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Ion–Molecule Reactions in Mixtures of Methane with Water, Hydrogen Sulfide, and Ammonia[1]

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Abstract: Ion–molecule reactions of ions formed by electron impact in mixtures of methane with water, hydrogen sulfide, and ammonia have been studied using ion–cyclotron resonance techniques. The reactions of primary ions are identified and their relative reaction rates measured using the resonant cyclotron ejection method. Absolute rates are determined by reference to the absolute rates previously measured for the major reactions occurring in the pure gases.

A study of the ion–molecule reactions occurring in mixtures of methane and ammonia using ion cyclotron resonance (icr) techniques has been previously reported.[2] The present work reports an extension of these studies in which the ion–molecule reactions occurring in mixtures of methane with water and hydrogen sulfide are also examined. In addition to the identification of reactions by the classical icr double resonance method, the relatively newer technique of resonant cyclotron ejection[3] is also used to measure the relative rates for these reactions. Absolute rates are determined by reference to absolute rate constants previously measured for the principal ion–molecule reactions in methane, ammonia, water, and hydrogen sulfide.[4]

Several early papers have appeared on mass spectrometric studies of ion–molecule reactions in methane–water[5,6] and methane–hydrogen sulfide mixtures.[7] These studies were not complete in their identification of reactions and measurement of rate constants. Because of the importance of ion–molecule reactions in discharges and in the radiation chemistry of mixtures of these particular gases in primordial atmospheres,[8] an extensive study of these reactions is reported here.

Experimental Section

The resonant cyclotron ejection method for the measurement of relative rates of ion–molecule reactions has been previously described.[3] Primary ions formed by electron impact are irradiated in the source region of a standard icr "flat" cell. The rf irradiation power used is sufficiently high to drive the resonant ion into the drift plates in the source region before the reaction can occur with the neutrals present in the cell. The irradiated ion is efficiently removed from the cell in this manner, and the resonant ion along with all product ions which would have resulted from reactions of this ion no longer appear in the mass spectrum. An ejection resolution of greater than $M/\Delta M = 30$ has been achieved with a flat cell at magnetic field strengths of 10 kg using this method.

Relative rates are determined from the cyclotron ejection method as follows. The decrease in the single-resonance intensity of a product ion is measured when a primary ion, coupled to the product ion by ion–molecule reaction, is ejected in the source region of the icr cell. Complete ejection of the primary ion is verified when no further decrease in secondary ion signal is observed as the rf irradiation power is increased. This results in the flat-bottomed appearance of the cyclotron ejection signal illustrated in Figure 1. The observed decrease in the product ion signal is then the contribution to the product ion signal from reaction of the irradiated primary ion and is proportional to the rate of the reaction. For two reactions

$$A^+ + M \xrightarrow{k_1} C^+ + X \tag{1}$$

$$B^+ + N \xrightarrow{k_2} D^+ + Y \tag{2}$$

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[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100 sponsored by the National Aeronautics and Space Administration.

[2] W. T. Huntress, Jr., and D. D. Elleman, *J. Amer. Chem. Soc.*, **92**, 3565 (1970).

[3] W. T. Huntress, Jr., M. Mosesman, and D. D. Elleman, *J. Chem. Phys.*, **54**, 843 (1971).

[4] W. T. Huntress, Jr., and R. F. Pinizzotto, Jr., submitted to *J. Chem. Phys.*, and references therein.

[5] (a) F. W. Lampe, F. H. Field, and J. L. Franklin, *J. Amer. Chem. Soc.*, **79**, 6132 (1957); (b) M. S. B. Munson and F. H. Field, *ibid.*, **87**, 4242 (1965).

[6] A. G. Harrison and J. C. J. Thynne, *Discuss. Faraday Soc.*, No. **44**, 945 (1967).

[7] F. H. Field and F. W. Lampe, *J. Amer. Chem. Soc.*, **80**, 5583 (1958).

[8] W. T. Huntress, Jr., and D. D. Elleman, "NASA Document SPS No. 37-61," Vol. III, Jet Propulsion Laboratory, 1970.

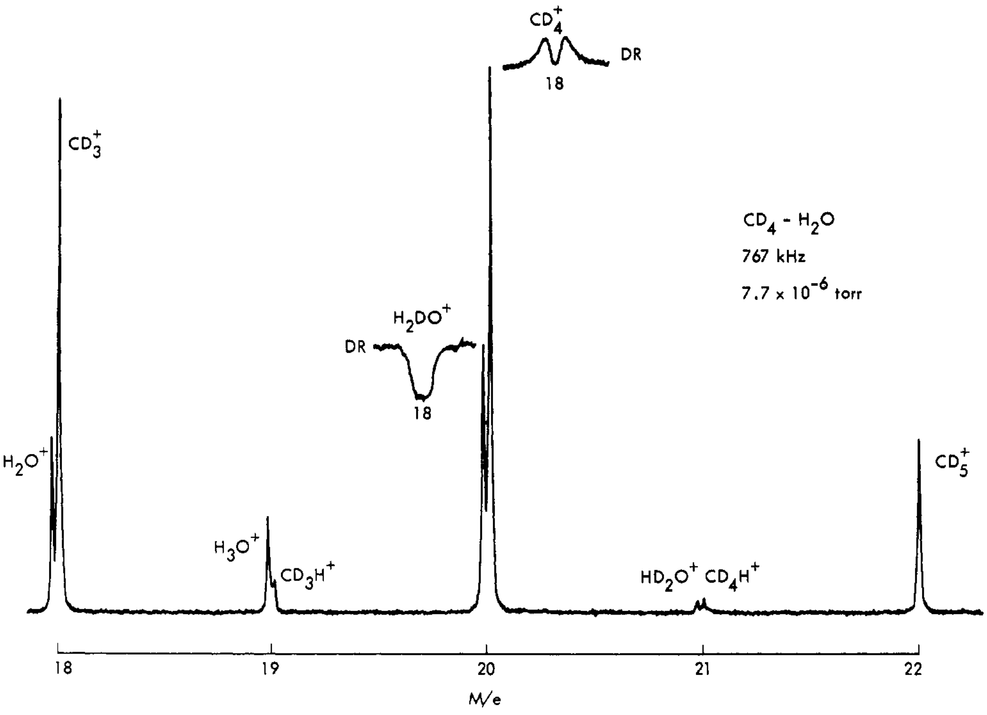

Figure 1. A portion of the icr spectrum of a 1:1 mixture of CD_4 and H_2O illustrating the splitting of peaks in these mixtures at high magnetic fields (~10 kG). Ion ejection spectra labeled "DR" are also illustrated for the two peaks at *m/e* 20, showing the different contributions to H_2DO^+ and CD_4^+ from the H_2O^+ ion at *m/e* 18. The identification of H_2O^+ as the reactant rather than CD_3^+ comes from ejection studies in CH_4–H_2O mixtures.

Table I. Absolute Rate Constants[a]

	Relative rates	Absolute rates	Lit. values
	Methane Reactions		
$CH_4^+ + CH_4 \xrightarrow{k_c} CH_5^+ + CH_3$		1.10	0.9–1.2
$CD_4^+ + CD_4 \xrightarrow{k_d} CD_5^+ + CD_3$	$k_d/k_c = 0.7 \pm 0.06$	0.80	0.7–1.0
$CH_3^+ + CH_4 \xrightarrow{k_{c'}} C_2H_5^+ + H_2$	$k_c/k_{c'} = 1.2 \pm 0.1$	0.90	0.9–1.3
	Proton Transfer Reactions		
$NH_3^+ + NH_3 \xrightarrow{k_n} NH_4^+ + NH_2$	$k_n/k_d = 1.9 \pm 0.1$	1.55	1.5–2.1
$H_2O^+ + H_2O \xrightarrow{k_o} H_3O^+ + OH$	$k_o/k_d = 2.6 \pm 0.2$	2.05	2.2–2.6
$H_2S^+ + H_2S \xrightarrow{k_s} H_3S^+ + SH$	$k_s/k_{c'} = 0.68 \pm 0.03$	0.58	0.7–0.9

[a] From ref 4. In units of 10^{-9} cm^3 molecule^{-1} sec^{-1}.

relative rates are obtained from the relation

$$\frac{k_1}{k_2} = \frac{m^2{}_D I(A \rightarrow C)}{m^2{}_C I(B \rightarrow D)} \frac{m_A P(B)[N]}{m_B P(A)[M]} \qquad (3)$$

where $I(A \rightarrow C)$ is the decrease in intensity of the C^+ ion when A^+ is ejected, $P(A)$ is the production rate of the primary ion A^+, m_A is the mass of the ion A^+, and [M] is the concentration or partial pressure of the neutral M. The mass factors are required in order to include the mass dependence of the power absorption and the variation of the drift velocity with the magnetic field.[3,4,9] The relative production rates for the primary ions are obtained from the relative single resonance intensities of the primary ions in the same mixture at low pressures where reactions are not observed.

Equation 3 is derived in the limit that $[N]k\tau \ll 1$, where τ is the residence time of an ion in the icr cell.[3,4,9] In order for this relation to be valid, it is necessary that the amount of conversion to product ions be low. Relative rates were measured in this work for conversion factors of less than 30%.

The relative pressures of neutral species [N]/[M] are measured using a GE 22GT103 ionization gauge calibrated with an MKS Baratron capacitance manometer coupled to the vacuum system just above the icr cell. The partial pressures of gases used varied between 1 and 5 × 10^{-6} Torr. The gauge constant for calibration of the ionization gauge pressure measurements was determined for each gas after each experiment by recording the output of the ionization gauge *vs.* the Baratron output as the pressure of each gas is continuously varied from 1 to 10 × 10^{-3} Torr.

From the relative rate constants determined for the reactions in this work, absolute rate constants can be obtained by comparison with the absolute rate constants for the set of reactions given in Table I. All of the relative rate constants measured in this work are referred to a rate constant for one of the reactions in Table I. The literature values for the absolute rate constants of these reactions have been recently reviewed,[4] and all have been measured by the icr trapped ion technique.[4] The values in Table I are taken from the icr trapped ion rate measurements given in ref 4.

The gases were obtained from commercial sources and used without further purification. The methane was obtained from Phillips, 99.56%; the CD_4, $^{15}NH_3$, and D_2O were obtained from Merck Sharpe and Dohme, 99 atom % grades; and the hydrogen sulfide and ammonia were obtained from J. T. Baker, anhydrous grade.

The electron energy used was 30 eV unless otherwise stated. Pulsed grid modulation was used at trapping potentials of 0.2–

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(9) S. E. Buttrill, Jr., *J. Chem. Phys.*, 50, 4125 (1969).

Table II. Ion–Molecule Reactions of Primary Ions Observed in Mixtures of Methane and Water

ΔH, kcal/mol	Reaction	Rel rate	Abs rate[a]	Lit. values
		CH_4–H_2O		
−41	$CH_4^+ + H_2O \xrightarrow{k_1} H_3O^+ + CH_3$	$k_1/k_c = 2.2 \pm 0.5$	2.4	0.57[b]
−52	$CH_2^+ + H_2O \xrightarrow{k_2} CH_2OH^+ + H$	$k_2/k_{c'} = 0.58 \pm 0.1$	0.52	
		CD_4–H_2O		
−40	$H_2O^+ + CD_4 \xrightarrow{k_3} H_2DO^+ + CD_3$	$k_3/k_o = 0.59 \pm 0.2$	1.2	2.52[c]
−40	$\xrightarrow{k_4} HD_2O^+ + CD_2H$	$k_4/k_3 = 0.055 \pm 0.03$	0.07	
−58	$OH^+ + CD_4 \xrightarrow{k_6} HD_2O^+ + CD_2$	$k_5/k_o = 0.015 \pm 0.002$	0.03	

[a] $\times 10^9$ cm^3 molecule^{-1} sec^{-1}. [b] Reference 6. [c] Reference 6, rate measured for the reaction $H_2O^+ + CH_4 \rightarrow H_3O^+ + CH_3$.

0.5 V with typical drift voltages of 0.2–0.6 V applied across a 1.2 × 2.4 cm cross-section flat cell.

Frequencies in the range 307–921 kHz were typically used. The marginal oscillator detector frequency used was determined by the mass of the heaviest ion observed and adjusted to take advantage of the maximum magnetic field possible in order to maximize resolution and signal/noise. Care was taken to avoid space charge effects in double resonance experiments, and operation was limited to low emission currents and to total ion currents less than 5×10^{-12} A.

Ion–Molecule Reactions in Mixtures of Methane and Water

Reactions and Relative Rates. The ion–molecule reactions detected by ejection experiments for primary ions in mixtures of methane and water, and their measured relative rates, are reported in Table II. The selection of the reaction to which each was compared for a relative rate measurement was made on the basis of maximum convenience in measurement, maximum signal/noise in ejection experiments for both reactions, and most immediate reference to a reaction with a known rate. By maximum convenience in measurement it is meant that closest proximity of the two product ions in the mass spectrum was required in order to minimize mass correction factors, and whereever possible, reactions originating from primary ions of different parent gases were avoided in order to reduce the necessity for measurement of relative production rates for ions between two separate gases. Isotopic substitution was used to identify hydrogen-atom abstraction reactions in the presence of proton-transfer reactions giving product ions at the same *m/e* value in normal mixtures.

Proton transfer is observed from the parent ion of methane to water.

$$\underset{16}{CH_4^+} + H_2O \longrightarrow \underset{19}{H_3O^+} + CH_3 \qquad (4)$$

This reaction is quite exothermic and exhibits a large rate comparable with the proton-transfer rate between H_2O^+ and H_2O. Reaction 4 has been reported by Harrison and Thynne,[6] but the rate constant these workers report is very low (Table II).

The methyl cation proves completely unreactive toward water. The exothermic reaction

$$\underset{15}{CH_3^+} + H_2O \longrightarrow \underset{31}{CH_2OH^+} + H_2 \qquad (5)$$

is not observed and must have a rate constant $k_5 < 10^{-11}$ cm^3 molecule^{-1} sec^{-1}. This is a surprising result since the methyl cation is a good condensation reagent and analogous condensations are observed in reactions of methyl cations with CH_4, NH_3, and H_2S. The reason for the lack of reactivity with water is not well understood. Recent icr data indicate that a kinetic barrier may exist to hydrogen loss in these reactions and that the barrier is of sufficient magnitude to prevent reaction 5 from occurring.[10] The condensation reactions in these mixtures are discussed later in more detail. The small amount of CH_2OH^+ ion at *m/e* 31 that is observed in these mixtures originates from the reaction

$$\underset{14}{CH_2^+} + H_2O \longrightarrow \underset{31}{CH_2OH^+} + H \qquad (6)$$

The H_2O^+ ion reacts with methane to produce the hydronium ion by what appears to be direct hydrogen-atom abstraction

$$\underset{18}{H_2O^+} + CD_4 \longrightarrow \underset{20}{DH_2O^+} + CD_3 \qquad (7)$$

A small amount of hydrogen-atom exchange is also observed for this reaction, however

$$\underset{18}{H_2O^+} + CD_4 \longrightarrow \underset{21}{HD_2O^+} + CD_2H \qquad (8)$$

which indicates that at least a small amount of intermediate complex formation must take place or that a complex is formed which lives long enough to allow at least a small amount of hydrogen atom exchange to occur. The reaction

$$\underset{18}{H_2O^+} + CH_4 \longrightarrow \underset{19}{H_3O^+} + CH_3 \qquad (9)$$

was reported by Harrison and Thynne,[6] but the rate constant for reaction 9 reported by these workers is significantly higher than the rate constant for reaction 7 determined in this work (Table II). The difference between our results and those of Harrison and Thynne appears to be too large to be explained on the basis of isotope effects.

The OH^+ ion reacts by what appears to be hydrogen-molecule abstraction from methane.

$$\underset{17}{OH^+} + CD_4 \longrightarrow \underset{21}{HD_2O^+} + CD_2 \qquad (10)$$

There are a large number of possible exothermic reactions of OH^+ with methane (Table III), but reaction 10 is the only one observed. Limiting rate constants are given in Table III for all unobserved exothermic reactions of primary ions in methane–water mixtures. Rate constants for the reactions of OH^+ and CH_2^+

[10] W. T. Huntress, Jr., and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, in press; M. T. Bowers, W. J. Chesnavich, and W. T. Huntress, Jr., *ibid.*, in press.

Table III. Exothermic Reactions Not Observed in Mixtures of Methane and Water

ΔH, kcal/mol	Reaction	Maximum rate constant[a]
−1	$CH_4^+ + H_2O \longrightarrow H_2O^+ + CH_4$	$<1 \times 10^{-11}$
−14	$\longrightarrow CH_3OH^+ + H_2$	
−31	$CH_3^+ + H_2O \longrightarrow CH_2OH^+ + H_2$	
−6	$CH_2^+ + H_2O \longrightarrow CH_3^+ + OH$	$<5 \times 10^{-11}$
−52	$\longrightarrow CH_2O^+ + H_2$	
−2	$\longrightarrow CHO^+ + H_2 + H$	
−13	$H_2O^+ + CH_4 \longrightarrow CH_3OH^+ + H_2$	$<1 \times 10^{-11}$
−28	$OD^+ + CH_4 \longrightarrow HDO^+ + CH_3$	$<5 \times 10^{-11}$
−12	$OH^+ + CD_4 \longrightarrow CD_4H^+ + O$	
−11	$+ CH_4 \longrightarrow CH_4^+ + OH$	
−92	$\longrightarrow CH_3^+ + H_2O$	
−123	$\longrightarrow CH_2OH^+ + H_2$	
−73	$\longrightarrow CHO^+ + 2H_2$	
−19	$\longrightarrow CH_2O^+ + H_2 + H$	
−40	$\longrightarrow CH_3OH^+ + H$	

[a] In units of cm^3 molecule^{-1} sec^{-1}.

ions have higher upper limits because of the lower single resonance intensities of these ions in the mass spectrum. Isotopic substitution was used in attempts at identification of reactions where interfering or overlapping peaks obscure identification in CH_4–H_2O mixtures. The hydroxyl cation is not observed to undergo either hydrogen-atom abstraction with methane in CH_4–D_2O mixtures nor proton transfer to methane in CD_4–H_2O mixtures. Change transfer from the hydroxyl cation to methane is not observed in either CH_4–H_2O, CD_4–H_2O, or CH_4–D_2O mixtures.

Tertiary reactions were also investigated in methane–water mixtures, although the relative rates for these reactions were not determined. In CH_4–H_2O mixtures

$$\underset{17}{CH_5^+} + H_2O \longrightarrow \underset{19}{H_3O^+} + CH_4 \qquad (11)$$

$$\underset{29}{C_2H_5^+} + H_2O \longrightarrow \underset{19}{H_3O^+} + C_2H_4 \qquad (12)$$

Water is known to have a higher proton affinity than either methane or ethylene: the proton affinity of water is 165 kcal/mol, methane 126 kcal/mol, and ethylene 160 kcal/mol.[11–13] Munson and Field[5b] reported observation of (11) and (12) in mass-spectrometric studies of CH_4–H_2O mixtures and gave approximate rates indicating both reactions to be very fast.

Exchange of hydrogen atoms in hydronium ions with both water and methane is also observed in CD_4–H_2O mixtures

$$\underset{19}{H_3O^+} + CD_4 \longrightarrow \underset{20}{H_2DO^+} + CD_3H \qquad (13)$$

$$\underset{20}{H_2DO^+} + H_2O \longrightarrow \underset{19}{H_3O^+} + HDO \qquad (14)$$

The occurrence of these reactions necessitates care in the examination of these mixtures for reactions 7, 8, and 10. At low conversion (low pressure), examination of ejection spectra shows the absence of reactions 13 and 14 where the relative rates for reactions 7, 8, and 10 are measured.

Pressure *vs.* intensity plots from 10^{-7} to 10^{-3} Torr in 1:1 mixtures of CH_4 and H_2O show that the CH_2OH^+ ion does not react further either with methane or water. Double resonance experiments confirm that proton transfer to water does not occur.

$$\underset{31}{CH_2OH^+} + H_2O \not\longrightarrow \underset{19}{H_3O^+} + CH_2O \qquad (15)$$

The reaction reverse to (15) has been observed in water–formaldehyde mixtures,[11] indicating that the proton affinity of formaldehyde is greater than that of water. Also, the CD_2OH^+ and CH_2OD^+ ions in CD_4–H_2O and CH_4–D_2O mixtures are not observed to undergo exchange reactions with water or methane.

High-Resolution Icr Spectra. Figure 1 shows a single resonance spectrum of a CD_4–H_2O mixture at 5×10^{-6} Torr. The marginal oscillator frequency is 757 kHz. At this frequency, sufficient resolution ($M/\Delta M \sim 500$) is obtained to resolve the peaks for the ions containing carbon from the ions containing oxygen. For example, H_2O^+ occurs at *m/e* 18.015 while CD_3^+ occurs at *m/e* 18.053. This resolution, coupled with double resonance techniques, proved to be invaluable for the identification of ion–molecule reactions and measurement of relative rates of reaction in CD_4–H_2O mixtures. If it were not possible to separate the mass peaks, then it would not have been possible to ascertain which of the following reactions was responsible for the 17 → 21 and 18 → 21 double resonance responses in this mixture

$$\underset{17}{OH^+} + CD_4 \begin{array}{ll} \longrightarrow \underset{21.035}{HD_2O^+} + CD_2 & (10) \\ \not\longrightarrow \underset{21.075}{CD_4H^+} + O & (16) \end{array}$$

and

$$\underset{18}{H_2O^+} + CD_4 \begin{array}{ll} \longrightarrow \underset{21.035}{HD_2O^+} + CD_2H & (8) \\ \not\longrightarrow \underset{21.075}{CD_4H^+} + OH & (17) \end{array}$$

Both reactions 10 and 16 are exothermic, and neither reaction can be identified in CH_4–H_2O mixtures. Since HD_2O^+ at *m/e* 21.035 and CD_4H^+ at *m/e* 21.075 are sufficiently resolved in the mass spectrum to tune the spectrometer to the resonant frequency of either one or the other of these ions, it was simple to show that only reactions 8 and 10 occur. A double resonance response is observed for 17 → 21.035, but not for 17 → 21.075. Reaction 17 is endothermic and is not observed in double resonance at *m/e* 21.075, while reaction 8 is observed in double response at *m/e* 21.035.

Similarly, it was possible to show that the 20 → 19 response in CD_4–H_2O mixtures is due to the exchange reaction

$$\underset{20}{H_2DO^+} + H_2O \longrightarrow \underset{19.023}{H_3O^+} + HDO \qquad (18)$$

and is not due to the reaction

$$\underset{20}{CD_4^+} + H_2O \longrightarrow \underset{19.061}{CD_3H^+} + HDO \qquad (19)$$

Reaction 19 is not observed in double resonance spectra at *m/e* 19.061. The CD_3H^+ and CD_4H^+ ions observed

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(11) J. L. Beauchamp and S. E. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).

(12) J. L. Beauchamp, D. Holtz, S. Patt, and S. Sample, *J. Amer. Chem. Soc.*, in press.

(13) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969).

Table IV. Ion–Molecule Reactions of Primary Ions Observed in Mixtures of Methane and Hydrogen Sulfide

ΔH, kcal/mol	Reaction	Rel rate	Abs rate[a]	Lit. values
	CH_4–H_2S			
−45	$CH_4^+ + H_2S \xrightarrow{k_1} H_3S^+ + CH_3$	$k_1/k_2 = 1.22 \pm 0.14$	0.72	
−52	$\xrightarrow{k_2} H_2S^+ + CH_4$	$k_2/k_{c'} = 0.65 \pm 0.10$	0.59	
−37	$CH_3^+ + H_2S \xrightarrow{k_3} CH_2SH^+ + H_2$	$k_3/k_{c'} = 0.56 \pm 0.03$	0.50	0.74[b]
−58	$CH_2^+ + H_2S \xrightarrow{k_4} CH_2SH^+ + H$	$k_4/k_3 = 0.78 \pm 0.15$	0.39	
−6	$\xrightarrow{k_5} CHS^+ + H_2 + H$	$k_5/k_4 = 0.50 \pm 0.10$	0.20	0.22[c]
−124	$CH^+ + H_2S \xrightarrow{k_6} CHS^+ + H_2$	$k_6/k_5 = 3.3 \pm 0.3$	0.66	
−40	$HS^+ + CH_4 \xrightarrow{k_7} CH_2SH^+ + H_2$	$k_7/k_8 = 0.70 \pm 0.05$	0.10	
−18	$S^+ + CH_4 \xrightarrow{k_8} CH_2SH^+ + H$	$k_8/k_3 = 0.28 \pm 0.05$	0.14	
	CD_4–H_2S			
−45	$CD_4^+ + H_2S \xrightarrow{k_9} H_2DS^+ + CD_3$	$k_9 \sim k_1$	~0.7	
	$\xrightarrow{k_{10}} HD_2S^+ + CD_2H$	$k_{10}/k_9 < 0.01$	<0.01	
−18	$\xrightarrow{k_{11}} CD_4H^+ + HS$	$k_{11}/k_d = 0.11 \pm 0.01$	0.09	0.15[d]
+7[e]	$(H_2S^+)^* + CD_4 \xrightarrow{k_{12}} H_2DS^+ + CD_3$	$k_{12}/k_s = 0.07 \pm 0.01$	0.04	0.14[d]

[a] $\times 10^9$ cm^3 molecule^{-1} sec^{-1}. [b] Reference 7, total appearance rate for CH_2SH^+. [c] Reference 7, appearance rate for CHS^+ without reaction 6. [d] Reference 7. [e] This reaction of excited H_2S^+ ions has been well established; see ref 7 and 13.

in these mixtures are due to incomplete isotopic substitution in the CD_4 sample.

Endothermic Charge-Transfer Reactions. Another example which shows the utility of high-resolution spectra in these mixtures is illustrated in Figure 1. Markedly different double resonance spectra are obtained for each of the individual peaks in the "doublet" at *m/e* 20. The separation of these two responses allows accurate measurement of the hydrogen-atom abstraction reaction 7 in the presence of possible interference from the charge-transfer reaction

$$\underset{18}{H_2O^+} + CD_4 \longrightarrow \underset{20}{CD_4^+} + H_2O \qquad (20)$$

The peculiar shape for the 18 → 20.067 peak in Figure 1 is due to an increase in the rate for the reaction as the ions are heated off-resonance by the rf field in the "wings" of the signal. At resonance in the center of the signal, the *m/e* 18 ions are completely ejected from the cell and the normal ejection spectrum is obtained. In this case, the reaction does not occur at thermal energies since the signal does not decrease below the base line at resonance, indicating a null response. At lower rf irradiation power, where the reactant ions are not ejected from the cell, a normal double resonance signal is obtained which indicates a rate increasing with ion kinetic energy. Charge transfer from H_2O to CH_4 is endothermic by about 0.1 eV at thermal kinetic energies. Reaction 20, therefore, does not proceed at thermal energies but is apparently readily forced by reactant ions containing excess kinetic energy.

The reaction reverse to (20) in CH_4–H_2O mixtures is exothermic

$$\underset{16}{CH_4^+} + H_2O \longrightarrow \underset{18}{H_2O^+} + CH_4 \qquad \Delta H = -0.1 \text{ eV} \quad (21)$$

but it is not observed at thermal kinetic energies, nor was it possible to force reaction 21 at excess CH_4^+ kinetic energies. This result is somewhat surprising, but may be explained on the basis of competing reactions. Reaction 21 is only very slightly exothermic and competes with a much more exothermic, very fast proton-transfer reaction, reaction 4. On the other hand, reaction 20 in CH_4–H_2O mixtures competes only with a slow hydrogen-atom transfer reaction, reaction 9. Charge-transfer processes may compete more favorably with hydrogen-atom transfer reactions than with proton-transfer reactions. Previous work[4] has shown that proton transfer appears to be fairly strongly favored over hydrogen-atom transfer when both yield the same product.

Double resonance responses were also observed for the reaction 18 → 15 in CH_4–H_2O mixtures indicating that the CH_4^+ ions produced by endothermic charge transfer from kinetically excited H_2O^+ ions are formed with sufficient internal energy at high enough reactant ion kinetic energies to undergo decomposition to the methyl cation.

$$H_2O^+ + CH_4 \xrightarrow[\text{KE}]{\text{excess}} [CH_4^+]^* + H_2O \qquad (22)$$

$$[CH_4^+]^* \longrightarrow CH_3^+ + H \qquad (23)$$

Ion–Molecule Reactions in Mixtures of Methane and Hydrogen Sulfide

Table IV shows the reactions of primary ions observed in methane–hydrogen sulfide mixtures and the measured relative rates. The variety of reactions observed in these mixtures is greater than observed in methane–water mixtures, particularly in the number of condensation reactions. Again, hydrogen-atom abstraction reactions were identified by isotopic substitution using CD_4–H_2S mixtures.

The CH_4^+ ion reacts with H_2S by charge transfer, by proton transfer, and by hydrogen-atom abstraction. Proton transfer is favored over hydrogen-atom abstraction. Charge transfer competes well with proton transfer in this case and is strongly exothermic. A very small amount of exchange is observed for the proton-

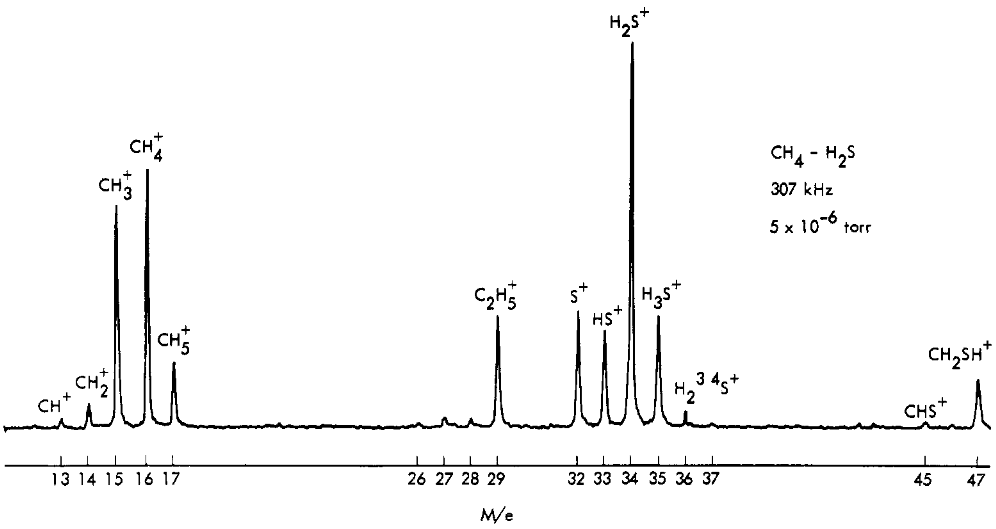

Figure 2. Icr spectra of a 3:1 mixture of CH_4 and H_2S at 50 eV electron energy. The S_2^+, S_2H^+, and $S_2H_2^+$ ions are not shown.

Table V. Exothermic Reactions Not Observed in Mixtures of Methane and Hydrogen Sulfide

ΔH, kcal/mol	Reaction	Maximum rate[a]
−44	$CH_4^+ + H_2S \longrightarrow CH_2S^+ + 2H_2$	$<1 \times 10^{-11}$
−57	$\longrightarrow CH_3SH^+ + H_2$	
−34	$CH_2^+ + H_2S \longrightarrow CH_3^+ + HS$	$<5 \times 10^{-11}$
−19	$\longrightarrow HS^+ + CH_3$	
−40	$\longrightarrow S^+ + CH_4$	
−3	$\longrightarrow CH_2S^+ + H_2$	
−5	$H_2S^+ + CH_4 \longrightarrow CH_3SH^+ + H_2$	$<1 \times 10^{-11}$
−3	$HS^+ + CH_4 \longrightarrow CH_3^+ + H_2S$	
−63	$S^+ + CH_4 \longrightarrow CH_2S^+ + H_2$	

[a] In units of cm^3 $molecule^{-1}$ sec^{-1}.

transfer reaction in CD_4–H_2S mixtures

$$\underset{20}{CD_4^+} + H_2S \longrightarrow \underset{36}{H_2DS^+} + CD_3 \qquad (24)$$

$$\longrightarrow \underset{37}{HD_2S^+} + CD_2H \qquad (25)$$

The amount of exchange observed is quite small, less than 1% of the rate for reaction 24, and it was not possible to obtain a good value for the rate of such a slow reaction. The hydrogen-atom abstraction reaction of CD_4^+ ions with H_2S in CD_4–H_2S mixtures has been previously reported.[7] The rate constant reported by Field and Lampe is in fair agreement with the rate constant measured in this work (Table IV).

The methyl cation is observed to undergo condensation with H_2S, in contrast to its behavior toward H_2O.

$$\underset{15}{CH_3^+} + H_2S \longrightarrow \underset{47}{CH_2SH^+} + H_2 \qquad (26)$$

The CH_2^+ and CH^+ ions also undergo condensation reactions with H_2S. The reaction of the CH_2^+ ion apparently proceeds at thermal kinetic energies with partial decomposition of the protonated thioformaldehyde product ion to give the CHS^+ ion.

$$CH_2^+ + H_2S \longrightarrow CH_2SH^+ + H \qquad (27)$$

$$\downarrow$$

$$CHS^+ + H_2 \qquad (28)$$

Attempts to force the reaction $CH_3^+ + H_2S \rightarrow CHS^+ + 2H_2$ by kinetic excitation of the methyl cation were unsuccessful.

Field and Lampe[7] reported the appearance of the CH_2SH^+ and CHS^+ ions in CH_4–H_2S mixtures, but were unable to determine the precursor ions. The rate constants measured by Field and Lampe for the appearance of these ions (Table IV) are in fair agreement with the rates obtained in this work for the appearance of CH_2SH^+ from reactions of CH_3^+ and CH_2^+ ions and for the appearance of CHS^+ from the reaction of CH_2^+ ions.

The reactions of H_2S^+, HS^+, and S^+ ions with CH_4 are very slow. It is noteworthy that the reactions observed for fragment ions from both neutrals are all condensation reactions. The HS^+ and S^+ ions from H_2S undergo condensation reactions with methane, whereas the OH^+ and NH_2^+ ions from water and ammonia do not. The hydrogen-atom abstraction reaction of H_2S^+ ions with CD_4 in CD_4–H_2S mixtures is endothermic,[7,13] indicating that excited H_2S^+ ions are present. It has been previously shown that the appearance potential of H_2DS^+ ions arising from this reaction is approximately 0.5 eV higher than the appearance potential of ground-state H_2S^+ ions.[7,13]

Two tertiary reactions are observed in CH_4–H_2S mixtures (Figure 2)

$$\underset{17}{CH_5^+} + H_2S \longrightarrow \underset{35}{H_3S^+} + CH_4 \qquad (29)$$

$$\underset{29}{C_2H_5^+} + H_2S \longrightarrow \underset{35}{H_3S^+} + C_2H_4 \qquad (30)$$

The proton affinity of H_2S is 170 kcal/mol, compared with 126 kcal/mol for CH_4 and 160 kcal/mol[11,13] for C_2H_4. Pressure *vs.* intensity studies to 0.001 Torr and double resonance experiments show that the CH_2SH^+, CHS^+, S_2^+, and $S_2H_2^+$ secondary ions present in these mixtures do not react with methane or hydrogen sulfide. The S_2H^+ ion reacts with H_2S[4] but not with CH_4. The fact that the CH_2SH^+ ion is not observed to undergo proton transfer with H_2S indicates that the proton affinity of thioformaldehyde is greater than H_2S. This

Table VI. Ion–Molecule Reactions of Primary Ions Observed in Methane–Ammonia Mixtures

ΔH, kcal/mol	Reaction	Rel rate	Abs rate[a]	Lit. values
	CH_4–NH_3 and CH_4–$^{15}NH_3$			
−82	$CH_4^+ + {}^{15}NH_3 \xrightarrow{k_1} {}^{15}NH_4^+ + CH_3$	$k_1/k_c = 0.60 \pm 0.05$	0.66	2.2 ± 0.7[b]
−58	$\xrightarrow{k_2} {}^{15}NH_3^+ + CH_4$	$k_2/k_1 = 1.05 \pm 0.15$	0.69	
−7	$CH_3^+ + {}^{15}NH_3 \xrightarrow{k_3} {}^{15}NH_4^+ + CH_2$	$k_3/k_1 = 0.25 \pm 0.05$	0.17	1.3 ± 0.2[b]
−71	$+ NH_3 \xrightarrow{k_4} CH_2NH_2^+ + H_2$	$k_4/k_{c'} = 0.73 \pm 0.05$	0.66	
−32	$CH_2^+ + {}^{15}NH_3 \xrightarrow{k_5} {}^{15}NH_4^+ + CH$	$k_5/k_3 = 1.8 \pm 0.5$	0.31	2.0 ± 0.8[b]
−92	$+ NH_3 \xrightarrow{k_6} CH_2NH_2^+ + H$	$k_6/k_4 = 1.8 \pm 0.2$	1.2	
	CD_4–NH_3			
−24	$NH_3^+ + CD_4 \xrightarrow{k_7} NH_3D^+ + CD_3$	$k_7/k_n = 0.25 \pm 0.03$	0.39	
−7	$CD_4^+ + NH_3 \xrightarrow{k_8} CD_4H^+ + NH_2$	$k_8/k_d = 0.04 \pm 0.01$	0.03	0.09,[c] 0.12[d]

[a] $\times 10^9$ cm^3 molecule^{-1} sec^{-1}. [b] Reference 5b, total disappearance rates. [c] Reference 14. [d] Reference 6.

difference is probably small, however, since it proved possible to force the proton-transfer reaction

$$\underset{47}{CH_2SH^+} + H_2S \xRightarrow[\text{KE}]{\text{excess}} \underset{35}{H_3S^+} + CH_2S \qquad (31)$$

by kinetic excitation of the CH_2SH^+ ion.

The H_3S^+ ion does not exchange with methane

$$\underset{35}{H_3S^+} + CD_4 \nrightarrow \underset{36}{H_2DS^+} + CD_3H \qquad (32)$$

but exchange is observed with hydrogen sulfide

$$\underset{36}{H_2DS^+} + H_2S \longrightarrow \underset{35}{H_3S^+} + HDS \qquad (33)$$

Exchange reactions of the CD_2SH^+ ion with CD_4 or H_2S are not observed in these mixtures.

Ion–Molecule Reactions in Mixtures of Methane and Ammonia

The reactions occurring in methane–ammonia mixtures have been the subject of a previous comprehensive icr study.[2] Relative rates for the reactions were not reported in that study, however, but are given here in Table VI. Because of overlap problems in the single resonance spectra of these mixtures, isotopic substitution using $^{15}NH_3$ proved convenient for identification of reactions and measurement of relative rates. Measurement of the rates of hydrogen-atom abstraction reactions necessarily required the use of CD_4–NH_3 mixtures.

The CH_4^+ ion reacts with ammonia by proton transfer, charge transfer, and hydrogen-atom abstraction, similar to its behavior in H_2S. Again, proton transfer is dominant over hydrogen-atom abstraction. Charge transfer competes well with proton transfer in this case also and is highly exothermic. The rate constants reported for the hydrogen-atom abstraction reaction by Lampe and Field[14] and by Harrison and Thynne[6] (Table VI) are only in qualitative agreement with the present results. The rate constants for the charge-transfer and proton-transfer reactions reported by Munson and Field[5b] are in fair agreement with the present results.

Table VII. Exothermic Reactions Not Observed in Mixtures of Methane and Ammonia

ΔH, kcal/mol	Reaction	Maximum rate[a]
−62	$CH_4^+ + NH_3 \longrightarrow CH_3NH_2^+ + H_2$	$<1 \times 10^{-11}$
−33	$\longrightarrow CH_2NH_2^+ + H_2 + H$	
−18	$CH_2^+ + NH_3 \longrightarrow CHNH^+ + H_2 + H$	$<5 \times 10^{-11}$
−4	$NH_3^+ + CH_4 \longrightarrow CH_3NH_2^+ + H_2$	$<1 \times 10^{-11}$
−44	$NH_2^+ + CH_4 \longrightarrow NH_4^+ + CH_2$	
−30	$\longrightarrow NH_3^+ + CH_3$	
−37	$\longrightarrow CH_3^+ + NH_3$	
−33	$\longrightarrow CH_3NH_2^+ + H$	
−108	$\longrightarrow CH_2NH_2^+ + H_2$	
−34	$\longrightarrow CHNH^+ + 2H_2$	

[a] In units of cm^3 molecule^{-1} sec^{-1}.

Both the methyl cation, CH_3^+, and the methylene cation, CH_2^+, react by condensation and by proton transfer with ammonia. These reactions were reported by Munson and Field,[5b] although they were unable to definitely establish the products of the reaction of methylene ions, nor were they able to report a branching ratio for reactions of either methyl cations or methylene cations. The total loss rate reported for these ions by Munson and Field is in fair agreement with our results considering the reported experimental errors. The charge-transfer reaction of methyl cations with ammonia reported in ref 2 does not occur at thermal kinetic energies. The rate constant for the condensation reaction of methyl cations with ammonia reported in ref 2 is too high by a factor of more than 2 because of errors in the use of the mass correction factor for field-swept icr mass spectra and in the value of the ionization cross section used for ammonia-pressure measurement. With this exception, the work of ref 2 is in general confirmed by the present studies.

Condensation Reactions

The mechanisms of the condensation reactions observed in this study were determined using methane-d_4 isotopic substitution to examine the origin of the hydrogen atoms lost during the reaction. The reaction of CD_3^+ with H_2S leads to three products. The ratio of these products is close to the statistical ratio expected on the basis of hydrogen-atom scrambling in an intermediate $[CD_3SH_2^+]^*$ complex (Table VIII). This is in contrast to the more specific mechanism in the CD_3^+–

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[14] F. W. Lampe, F. H. Field, and J. L. Franklin, *J. Amer. Chem. Soc.*, 79, 6132 (1957).

Table VIII. Condensation Mechanism of the $CD_3^+ + H_2S$ Reaction

Reactants	Products	Obsd ratio	Statistical ratio
$CD_3^+ + H_2S$	→ $CDSH_2^+$ ($CDHSH^+$) + D_2	0.20	0.30
	→ CD_2SH^+ + HD	0.73	0.60
	→ CD_3S^+ (CD_2SD^+) + H_2	0.07	0.10

NH_3 condensation reaction, which proceeds mainly *via* vicinal elimination of a hydrogen molecule across the C–N bond, although a significant percentage of germinal loss at the heteroatom site is also observed.[2] The methylene cation, CD_2^+, condenses with H_2O, H_2S, and NH_3 with loss of a hydrogen atom from the heteroatom site in the intermediate complex (Table IX). The HS^+ ion condenses with CD_4 to produce a statistical ratio of products (Table X).

Table IX. Condensation Mechanisms of CH_2^+ Ions

Reactants	Products	Obsd ratio	Statistical ratio
$CH_2^+ + D_2O$	→ CH_2OD^+ + D	1.00	0.50
	→ $CHDOD^+$ + H	0.00	0.50
$CD_2^+ + H_2S$	→ CD_2SH^+ + H	1.00	0.50
	→ $CDHSH^+$ + D	0.00	0.50
$CH_2^+ + ND_3$	→ $CH_2ND_2^+$ + D	1.00	0.60
	→ $CHDND_2$ + H	0.00	0.40

Table X. Condensation Mechanism of the $HS^+ + CD_4$ Reaction

Reactants	Products	Obsd ratio	Statistical ratio
$HS^+ + CD_4$	→ CD_2SH^+ + D_2	0.6	0.60
	→ CD_3S^+ (CD_2SD^+) + HD	0.4	0.40

Unlike $CH_2NH_2^+$ ion in CH_4–NH_3 mixtures,[2] the CH_2OH^+ and CH_2SH^+ ions do not appear to be formed initially in an excited state in CH_4–H_2O and CH_4–H_2S mixtures and do not react further with the hydride in the mixture either by proton transfer or by exchange reactions. It is surprising that methyl cation is unreactive toward H_2O. Reaction 5 is exothermic and is quite similar to the observed condensation reactions with H_2S and NH_3. Although the reasons for this behavior remain obscure, a possible explanation has been proposed.[10] In this latter work, proton-transfer reactions from H_3^+ ions to CH_3NH_2, CH_3OH, and CH_3SH molecules were used to produce the complex intermediate $[CH_3NH_3^+]^*$, $[CH_3OH_2^+]^*$, and $[CH_3SH_2^+]^*$ ions with varying degrees of internal energy. These intermediates are the same ones involved in the condensation reactions of CH_3^+ ions with NH_3, H_2S, and H_2O. The excited intermediates formed by the proton-transfer reactions decompose either by H_2 loss to give the $CH_2XH_n^+$ ion, or by C–X bond scission to give the CH_3^+ ion and the corresponding hydride. The latter reaction is the reverse of the condensation reaction. From the change in the branching ratio of these two decomposition pathways with internal energy in the intermediate complex, it was possible to show that a kinetic barrier apparently exists to decomposition of the intermediate complex by loss of a hydrogen molecule. The existence of such a barrier may explain the failure to detect the condensation reaction of methyl cations with water. Subtraction of the barrier heights derived in ref 10 from the excess energies of the condensation reactions reduces the apparent exothermicities for all the condensation reactions but the apparent exothermicity of the CH_3^+–H_2O reaction is reduced to near zero. That a barrier should exist to hydrogen-molecule loss is reasonable since a fair amount of rearrangement is necessary in the four-centered activated complex.

Comparison of Rates with Theory

Table XI shows the experimental total rate constants for reactions of the various ion–neutral pairs studied in this work. The experimental total rates are compared in Table XI to two theoretical models; the Gioumousis–Stevenson theory (GS)[15] or polarization limit, and the locked-dipole (LD) limit.[16] The GS theory is the maximum rate predicted by the Langevin theory using the ion-induced dipole polarization potential to describe the collision interaction between the ion and neutral molecule. The important parameters in this theory are the polarizability of the neutral molecule and the reduced mass of the ion–neutral pair. The ion is treated as a point charge. The locked-dipole limit for polar molecules expands the GS theory to include the effect of a dipole moment in the neutral molecule by assuming that the dipole moment is always "locked-on" to the ion so that complete alignment between the dipole moment of the neutral with the charge on the ion is maintained.

Table XI. Comparison of Experimental Rates of Ion–Neutral Pairs with Theory

Ion	Neutral	Experimental rate[a]	GS rate[a]	LD rate[a]
CH_4^+	H_2O	2.4	1.3	6.1
	H_2S	1.4	1.3	3.7
	NH_3	1.4	1.1	5.4
CH_3^+	H_2O	<0.01	1.3	6.2
	H_2S	0.5	1.3	3.8
	NH_3	0.8	1.1	5.5
CH_2^+	H_2O	0.5	1.3	6.3
	H_2S	0.6	1.4	3.9
	NH_3	1.5	1.1	5.6
H_2S^+	CD_4	0.04	1.1	
HS^+	CH_4	0.1	1.2	
S^+	CH_4	0.14	1.2	
H_2O^+	CD_4	1.3	1.2	
OH^+	CD_4	0.03	1.2	
NH_3^+	CD_4	0.4	1.2	
NH_2^+	CH_4	<0.01	1.3	

[a] All rates in units of 10^{-9} $cm^3/molecule^{-1}$ sec^{-1}.

The results in Table XI show that for reactions of the CH_4^+ ion with polar neutrals (H_2O, H_2S, and NH_3) the values of the experimental rate constant lie between

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[15] G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

[16] T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).

theoretical rate constants for the polarization and locked-dipole limits. Recent work[17] has shown that this phenomenon is often observed for ion–molecule reactions, involving polar neutrals, and that the observed rate constant is generally closer to the polarization limit, indicating that the effect of the dipole moment is to a large extent averaged out by molecular rotation of the neutral molecule.

In contrast to the general observation, the reactions of the CH_3^+ and CH_2^+ ions, which proceed mainly by condensation, exhibit rates even less than the polarization limit. An apparent exception is the CH_2^+–NH_3 reaction. This observation tends to support the idea[10] that significant barriers to some dissociation channels of intermediate complexes in ion–molecule reactions may exist as a result of the large amount of molecular rearrangement required to form condensation products. The result is simply back reaction where no other exothermic reaction channels are available. Also, comparison of the observed reactions in CH_4–H_2S *vs.* CH_4–H_2O mixtures, and in CH_4–NH_3 *vs.* CH_4–PH_3[18] mixtures, shows that a larger number of condensation reactions are observed in mixtures with second-row hydrides compared with hydrides of the first-row elements. Rearrangement apparently occurs more readily in reactions involving ions and neutrals of the larger second-row hydrides.

The most surprising observation to be made from Table XI is that the reactions of the hydride ions with methane are so slow, the apparent exception in this case being the H_2O^+–CD_4 reaction. A possible explanation is that there are no exothermic proton-transfer or charge-transfer reaction channels available in these reactions (the OH^+ ion being the exception in this instance). The exothermic reaction channels for these reactions consist of abstraction reactions (of H_2, H, or H^- from the neutral) and condensation reactions. Abstraction reactions all seem to exhibit slow rates when observed at all (again the H_2O^+–CD_4 reaction excepted), and evidence has already been presented for the existence of barriers to condensation reactions.

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[17] T. Su and M. T. Bowers, *J. Chem. Phys.*, in press.

[18] D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970).

Mechanism for Scrambling and Dissociation of Short-Lived Intermediate in a Crossed-Beam Reaction of Methyl Cation and Methane

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Abstract: Crossed-beam studies of the ion–molecule reaction $CD_3^+ + CH_4 \rightarrow C_2X_5^+ + X_2$ (X = H, D) and its isotopic complement $CH_3^+ + CD_4 \rightarrow C_2X_5^+ + X_2$ (X = H, D) yield the following results. (a) All $C_2X_5^+$ products arise from a direct reaction mechanism with no evidence of long-lived intermediate formation. (2) Total reaction cross sections calculated from probability contour plots show a marked trend toward nonrandom H, D scrambling with increasing collision energy. A kinetic model of scrambling and dissociation in the short-lived intermediate is proposed to account for the results.

Although Herman, *et al.*,[1] have convincingly demonstrated that the reaction of methyl cation with methane does not proceed through a long-lived intermediate, the mechanism is still far from clear since tandem mass spectrometer (TMS)[2] and ion cyclotron resonance (icr)[3] studies both show extensive H–D scrambling in isotopically labeled products. A possible inference is that the $C_2H_ND_{7-N}^+$ intermediate exists as a structural entity long enough for exchange to take place (a few vibrational periods) but not long enough to exist as a persistent collision complex[4] (a few rotational periods).

Here we report studies of two isotopic systems

$$CD_3^+ + CH_4 \longrightarrow C_2H_ND_{5-N}^+ + H_{4-N}D_{N-2} \qquad (N = 2, 3, 4) \qquad (1a)$$

$$CH_3^+ + CD_4 \longrightarrow C_2H_{5-N}D_N + H_{N-2}D_{4-N} \qquad (N = 2, 3, 4) \qquad (1b)$$

using the crossed-beam electron volt accelerator (EVA).[5] Our purpose in studying this system is twofold: first, to determine if reactions 1a and 1b proceed *via* a direct mechanism for all isotopic products or whether some products are formed in, say, a "stripping" mechanism[5] while others are formed through a long-lived interme-

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[1] Z. Herman, P. Hierl, A. Lee, and R. Wolfgang, *J. Chem. Phys.*, **51**, 454 (1969).

[2] F. P. Abramson and J. H. Futrell, *J. Chem. Phys.*, **45**, 1925 (1966).

[3] W. T. Huntress, Jr., *J. Chem. Phys.*, **56**, 5111 (1972).

[4] A persistent collision complex is defined as an intermediate which lives long enough to scramble completely the *momenta* of the reactant species so that memory of the initial orientation of the momenta is completely lost to the products. Total linear momentum, of course, is conserved. Note the distinction between momentum scrambling and chemical (hydrogen–deuterium) scrambling. For an example of a persistent complex in ion–molecule reactions, see Z. Herman, A. Lee, and R. Wolfgang, *J. Chem. Phys.*, **51**, 452 (1969). See also W. B. Miller, S. A. Safron, and D. R. Herschbach, *Discuss. Faraday Soc.*, **No. 44**, 108 (1967), for a discussion of persistent collision complexes in thermal neutral–neutral reactions.

[5] Z. Herman, J. D. Kerstetter, T. L. Rose, and R. Wolfgang, *Discuss. Faraday Soc.*, No. **44**, 123 (1967).