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Reactions of Gaseous Ions. V. Methane–Hydrogen Chloride and Methane–Hydrogen Sulfide

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Specific reaction rates and cross-sections of the gaseous ion reactions occurring in mixtures of methane with hydrogen chloride and methane with hydrogen sulfide have been measured at a field strength of 10 volts per cm. Extrapolation of these values to zero field strength has been made in the methane–hydrogen chloride system. The reactions that do proceed in these systems allow the calculation of lower limits of 120 and 175 kcal./mole for the proton affinities of hydrogen chloride and hydrogen sulfide, respectively.

Introduction

The formation of H_2Cl^+ by an ion–molecule reaction in hydrogen chloride with a specific reaction rate of 4×10^{-10} cm.^{3}/molecule-sec. has been reported by Schissler and Stevenson.[1] The analogous formation of the H_2Br^+ ion was first proposed by Eyring, Hirschfelder and Taylor[2] as a step in the α-particle radiolysis of hydrogen bromide. In a recent communication[3] we reported the existence of several ion–molecule reactions in mixtures of tetradeuteriomethane with hydrogen chloride and hydrogen sulfide, which result in the formation of the CD_4H^+, $HDCl^+$, H_3S^+ and H_2DS^+ ions.

This paper comprises a detailed study of these reactions and of two previously unreported reactions between methane and hydrogen sulfide.

Experimental

The experimental techniques employed have been described in detail in previous papers of this series.[4,5] In general, the allowance of 30 minutes for mixing of the two gases proved to be satisfactory, as indicated by the identity of the known rate of given reaction (determined in a pure compound study) with the observed rate of the same reaction in a mixture. For example, in mixtures of CD_4 and HCl, the observed rate of the reaction between CD_4^+ and CD_4 to form CD_5^+ was identical to the rate observed in CD_4 alone. This would not be possible if the CD_4 concentrations in the mixtures were different from those calculated with the assumption of complete mixing. However, one exception was noted. In the pressure studies of CD_4–H_2S mixtures, the set of experiments in which CD_4 was varied yielded an observed rate of formation of CD_5^+ that was 18% lower than that found in pure CD_4. Since, over an extended period, we have found the rate of CD_5^+ formation to be quite reproducible, we conclude that mixing was incomplete and that the actual CD_4 concentration in these experiments was lower than that calculated assuming complete mixing. The direction of this variance is consistent with the fact that, in these experiments, CD_4 was admitted after H_2S. We do not understand why mixing should have been complete in the inverted set of experiments (those in which H_2S was added last and varied) but the identity of the rate of formation of H_3S^+ in the mixtures with the rate observed in pure H_2S indicates that this was the case. The concentrations of CD_4, in those experiments in which incomplete mixing was indicated, were therefore calculated from the ion-current ratios and the known rate of formation of CD_5^+.

In the studies of the CH_4–H_2S system we were unable to obtain meaningful data on the formation of the CH_5^+ ion. This difficulty was due to a very high water background brought about by the moving and reinstallation of the instrument, just prior to the measurements.

The rate studies were carried out in a Consolidated Electrodynamics Corporation (CEC) Model 21-620 cycloidal focusing mass spectrometer. The ionization chamber of this instrument was calibrated for pressure using total ionization cross-sections for 75 v. electrons recently reported.[6] Appearance potential measurements were made in a Westinghouse Type LV mass spectrometer.

The tetradeuteriomethane (minimum purity 95%) was obtained from Tracerlab, Inc., and used as received. The methane was Phillips Research Grade with a stated purity of 99.58%. Hydrogen chloride (99.0%) and hydrogen

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[1] D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **24**, 926 (1956).

[2] H. Eyring, J. O. Hirschfelder and H. S. Taylor, *ibid.*, **4**, 570 (1936).

[3] F. W. Lampe and F. H. Field, THIS JOURNAL, **79**, 4244 (1957).

[4] F. H. Field, J. L. Franklin and F. W. Lampe, *ibid.*, **79**, 2419 (1957).

[5] F. W. Lampe, F. H. Field and J. L. Franklin, *ibid.*, **79**, 6132 (1957).

[6] F. W. Lampe, J. L. Franklin and F. H. Field, *ibid.*, **79**, 6129 (1957).

sulfide (99.5%) were obtained from the Matheson Company and were used without further purification.

Results and Discussion

Specific reaction rates and cross-sections for the reactions occurring in CH_4–HCl and CD_4–HCl mixtures are shown in Table I. Unfortunately, the ionization potentials of methane and hydrogen chloride differ by only about 0.2 of a volt which makes a positive identification of the reactions by appearance potential measurements impossible. Therefore, while the rate constants and cross-sections listed are calculated on the basis of the reactions as written, it must be kept in mind that the choice as to which reacting species is the ion and which is the molecule is somewhat arbitrary. For reaction 1 of Table I, there is, of course, little doubt. The basis for selecting CD_4^+ as the ionic reactant in (4) is our observation that, for mixtures of CD_4 with hydrogen-containing substances in which appearance potential measurements are feasible, the only appearance potential observed for CD_4H^+ is closer to the ionization potential of CD_4 than to the critical potential of any other possible ion in the system. Furthermore, if HCl^+ is the ionic reactant and if our estimate of the heat of formation of CH_5^+ is correct,[3] the reaction would be some 6–7 kcal./mole endothermic. Reaction 5 follows also from the above considerations and, of course, there is no doubt about (6) and (7). The choice for (2) and (3) is completely arbitrary and is written as shown only because the inverse cases, (4) and (5), were written as atom transfer reactions.

TABLE I

GASEOUS ION REACTIONS IN METHANE–HYDROGEN CHLORIDE MIXTURES

Reaction	$\left(\frac{dv}{dx}\right)\frac{v.}{cm.}$	$f\sigma \times 10^{16}$, cm.^{2}	$k \times 10^{10}$, $\frac{cm.^3}{molecule\text{-}sec.}$
(1) $HCl^+ + HCl \rightarrow H_2Cl^+ + Cl$	10	48	4.4
(2) $HCl^+ + CD_4 \rightarrow HDCl^+ + CD_3$	10	109	10.2
(3) $HCl^+ + CH_4 \rightarrow H_2Cl^+ + CH_3$	10	129	12.0
(4) $CD_4^+ + HCl \rightarrow CD_4H^+ + Cl$	10	41	5.1
(5) $CH_4^+ + HCl \rightarrow CH_5^+ + Cl$	10	33	4.6
(6) $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	10	60.6	8.50
(7) $CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3$	10	63.4	7.94
(1A) $HCl^+ + HCl \rightarrow H_2Cl^+ + Cl$	0	113	8.0
(2A) $HCl^+ + CD_4 \rightarrow HDCl^+ + CD_3$	0	185	15
(3A) $CD_4^+ + HCl \rightarrow CD_4H^+ + Cl$	0	96	8.0

The specific reaction rates and cross-sections at 10 volts/cm. listed in Table I were obtained from experiments in which the ionization chamber concentrations were varied. In the HCl–CH_4 system, for example, the CH_5^+ ion can be formed by reactions 5 and 6. It has been shown previously[4,5] that for such a situation we can write

$$\frac{1}{[HCl]}\frac{I_{CH_5^+}}{I_{CH_4^+} + I_{CH_5^+}} = k_5\,\tau_{CH_4^+} + k_6\,\tau_{CH_4^+}\frac{[CH_4]}{[HCl]} \quad (E1)$$

or the inverted form which is obtained by multiplying through by [HCl]/[CH_4]. In (E1), the I's are the observed ion-currents, $\tau_{CH_4^+}$ is the residence time of CH_4^+ in the ionization chamber and the k's are the specific reaction rates.

The calculation of the ion-current ratios in these systems is complicated by the appreciable isotope abundances in chlorine. In the CH_4–HCl system two sets of ion-current ratios were calculated for the formation of the H_2Cl^+ ion as

$$\frac{I_{H_2Cl_{35}^+}}{I_{HCl_{35}^+} + I_{H_2Cl_{35}^+}} = \frac{I_{37} - \left(\frac{Cl_{37}}{Cl_{35}}\right) I_{35}}{I_{36} + I_{37} - \left(\frac{Cl_{37}}{Cl_{35}}\right) I_{35}} \quad (E2)$$

$$\frac{I_{H_2Cl_{37}^+}}{I_{HCl_{37}^+} + I_{H_2Cl_{37}^+}} = \frac{I_{39}}{I_{38} + I_{39}} \quad (E3)$$

Excellent agreement between these ratios was obtained in all experiments. For the formation of $HDCl^+$ in CD_4–HCl mixtures the Cl_{37} isotope was used. The ion-current ratio concerned was

$$\frac{I_{HDCl_{37}^+}}{I_{HCl_{37}^+} + I_{HDCl_{37}^+} + I_{H_2Cl_{37}^+}} = \frac{I_{40}}{\left(\frac{Cl_{37}}{Cl_{35}}\right) I_{36} + I_{40} + I_{39}} \quad (E4)$$

A plot according to (E1), for sets of experiments in which the HCl concentration was held constant at a low level and the CH_4 concentration varied, is shown in Fig. 1. A plot of the inverted form of (E1) for experiments in which the CH_4 concentration was held constant and the HCl concentration varied is shown in Fig. 2. The slope from one form of plot is in satisfactory agreement with the intercept from the inverted form, as required.

However, it is seen that the plot for which [HCl] is varied to high levels shows curvature while that for the case where [CH_4] is varied does not. We have shown previously[4] that such curvature at high pressures (by mass spectrometer standards) in our instrument is due to differential scattering in the analyzer. In previous work we have never observed such differential scattering for ions differing by only one mass unit, and since we observe it in this work only when the [HCl] is increased to quite high values, we are led to the conclusion that HCl has an enhanced scattering cross-section, probably due to contributions of the permanent dipole. In our investigations of water[5] we were not able to raise the [H_2O] to such levels because of vapor pressure limitations and did not observe differential scattering.

The reaction rates and cross-sections for (6) and (7) were obtained from the mixtures and are in excellent agreement with values previously determined from the pure compounds.[4] The reaction rate difference between (2) and (3) may be partially due to an isotope effect. However, in view of the uncertainty involved as can be seen by comparing (4) and (5), it is pointless to pursue this further. The specific reaction rate of (1) appears to be in quite good agreement with that reported by Schissler and Stevenson[1] although, since we do

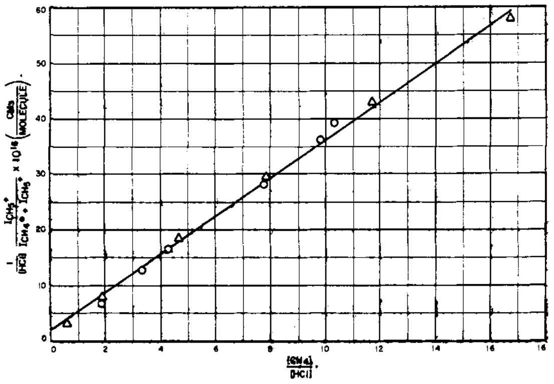

Fig. 1.—Formation of CH_5^+ in HCl–CH_4 mixtures.

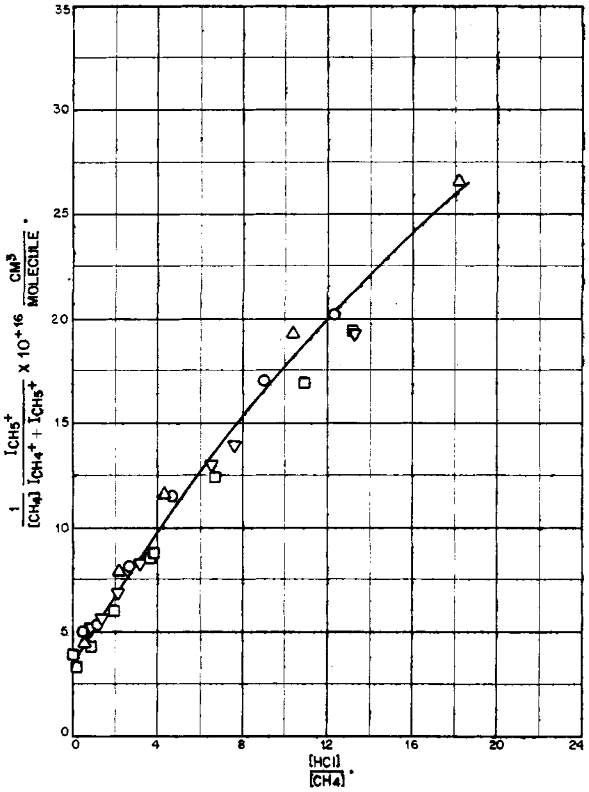

Fig. 2.—Formation of CH_5^+ in CH_4–HCl mixtures.

not know exactly under what conditions they obtained their value, comparison is difficult.

The reaction cross-sections at zero field strength shown in Table I were determined by extrapolation of data obtained, at constant ionization chamber pressures, over a voltage gradient range of 2–100 volts/cm. The extrapolation procedure was described in previous papers.[4,5] The variation of reaction cross-section of (2) in Table I with ionization chamber field strength is shown in Fig. 2.

Specific reaction rates and cross-sections at 10 volts/cm. for the reactions occurring in pure H_2S, CH_4–H_2S and CD_4–H_2S mixtures are shown in Table II. The reactions occurring in this system were deduced, in so far as possible, by appearance potential measurements.

TABLE II

GASEOUS ION REACTIONS IN METHANE–HYDROGEN SULFIDE MIXTURES

Reaction	$f\sigma \times 10^{16}$, cm.^{2}	$k \times 10^{10}$, cm.^{3}/molecule-sec.
(8) $H_2S^+ + H_2S \rightarrow H_3S^+ + HS$	31	3.0
(9) $H_2S^+ + CD_4 \rightarrow H_2DS^+ + CD_3$	14	1.4
(10) $H_2S^+ + CH_4 \rightarrow H_3S^+ + CH_3$	15	1.5
(11) $CD_4^+ + H_2S \rightarrow CD_4H^+ + HS$	12	1.5
(12) CH_3^+ (or CH_4^+) + $H_2S \rightarrow$ $CHS^+ + 2H_2(+H)$	16	2.2
(13) CH_3^+ (or CH_4^+) + $H_2S \rightarrow$ $CH_2S^+ + H_2(+H)$	52	7.4

The appearance potential of the H_3S^+ ion in pure H_2S was found to be 10.6 volts which when compared to the value of 10.50 volts for the ionization potential of H_2S[7] leaves little doubt that (8) is the reaction involved. The choice of the ionic reactant in reaction 9 is somewhat arbitrary. The only appearance potential found for the H_2DS^+ ion was 10.9 volts, but it cannot be definitely concluded from this that H_2S^+ is the ionic species involved in the reaction. The $H_2S_{34}^+$ isotopic ion is in sufficient abundance (4.2%) to mask any higher appearance potential of the secondary ion, $H_2DS_{32}^+$. Similar considerations apply, of course to reaction 10. Only one appearance potential was found for the CD_4H^+ ion and this was at 13.0 volts, which is to be compared with a value of 13.2 volts for the ionization potential of CD_4. There is little doubt that CD_4^+ is the ionic species in reaction 11.

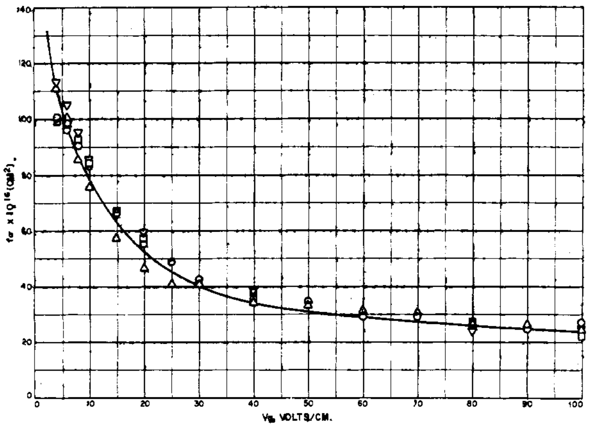

Fig. 3.—Effect of field strength on reaction cross-section.

Reactions 12 and 13 in which a carbon–sulfur bond is formed are quite interesting. They both show the correct pressure dependence for secondary ions. Moreover, when CD_4 is substituted for CH_4, the CHS^+ (mass 45) is replaced by CDS^+ (mass 46) and the CH_3S^+ ion (mass 47) is replaced by CH_2DS^+, CHD_2S^+, CD_3S^+ (masses 48, 49 and 50). Thus these ions are products of ion–molecule reactions between H_2S and CH_4. The CHS^+ ion exhibits two appearance potentials, one at 13.0 volts and the second at 14.5 volts. The CH_3S^+ ion has appearance potentials at 13.0 and 14.3 volts. We therefore conclude that both CH_4^+ (I.P. = 13.12 volts) and CH_3^+ (A.P. = 14.39 volts) are the ionic reactants involved in the formation of these two secondary ions.

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(7) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, N. Y., 1957.

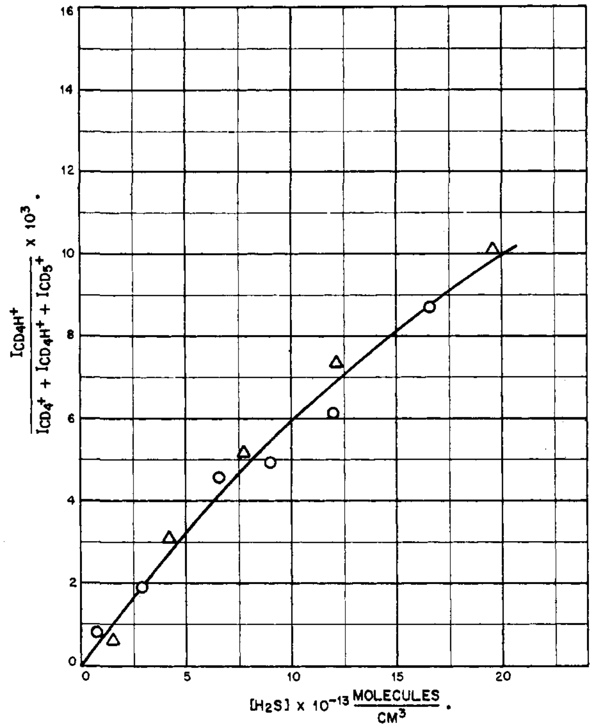

Fig. 4.—Formation of CD_4H^+ in H_2S–CD_4 mixtures.

The specific reaction rates and cross-sections in Table II were obtained in the same manner as the analogous values for the CH_4–HCl system. However, since secondary ion peaks decrease with field strength, are considerably smaller in the CH_4–H_2S system than in the HCl–CH_4 mixtures and involve much more extensive isotope corrections, no attempt was made to extrapolate the rather scattered data to zero field strength.

It can be shown that in the H_2S and H_2S–CH_4 systems the necessary isotope corrections lead to the following equation for the calculations involved in the formation of H_3S^+

$$\frac{I_{\mathrm{H_3S^+}}}{I_{\mathrm{H_2S^+}} + I_{\mathrm{H_3S^+}}} = \frac{I_{35} - aI_{34} - bI_{33} + 2abI_{32}}{I_{35} + (1 - a)I_{34} - (a + b)I_{33} - bI_{32}} \tag{E5}$$

In mixtures of H_2S and CD_4, the ion-current ratios for calculation of the rates of formation of H_3S^+ and H_2DS^+ are

$$\frac{I_{\mathrm{H_3S^+}}}{I_{\mathrm{H_2S^+}} + I_{\mathrm{H_3S^+}} + I_{\mathrm{H_2DS^+}}} = \frac{I_{35} - aI_{34} - bI_{33} + 2abI_{32}}{I_{36} + I_{35} + (1 - a - b)I_{34} - (a + b)I_{33} - bI_{32} - cI_{22}} \tag{E6}$$

$$\frac{I_{\mathrm{H_2DS^+}}}{I_{\mathrm{H_2S}} + I_{\mathrm{H_3S^+}} + I_{\mathrm{H_2DS^+}}} = \frac{I_{36} - bI_{34} + abI_{33} + bI_{32}}{I_{36} + I_{35} + (1 - a - b)I_{34} - (a + b)I_{33} - bI_{32} - cI_{22}} \tag{E7}$$

In equations E5-E7, *a* is the ratio of S_{33} to S_{32}, *b* is the ratio of S_{34} to S_{32} and *c* is the ratio of $C_2D_5^+$ (mass 34) to CD_5^+ (mass 22) determined in pure CD_4.

In view of such extensive corrections in the H_2S systems, it is not surprising that some scatter is observed. However, agreement is observed between the rate of formation of H_3S^+ in pure H_2S and that found in H_2S–CD_4 mixtures as well as between reactions 9 and 10 of Table II, which indicates that the corrections have been properly made.

A typical plot for the CD_4–H_2S system is shown in Fig. 4, which relates to the formation of CD_4H^+ by reaction 11. We have shown previously[4,5] that the initial slope of such a plot is $k\tau$, where k is the specific reaction rate and τ is the residence time of of the ionic reactant.

It is of interest that in this system as in the HCl–CH_4 system, curvature is observed when the polar component is raised to high concentration but a linear plot is observed when the non-polar component concentration is increased. This occurrence in the CH_4–H_2S system strengthens our view expressed earlier that the scattering cross-section is much enhanced in compounds with a permanent dipole, such as HCl and H_2S.

It is impossible in this system to separate from each other the two reactions forming CHS^+ and the two forming CH_3S^+. The reaction rate constants and cross-sections for the formation of these secondary ions were calculated as average values of the two reactions involved for each.

Since only exothermic reactions can be observed in these mass spectrometer studies, the reactions that are observed allow us to assign lower limits to the proton affinity of HCl and H_2S. The observation of reaction 1 in Table I leads to a proton affinity for HCl > 120 kcal./mole. The observation of reaction 10 in Table II leads to a value for the proton affinity of H_2S > 175 kcal./mole.

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