1.65\times10^{-6}$ Torr, and (2) crosses, with $2.15\times10^{-6}$ Torr of $H_2$ added for a total of $3.70\times10^{-6}$ Torr.

$CO^+$, $CH_3^+$, $CH_4^+$, $NH_3^+$, and $H_2O^+$ ions are considerably affected on addition of $H_2$. These ions are formed by $H_2^+$ or $H_3^+$ ions in the mixtures used, and two methods were used to eliminate these secondary processes. In the first method electron energies below the I. P. of $H_2$ were used, and in the second method an electron energy of 40 eV was used with continuous cyclotron ejection of the $H_2^+$ ion (which also prevents formation of $H_3^+$ ions). Complete ejection of the $H_2^+$ ion is verified when further increases in rf irradiation power at the cyclotron frequency of $H_2^+$ results in no further reduction of the total ion signal. The rate constants obtained by either of these methods are identical, but the data obtained by $H_2^+$ ion ejection are more precise because of the much larger ion signal which can be obtained at high electron energies. The errors quoted are for precision only. The estimated accuracy of the measurements is estimated to be on the order of 10–15%.

The reactions with $H_2$ indicated by the ion trapping experiments were confirmed by performing standard ICR double resonance ejection experiments.[13] For the ions which do not react with $H_2$, upper limits for the rate constants were obtained by using standard continuous-drift ICR methods at electron energies below the I. P. of $H_2$. The neutral hydride was admitted to the spectrometer at low pressures where little or no reaction between ions and the neutral hydride are observed (short drift times, ~1–2 msec). Hydrogen (or $D_2$) was then added to pressures as high as $2\times10^{-3}$ Torr and the upper limit determined from the ratio of intensities of the $m+1$ ion (or $m+1$ and $m+2$ ions in the case of added $D_2$) to the $m$ ion. Better upper limits can be obtained by searching for the product ion than by searching for small differences in slopes in semilogarithmic ion decay plots. Short reaction times are also required in order to prevent formation of the $m+1$ ion by reactions with the neutral hydride itself (rather than with $H_2$) so that the ion trapping mode is not applicable in this case.

The upper limits for the abstraction reactions of $CH_3^+$, $H_2S^+$, $CH_3NH_2^+$, and $CH_3OH^+$ ions with $H_2$ (or $D_2$) were determined by the continuous-drift ICR method given above. For several ions that are not reactive with hydrogen, the possibility of hydrogen atom exchange in nonreactive collisions was examined using this same method (Table II). In order to examine for exchange reactions of protonated ions ($NH_4^+$, $H_3O^+$, $H_3S^+$, and $CD_5^+$), the neutral hydride gas was added at high pressures where extensive reaction results in nearly complete conversion of primary ions to the protonated (deuteronated) ion. Hydrogen (or $D_2$) is then added as before to examine for the exchange reaction (Fig. 2).

## III. RESULTS AND DISCUSSION

### A. Methane-hydrogen mixtures

The $CH^+$, $CH_2^+$, $CH_3^+$, and $CH_4^+$ ions were obtained by electron impact of $CH_4$. Figure 1 illustrates the measurement of the rate constants for the reactions

$$CH^+ + H_2 \rightarrow CH_2^+ + H\ , \qquad (1)$$

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H \qquad (2)$$

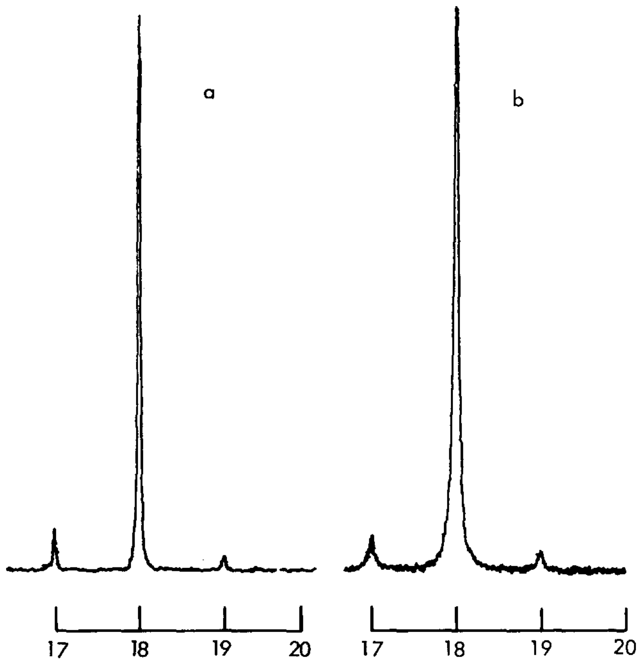

FIG. 2. Conventional ICR spectra of (a) $NH_3$ at $2.9\times10^{-5}$ Torr, (b) same as (a) with $9.2\times10^{-4}$ Torr of added $D_2$. Electron energy 13.5 eV, drift time $1.5\times10^{-3}$ sec. From the lack of change in relative intensities of the $m/e=18$ and 19 ions with added $D_2$, an upper limit of $\sim1\times10^{-13}$ cm$^3$/sec is obtained for the reaction $NH_4^+ + D_2 \rightarrow NH_3D^+ + HD$.

TABLE I. Reactions of ions with hydrogen.

| ΔH (kcal/mole) | Reaction | Rate constant[a] ($10^{-9}$ $cm^3/sec$) | Lit. values | $E_a$ (kcal/mole) |
|---|---|---|---|---|
| −14 | $CH^+ + H_2 \rightarrow CH_2^+ + H$ | 1.01 ± 0.04 | 0.58,[7] (0.49)[7,b] | 0.2 |
| −21 | $CH_2^+ + H_2 \rightarrow CH_3^+ + H$ | 0.72 ± 0.04 | 0.23,[7] (0.31)[7,b] | 0.4 |
| +66 | $CH_3^+ + H_2 \rightarrow CH_4^+ + H$ | ≤ 0.0005 | | > 4.1 |
| 0 | $CH_4^+ + H_2 \rightarrow CH_5^+ + H$ | 0.041 ± 0.002 | | 2.2 |
| −14 | $N^+ + H_2 \rightarrow NH^+ + H$ | 0.48 ± 0.02 | 0.47[4] | 0.7 |
| −26 | $NH^+ + H_2 \rightarrow NH_2^+ + H$ | 0.95 ± 0.10 | ~2.0[4] | 0.3 |
| −29 | $NH_2^+ + H_2 \rightarrow NH_3^+ + H$ | 0.12 ± 0.02 | 0.25[4] | 1.5 |
| −23 | $NH_3^+ + H_2 \rightarrow NH_4^+ + H$ | $(3 \pm 1) \times 10^{-4}$[b] | $(\leq 5 \times 10^{-4})$,[4] (0.076)[10,b] | 5.1 |
| −10 | $O^+ + H_2 \rightarrow OH^+ + H$ | 1.58 ± 0.04 | 2.0[3] | ~0 |
| | | (1.32 ± 0.03)[c] | | |
| −27 | $OH^+ + H_2 \rightarrow H_2O^+ + H$ | 1.05 ± 0.08 | ~1.5[3] | 0.2 |
| −38 | $H_2O^+ + H_2 \rightarrow H_3O^+ + H$ | 0.61 ± 0.03 | ~1.4,[3] (0.41),[10,b] (0.64)[6,d] | 0.5 |
| −48 | $CO^+ + H_2 \rightarrow COH^+ + H$ | 1.39 ± 0.04 | 2.0,[3] (1.5),[5,b] (1.5),[9,b] (0.72)[8,b] | 0.1 |
| −57 | $N_2^+ + H_2 \rightarrow N_2H^+ + H$ | 1.73 ± 0.05 | 1.7,[3] 2.1,[11] (1.7)[5,b] | ~0 |
| −23 | $C_2^+ + H_2 \rightarrow C_2H^+ + H$ | 1.12 ± 0.11 | | 0.2 |
| −30 | $C_2H^+ + H_2 \rightarrow C_2H_2^+ + H$ | 0.78 ± 0.05 | | 0.4 |
| −5 | $CH_3NH_2^+ + D_2 \rightarrow CH_3NH_2D^+ + H$ | ≤ 0.0005 | | > 4.1 |
| −12 | $CH_3OH^+ + D_2 \rightarrow CH_3OHD^+ + H$ | ≤ 0.0005 | | > 4.1 |

[a] Errors quoted are for precision only.

[b] For reaction with $D_2$.

[c] For $O^+$ ions from $O_2$, where approximately 28% of the ions are excited.

[d] For the reaction $D_2O^+ + H_2$.

by the trapped ion method in $CH_4$–$H_2$ mixtures. The rate constant for the reaction

$$CH_4^+ + H_2 \rightarrow CH_5^+ + H \quad (3)$$

was also measured in this manner, and the results are given in Table I. The values obtained for $k_1$ and $k_2$ do not agree well with the early work of Munson *et al.*,[7] probably because the average ion kinetic energy was much higher in their experiments. The occurrence of Reactions (1) and (2) were confirmed by double resonance ejection experiments in $CH_4$–$H_2$ mixtures. Double resonance ejection signals for the reactions 13 → 14 and 14 → 15 are observed only in the presence of hydrogen in these mixtures. The reaction

$$CH_4^+ + D_2 \rightarrow CH_4D^+ + D \quad (4)$$

was confirmed by double resonance ejection in $CH_4$ – $D_2$ mixtures at low electron impact energies (14 eV).

TABLE II. Exchange reactions with hydrogen.

| Reaction | Rate constant ($10^{-9}$ $cm^3/sec$) | Lit. values. |
|---|---|---|
| $CD_5^+ + H_2 \rightarrow CD_4H^+ + HD$ | ≤ 0.0005 | |
| $CD_4^+ + H_2 \rightarrow CD_3H^+ + HD$ | ≤ 0.001 | |
| $CD_3^+ + H_2 \rightarrow CH_2H^+ + HD$<br>$\rightarrow CDH_2^+ + D_2$ | 0.51 ± 0.05 | (0.55)[16,a] |
| $NH_4^+ + D_2 \rightarrow NH_3D^+ + HD$ | ≤ 0.0001 | |
| $NH_3^+ + D_2 \rightarrow NH_2D^+ + HD$ | ≤ 0.002 | |
| $H_3O^+ + D_2 \rightarrow H_2DO^+ + HD$ | ≤ 0.001 | |
| $H_2S^+ + D_2 \rightarrow HDS^+ + HD$ | ≤ 0.0005 | |
| $H_3S^+ + D_2 \rightarrow H_2DS^+ + HD$ | ≤ 0.001 | |

[a] For the reaction $CH_3^+ + D_2 \rightarrow (CH_2D^+, CHD_2^+) + (HD, H_2)$.

There are no exothermic reaction channels available in collisions between $CH_3^+$ ions and $H_2$ at thermal kinetic energies. Trapped ion experiments show no change in the decay rate of $CH_3^+$ ions on addition of $H_2$. However, the methyl cation has been shown to undergo hydrogen atom exchange in collisions with $H_2$.[14,15] Double resonance ejection experiments in $CD_4$–$H_2$ mixtures identify the reaction:

$$CD_3^+ + H_2 \rightarrow CD_2H^+ + HD , \quad (5)$$

and trapped ion studies on these mixtures yield the value $0.51 \times 10^{-9}$ $cm^3/sec$ for the total disappearance rate constant of $CD_3^+$ ions in $H_2$ (Table II). This result is in excellent agreement with the value $0.55 \times 10^{-9}$ $cm^3/sec$ obtained by Harrison and Keyes[16] for the disappearance rate constant of $CH_3^+$ ions in $D_2$. Harrison and Keyes also determined the product distribution in this reaction

$$CH_3^+ + D_2 \rightarrow CH_2D^+ + HD \quad (6)$$

$$\rightarrow CHD_2^+ + H_2 \qquad (7)$$

and found that $k_6/k_7 = 2.0 \pm 0.4$, indicating that equilibration of the hydrogen atoms occurs in an intermediate complex for these reactions.

### B. Ammonia-hydrogen mixtures

$NH^+$, $NH_2^+$, and $NH_3^+$ ions were obtained by electron impact of $NH_3$, and the rate constants obtained for the reactions

$$NH^+ + H_2 \rightarrow NH_2^+ + H\ , \qquad (8)$$

$$NH_2^+ + H_2 \rightarrow NH_3^+ + H \qquad (9)$$

in $NH_3$–$H_2$ mixtures are given in Table I. The ICR values do not agree well with those reported from flowing afterglow experiments by Fehsenfeld *et al.*[3,4] However, both the ICR and flowing afterglow experiments show that the exothermic reaction

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \qquad (10)$$

is extremely slow.

The intensity of $NH^+$ ions obtained by electron impact of $NH_3$ was insufficient for reliable identification of Reaction (8) in double resonance experiments. A reaction between $NH^+$ and $H_2$ is, however, clearly observed in ion trapping experiments. Fehsenfeld *et al.* have shown in flowing afterglow experiments that Reaction (8) does occur and that the only alternative reaction pathway,

$$NH^+ + H_2\ \mathrm{X}\ H_3^+ + N\ , \qquad (11)$$

does not occur at thermal energies.

Cyclotron ejection experiments in conventional, continuous-drift ICR studies of $NH_3$–$D_2$ mixtures confirm the occurrence of Reaction (12),

$$NH_2^+ + D_2 \rightarrow NH_2D^+ + D\ , \qquad (12)$$

16 18

in the presence of the reaction

$$NH_2^+ + NH_3 \rightarrow NH_4^+ + NH \qquad (13)$$

16 18

by an increase in the double resonance ejection intensity for 16 → 18 on addition of $D_2$ when compared to the double resonance intensity for 17 → 18,

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2\ . \qquad (14)$$

17 18

Exchange of $NH_3^+$ ions with $D_2$ to give $NH_2D^+$ ions was not observed in $NH_3$–$D_2$ mixtures below the I. P. of $D_2$.

Because of the failure to observe reaction (10) in $NH_3$–$H_2$ mixtures, and the ultimate importance of this reaction for the possible synthesis of ammonia in interstellar clouds,[17] this reaction was examined in more detail using $NH_3$–$D_2$ mixtures. Figure 3 shows the results of a trapped ion experiment below the I. P. of $D_2$ at very high $D_2$ pressures. The absence of any observable change in the slope for the $NH_3^+$ ion decay plot gives an upper limit of about $5 \times 10^{-12}$ cm³/sec for any reaction between $NH_3^+$ and $D_2$. However, a very small amount of product ion is observed at $m/e = 19$ which in the absence of $D_2$ corresponds to the natural isotopes of the $m+1$ ion ($^{15}NH_4^+$, $^{14}NH_3D^+$). The $m/e = 19$ signal does show a significant and reproducible increase on addition of $D_2$. This increase could correspond either to the reaction

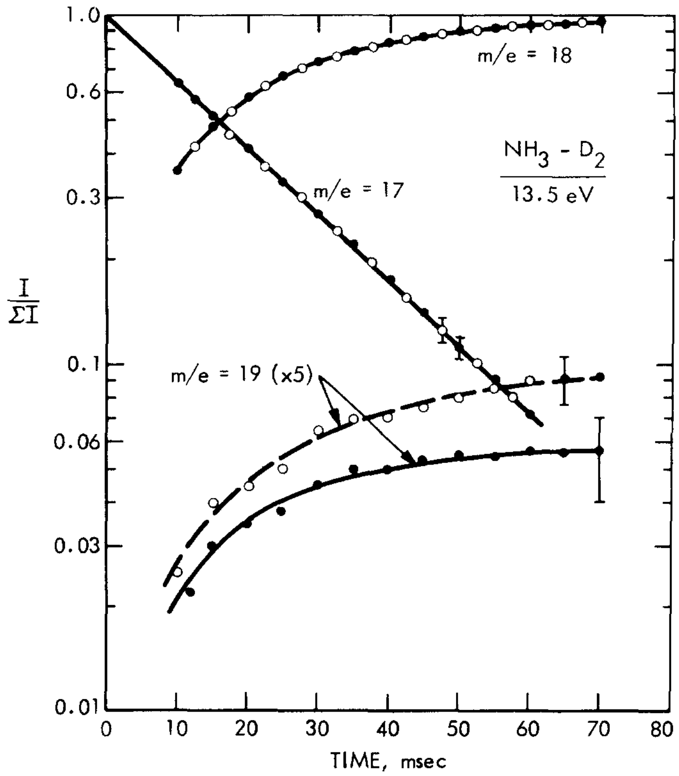

FIG. 3. Ion intensities vs time in $NH_3$ (solid circles, $8.35 \times 10^{-7}$ Torr $NH_3$) and in a $NH_3$–$D_2$ mixture (open circles, $8.35 \times 10^{-7}$ Torr $NH_3$ and $1.21 \times 10^{-5}$ Torr $D_2$). Electron energy 13.5 eV. Error bars are given for intensities measured at long storage times.

$$NH_3^+ + D_2 \rightarrow NH_3D^+ + D \qquad (15)$$

17 19

or to reactions with water impurity in the $D_2$ sample,

$$(NH_3^+)^* + H_2O \rightarrow H_3O^+ + NH_2\ , \qquad (16)$$

17 19

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH\ . \qquad (17)$$

18 19

The electron energy used in the experiment illustrated in Fig. 3 was 13.5 eV, which has been shown to produce $NH_3^+$ ions in a distribution of excited vibrational states.[13] Reaction (16) has been identified in $NH_3$–$H_2O$ mixtures.[18] Also, the water impurity in the $D_2$ sample was found to be ~ 10 ppm, which might account for the increase in the $m/e = 19$ intensity via reactions (16) and (17), except for the fact that $H_3O^+$ ions are rapidly converted to $NH_4^+$ ions ($m/e = 18$) via the very fast reaction

$$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O\ . \qquad (18)$$

Reaction (18) should completely remove any $H_3O^+$ ions at 70 msec and $8.35\times10^{-7}$ Torr $NH_3$. The reaction reverse to (18) has not been identified, but must have an immeasurably small rate constant. The difference in the proton affinities of water and ammonia is on the order of 40 kcal/mole,[19] so that the equilibrium constant for Reaction (18) is on the order of $10^{29}$. This yields a reverse rate constant on the order of $10^{-38}$. Reactions with water impurity can therefore be eliminated.

An alternate possibility for the increase in $m/e = 19$ signal with added $D_2$ pressures might be the occurrence of an exchange reaction,

$$\underset{18}{NH_4^+} + D_2 \rightarrow \underset{19}{NH_3D^+} + HD \quad . \qquad (19)$$

However, experiments using the conventional, continuous-drift ICR method show that the rate constant for reaction (19) is less than $1.0\times10^{-13}$ cm$^3$/sec (Fig. 2). The rate constant derived for reaction (15) from Fig. 3 is $(3\pm1)\times10^{-13}$ cm$^3$/sec, so that Reaction (19) is not sufficient to explain the magnitude of the increase of $m/e = 19$ with added $D_2$. Also, no ions were observed at $m/e = 20$. Another observation which is pertinent in the conventional ICR data in Fig. 2 is the small signal at $m/e = 19$ (short times and high $NH_3$ pressures). This is the $H_3O^+$ ion formed by Reaction (16) of excited $NH_3^+$ ions with the background residual water impurity, which is always present in very small quantities. The reaction time (~1 msec) is sufficiently short in this case to prevent extensive conversion of $H_3O^+$ to $NH_4^+$ ions. Addition of a large amount of $D_2$ does not appear to result in an increase in water background signal in Fig. 2.

Based on the present results, it seems fairly certain that Reaction (15) is indeed occurring, at least for the distribution of vibrationally excited $NH_3^+$ ions formed by electron impact at 13.5 eV, and that the rate constant is $k_{15} = (3\pm1)\times10^{-13}$ cm$^3$/sec. Figure 4 shows rf double resonance spectra of the $m/e = 19$ ion at 95 msec in the experiment illustrated in Fig. 3. Continuous rf power was applied over the entire storage time of the ions. A significant observation in Fig. 4 is that the sum of the ion-ejection intensitites is greater than the total single resonance signal, a symptom of excessive ion densities where coulombic couplings are observed in double resonance spectra. Unfortunately, large ion densities are required in order to observe the very small signal at $m/e = 19$, so that coulombic coupling cannot be avoided in this case. The ejection intensities are therefore not reliable. However, at low rf powers where ions are not ejected, but are translationally heated, coulombic coupling is not as severe a problem. Under these conditions, the double resonance signal at $m/e = 18$ disappears and the response at $m/e = 17$ indicates a large increase in the $m/e = 19$ signal. This "positive-going" signal disappears in the absence of $D_2$. These observations at low rf powers rigorously identify Reaction (15) at elevated ion kinetic energies and show a rate constant increasing rapidly with increasing ion kinetic energy. This change might explain why Harrison and Thynne[10] report such a large rate constant for this reaction. The exit ion energy in their experiments was approximately 3.7 eV.

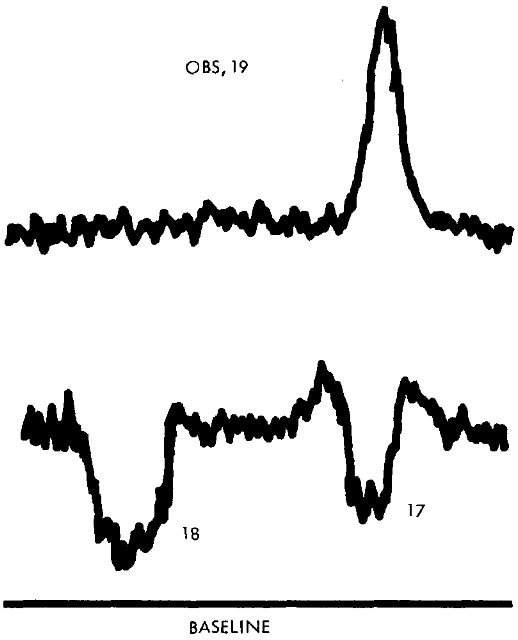

FIG. 4. Double resonance spectra of the $m/e = 19$ ion in the $NH_3$–$D_2$ mixture shown in Fig. 3 at 95 msec reaction time. Lower trace is a high rf power, ion-ejection spectrum with the baseline as shown. The upper trace is a low rf power, ion-heating spectrum on the same sensitivity scale as the lower trace but with the baseline raised.

Since it is known that $NH_3^+$ ions are formed by electron impact at 13.5 eV in a distribution of vibrationally excited states, it cannot be determined in the present work whether the rate constant determined for Reaction (15) is applicable to $NH_3^+$ ions in the ground vibrational state. The failure to observe any increase in the loss rate for $NH_3^+$ ions with addition of $D_2$ in Fig. 3 can only place an upper limit of about $5\times10^{-12}$ cm$^3$/sec on the rate constant for deactivation of vibrationally excited $NH_3^+$ ions in nonreactive collisions with $D_2$. The rate constant for reaction (14) is significantly larger for $NH_3^+$ ions in the ground vibrational state than for $NH_3^+$ ions formed by electron impact at 13.5 eV.[13] Collisional deactivation would therefore have been expected to produce some curvature in the semilogarthmic plot in Fig. 3 if the rate constant $k_{14}$ were to have increased at longer storage times.

### C. Water-hydrogen mixtures

The reactions

$$OH^+ + H_2 \rightarrow H_2O^+ + H \ , \qquad (20)$$

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H \qquad (21)$$

occur with appreciable rate constants at thermal kinetic energies. The values for $k_{20}$ and $k_{21}$, measured in this work by the trapped ion method in $H_2O$–$H_2$ mixtures, are given in Table I. The rate constant $k_{21}$ obtained is in good agreement with the values reported earlier by Lampe *et al.*[6] and by Harrison and Thynne[10] but both $k_{20}$ and $k_{21}$ are significantly less than the approximate values reported by Fehsenfeld *et al.*[3] Reaction (21) is confirmed in conventional ICR experiments both as an increase in the single resonance intensity ratio $I(H_3O^+)/I(H_2O^+)$ with increasing $H_2$ pressure at electron energies below the I. P. of $H_2$, and as the appearance of an ion at $m/e = 20$ in $H_2O$–$D_2$ mixtures due to the reaction

$$\underset{18}{H_2O^+} + D_2 \rightarrow \underset{20}{H_2DO^+} + D \ . \tag{22}$$

Reaction (20) is identified in conventional ICR studies of $H_2O$–$D_2$ mixtures as an increase in the double resonance ejection intensity for the reactions

$$\underset{17}{OH^+} + D_2 \rightarrow \underset{19}{HDO^+} + D \ , \tag{23}$$

$$+ H_2O \rightarrow \underset{19}{H_3O^+} + O \tag{24}$$

with increasing $D_2$ pressure when compared to the double resonance ejection intensity for the reaction

$$\underset{18}{H_2O^+} + H_2O \rightarrow \underset{19}{H_3O^+} + OH \ . \tag{25}$$

### D. Mixtures of oxygen and carbon dioxide with hydrogen

Both oxygen and carbon dioxide were used as sources of the atomic oxygen ion. The $O^+$ ion is a very minor fragment ion for electron impact on these molecules. Nevertheless, sufficient $O^+$ ion intensity was obtained at electron impact energies of 40 eV for good ion decay curves to be observed in trapped ion experiments. Two different sources were used for production of $O^+$ since it has been shown[20,21] that these ions are readily produced in the metastable $^2D$ and $^2P$ states by dissociative ionization of various molecules. Turner *et al.*[20] have shown that ~28% of the $O^+$ ions initially produced from $O_2$ by electron impact at 60 eV are in electronically excited states, whereas Hughes and Tiernan[21] have shown that only ~4% of the $O^+$ ions initially produced from $CO_2$ by electron impact at 60 eV are in electronically excited states. In the present work, different rate constants were obtained with $H_2$ for the reaction of $O^+$ ions produced from $O_2$ and $CO_2$ (Table I).

The value of the rate constant for the reaction

$$O^+ + H_2 \rightarrow OH^+ + H \ , \tag{26}$$

obtained from $CO_2$–$H_2$ mixtures, $1.58 \times 10^{-9}$ $cm^3/sec$, agrees very well with the Langevin rate constant for this reaction, $1.56 \times 10^{-9}$ $cm^3/sec$, and is probably the rate constant appropriate for ground state $O^+$ ions. These values are in poor agreement, however, with the rather high value from early flowing afterglow experiments, $2.0 \times 10^{-9}$ $cm^3/sec$.[3] The value of the rate constant for Reaction (26), obtained from $O_2$–$H_2$ mixtures, $1.32 \times 10^{-9}$ $cm^3/sec$, is decidedly less than the value from $CO_2$–$H_2$ mixtures. This is possibly the result of the formation of metastable electronically excited $O^+$ ions by electron impact of $O_2$, and indicates that the rate constant for reaction (26) may be significantly smaller for $O^+$ ions in these excited states.

### E. Mixtures of nitrogen with hydrogen

Electron impact of molecular nitrogen at 40 eV was used as a source of the atomic nitrogen ion. The rate constant determined for the reaction

$$N^+ + H_2 \rightarrow NH^+ + H \tag{27}$$

in $N_2$–$H_2$ mixtures is given in Table I. The value obtained is in excellent agreement with the most recent value from flowing afterglow experiments.[4] The rate constant for the reaction

$$N_2^+ + H_2 \rightarrow N_2H^+ + H \tag{28}$$

was also measured in $N_2$–$H_2$ mixtures, and the value obtained is again in excellent agreement with the flowing afterglow experiments. The value reported by Aquilanti *et al.*[11] may be somewhat high because of excess $N_2^+$ ion kinetic energy in their high pressure mass spectrometer experiments (~ 2.0 eV ion exit energy).

Both Reactions (27) and (28) have alternate exothermic reaction pathways:

$$N^+ + H_2 \rightarrow H^+ + NH + 3 \text{ kcal} \ , \tag{29}$$

$$N_2^+ + H_2 \rightarrow H_2^+ + N_2 + 3.4 \text{ kcal} \ . \tag{30}$$

The intensity of $N^+$ ions obtained by electron impact of molecular nitrogen at 40 eV was insufficient to eliminate the possibility of the occurrence of Reaction (29), but double resonance ejection experiments appear to indicate that Reaction (27) is the main reaction channel in $N^+$–$H_2$ collisions. Double resonance ejection experiments clearly show reaction (28) as the major reaction channel for $N_2^+$–$H_2$ collisions. The probability for charge transfer from $N_2^+$ to $H_2$ is determined from the present experiments to be less than $10^{-2}$ times the probability for hydrogen atom abstraction at thermal ion kinetic energies.

Ionization of molecular nitrogen at 40 eV electron impact energy is known to produce a significant fraction of $N_2^+$ ions in electronically excited states.[22-24] However, the lifetimes of the optically observed states are sufficiently short[22-24] ($\lesssim 10^{-5}$ sec) compared to the time between collisions in the ICR experiment ($\gtrsim 10^{-3}$ sec) that contributions from these states are not expected in the present experiments. To eliminate the possibility that vibrationally excited states or metastable electronically excited states of $N_2^+$ may be present, experiments were run on $N_2$–$H_2$ mixtures at 16.5 eV, below the A. P. of the first optically allowed electronically excited state of $N_2^+$. Photoelectron spectra[25] show that $N_2^+$ ions formed at 16.5 eV should be principally in the ground vibronic state at this energy. The same rate constant was obtained for reaction (28) for electron impact energies of 16.5 and 40.0 eV.

The rate constant for the reaction of $N_2^+$ with $H_2$ is the largest measured in this series: $(1.73 \pm 0.05) \times 10^{-9}$ $cm^3/sec$. It is interesting that the experimental value is actually significantly larger than the Langevin value $1.49 \times 10^{-9}$ $cm^3/sec$. If grazing collisions are included in the Langevin formalism,[26] and if the maximum component of the polarizability tensor[27] is used, the theoretical value can be raised to $1.78 \times 10^{-9}$ $cm^3/sec$. It has also been suggested[28] that the quadrupole moment of $H_2$ may have to be included in calculating rate constants for reactions of ions with $H_2$. A large rate constant for the $N_2^+$–$H_2$ reaction might possibly be explained by some combination of these latter effects.

### F. Mixtures of carbon monoxide with hydrogen

The rate constant for the reaction,

$$CO^+ + H_2 \rightarrow COH^+ + H \ , \tag{31}$$

measured in CO–$H_2$ mixtures, is given in Table I. The value obtained is not in good agreement with the approximate value obtained from the early flowing afterglow experiments.[3] Good agreement is obtained with several other values[5,9] reported for the $CO^+$–$D_2$ reaction, but direct comparison may not be applicable because of the significantly larger reduced mass in the latter collisions. To eliminate the possibility of contributions from vibrationally excited or metastable electronically excited states of $CO^+$, experiments were run on CO–$H_2$ mixtures at 16.0 eV, below the A. P. of the first optically allowed electronically excited state of $CO^+$. Photoelectron spectra show that $CO^+$ ions formed at 16.0 eV should be principally in the ground vibronic state at this energy. The same rate constant was obtained for reaction (31) for electron impact energies of 16.0 and 40.0 eV.

### G. Mixtures of hydrogen sulfide with hydrogen

There are no exothermic reactions between $H_2$ and $S^+$, $HS^+$, or $H_2S^+$ ions at thermal kinetic energies. The reaction of $H_2S^+$ with $H_2$ is endothermic by about 8 kcal/mole:

$$H_2S^+ + H_2 \rightarrow H_3S^+ + H, \ \ \Delta H \cong +8 \text{ kcal/mole} \ . \tag{32}$$

However, an endothermic reaction of vibrationally excited $H_2S^+$ ions has been previously observed in ICR experiments[29]:

$$(H_2S^+)^* + CD_4 \rightarrow H_2DS^+ + CD_3, \ \ \Delta H \cong +8 \text{ kcal/mole.} \tag{33}$$

Reaction (33) is also endothermic by about 8 kcal/mole. An attempt was therefore made to observe Reaction (32) by using the conventional ICR method and looking for an increase in the single resonance intensity ratio $I(H_3S^+)/I(H_2S^+)$ with increasing $H_2$ pressure at electron impact energies below the I. P. of $H_2$ (14 eV). No increase was observed, and an upper limit was placed on the rate constant for Reaction (32) of approximately $k_{32} \leq 5 \times 10^{-13}$ cm$^3$/molecule-sec.

### H. Acetylene-hydrogen mixtures

The reactions

$$C_2^+ + H_2 \rightarrow C_2H^+ + H \ , \tag{34}$$

$$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H \tag{35}$$

were identified in $C_2H_2$–$H_2$ mixtures where the $C_2^+$ and $C_2H^+$ ions were obtained by electron impact of $C_2H_2$ at 40 eV. The rate constants measured for Reactions (34) and (35) are given in Table I. The reaction of the parent ion,

$$C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H \ , \tag{36}$$

is endothermic by about 1 kcal/mole. A previous study[30] has shown that Reaction (36) does not occur for $C_2H_2^+$ ions in the ground vibronic state, but that acetylene ions with at least one quantum of excess vibrational energy do react with $H_2$ to give $C_2H_3^+$ ions. There are no exothermic reaction pathways available in collisions between $H_2$ and $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$, or $C_2H_6^+$ ions at thermal kinetic energies, and no reactions were observed between $H_2$ and these ions in $C_2H_4$–$H_2$ and $C_2H_6$–$H_2$ mixtures.

### I. Mixtures of $CH_3NH_2$ and $CH_3OH$ with hydrogen

The reactions

$$CH_3NH_2^+ + D_2 \rightarrow CH_3NH_2D^+ + D \ , \tag{37}$$

$$CH_3OH^+ + D_2 \rightarrow CH_3OHD^+ + D \tag{38}$$

are both exothermic, but a previous study[31] using the conventional ICR method has shown that they do not occur. The upper limits for the rate constants of Reactions (37) and (38) determined in this study are $k_{37}$, $k_{38} \leq 5 \times 10^{-13}$ cm$^3$/molecule-sec.

## IV. SUMMARY AND CONCLUSIONS

Except for the reactions of $N^+$, $NH^+$, and $N_2^+$ with $H_2$, hydrogen atom abstraction is the only available exothermic reaction pathway at thermal energies for the reactions listed in Table I. Even in the case of $NH^+$ and $N_2^+$, it has been shown that the alternate reaction pathway is not observed and that the reaction occurs principally via hydrogen atom abstraction. The rate constants measured for these reactions range from a low of $(3 \pm 1) \times 10^{-13}$ cm$^3$/sec for the $NH_3^+$–$H_2$ reaction to $(1.73 \pm 0.04) \times 10^{-9}$ cm$^3$/sec for the $N_2^+$–$H_2$ reaction. When compared to the Langevin value of $\sim 1.5 \times 10^{-9}$ cm$^3$/sec, it is clear that a large fraction of the collisions between these ions (except for $O^+$, $CO^+$, and $N_2^+$) are not reactive. This observation contrasts with the traditional view that exothermic ion–molecule reactions have little or no activation energy and should therefore occur with nearly every collision. There has been some recent discussion in the literature about barriers to simple ion–molecule reactions,[32] and if the simple expression

$$k_{\text{obs}} = k_{\text{collision}} e^{-E_a/kT} \tag{39}$$

is used for deducing magnitudes of activation energies for ion–molecule reactions, then barriers on the order of several kcal/mole are obtained for the reactions studied in this work. Using expression (39) and a value of $1.5 \times 10^{-9}$ cm$^3$/sec for $k_{\text{collision}}$, the values of $E_a$ given in Table I are obtained. It does appear that successive substitution of hydrogen on the active site (C, N, or O ion) increases the activation energy (i.e., $O^+$, $OH^+$, and $OH_2^+$; or the isoelectronic series $CH_2^+$, $NH^+$, and $O^+$). Hence the number of unfilled $sp^n$ hybrid orbitals may be important. Also, substitution of $CH_3$ for H may increase the activation energy dramatically (i.e., $CH_3OH_2^+$ and $OH_2^+$). Hence steric or change delocalization effects may be important.

The examples obtained in the present work add to the mounting evidence that considerable barriers can exist to even very simple ion–molecule reactions, and suggest the need for further theoretical and mechanistic study in this area. One observation can also be made concerning mechanism with regard to the data on exchange reactions in Table II. It would seem reasonable to expect that exchange will only be observed for reactions in which a stable intermediate complex ion is formed with a sufficiently long lifetime so that many vibrations can occur before dissociation. In fact, the only exchange reaction observed among those listed in Table II, Reaction (5), is one for which the collision complex has the appearance of a known, stable ion. The $CH_5^+$ ion is a stable well-known ion, whereas none of the remaining reactant ions in Table II can form known, stable ions by forming complexes with molecular hydrogen.

The present work shows the necessity for obtaining laboratory data in order to confidently model ion–molecule reactions in the interstellar medium. Most of the present models are based on the premise that a reaction can be presumed to occur at the Langevin rate if exothermic. Other observations pertinent to interstellar chemistry:

(1) The large rate constants measured for Reactions (1) and (2) raise some difficulties in explaining the concurrent high abundance of both $CH^+$ and CH in dense interstellar clouds containing molecular hydrogen[1,2].

(2) The identification and measurement of a finite, if small, rate constant for the reaction $NH_3^+ + H_2 \rightarrow NH_4^+ + H$ relieves some of the difficulty in accounting for the high abundance of neutral $NH_3$ observed in these same regions.[17]

Because of the possibility that there are significant kinetic barriers to hydrogen atom abstraction reactions, it is quite possible that a significant temperature dependence will be exhibited by rate constants (Table I) which are already small at 300 °K. Variable temperature measurements will be required in order to measure any activation energies for the reactions in Table I and to determine the applicability of the values given in this table to the temperatures in interstellar clouds. One particular case in point is Reaction (3), which is thermoneutral or very nearly so. On this basis, the equilibrium constant should be close to unity; an examination of the reverse reaction would be interesting.

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