Reactions of Gaseous Ions. XIII. The System Methane–Hydrogen[1]

BY M. S. B. MUNSON, F. H. FIELD, AND J. L. FRANKLIN

Studies have been made of ion–molecule reactions in mixtures of CH_4 with H_2 and D_2 and of CD_4 with H_2. At low electron energies where only methane ions are formed, both CH_4D^+ and CH_3D^+ were formed at very small rates. At higher electron energies hydrogen molecular ions attack methane to produce methyl ions which, where D–H exchange can occur, will be extensively exchanged. Methyl ions also undergo exchange reactions with hydrogen. The exchanged methyls account for most of the exchanged ethyl ions observed. H_3^+ ions react with methane to produce CH_5^+, and H_2^+ reacts slowly with methane to form H_3^+. Both CH_2^+ and CH^+ react with H_2 to form CH_3^+ and CH_2^+, respectively.

Pratt and Wolfgang[2a] in their work on exchange of T_2 with CH_4 suggested that ion–molecule reactions were directly involved in part of the exchange, and Wexler[2b] has recently reported a mass spectrometric study on mixtures of D_2 and CH_4 that suggested lines for further work in obtaining quantitative data for the ion–molecule reactions which might be involved in exchange reactions of CH_4 with D_2 or T_2. Accordingly, we have studied mixtures of CH_4 and H_2, CH_4 and D_2, and CD_4 and H_2 in an attempt to determine the kinetics of the ionic reactions of methane and hydrogen.

Experimental

The mass spectrometer is that described previously by Field[3] and used in several previous papers reported from this Laboratory.[4] The CH_4 was Phillips research grade (99.6 mole %) which was purified by double fractionation from Linde Molecular Sieve. D_2 and H_2 (Matheson) were purified by sorption and desorption from a Molecular Sieve at liquid N_2 temperatures. The CD_4 (purified in the same manner as CH_4) was from Tracer-Lab and contained about 7.5% CD_3H and not more than 1% CD_2H_2. Pressure calibrations for CH_4 were obtained in the manner previously described[5a] while calibrations for D_2 and H_2 were obtained from the kinetics of $D_2^+ + D_2 = D_3^+$ (or the hydrogen analog) using the rate constant given by Stevenson and Schissler.[5b] The pressure calibration for CD_4 was obtained from the reactions of CD_4^+ and CD_3^+ using the rate constants given in our recent paper of ionic reactions in CH_4.[4]

Most of the experiments were done with an electron current of 0.02 μa. with 70-e.v. electrons and a repeller field strength of 12.5 v./cm. For the experiments at low electron voltage a lower repeller field strength and higher electron current were used. For some of the low energy experiments the relative rate constants were determined with a pulsed electron beam so that the electron energy could be controlled more precisely.
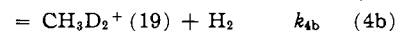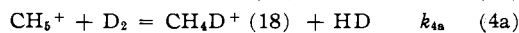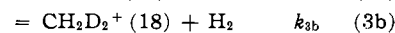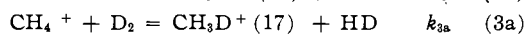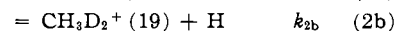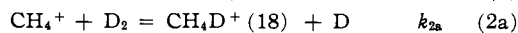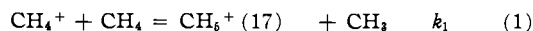
The methane and hydrogen were in separate reservoirs and the pressure studies from which the kinetic data were obtained were made by determining the mass spectrum with a fixed pressure of methane in one reservoir and then determining the mass spectrum after each successive addition of hydrogen in the other reservoir. Perhaps because of the flow properties of hydrogen and the difficulties of focusing and collecting ions of mass 2–6, the data reported here do not have the precision which we have recently been able to attain.

In this study we have elected to present rate data in terms of specific reaction rate constants, k, rather than cross sections. The two are, of course, equivalent because of the relation $k = \sigma v$ where σ and v are, respectively, cross section and relative velocity. We prefer the rate constants since they are less sensitive to velocity effects than are cross sections. In many instances $\sigma \propto 1/v$ so that k is independent of v. When this relationship is correct the rate constants determined in the presence of repeller field are the same as those for thermal ions. Unfortunately, this is not always the case and so we must consider our rate constants to be valid only at the average relative velocities corresponding to the repeller field strength employed when the measurements were made. In most studies a field strength of 12.5 v./cm. was employed (maximum ion energy of 2.5 v.). In a few experiments the field strength was 2.5 v./cm. corresponding to a maximum ion energy of 0.5 v. A more complete discussion is given by Lampe, Franklin, and Field.[6]

Results

Reactions of CH_4^+.—Using electrons of energy too low to form any primary ions other than CH_4^+, we were able to study the reactions of CH_4^+ with H_2 and D_2 without interference.

$$CH_4^+ + CH_4 = CH_5^+ (17) \quad + CH_3 \qquad k_1 \qquad (1)$$
$$CH_4^+ + D_2 = CH_4D^+ (18) + D \qquad k_{2a} \qquad (2a)$$
$$= CH_3D_2^+ (19) + H \qquad k_{2b} \qquad (2b)$$
$$CH_4^+ + D_2 = CH_3D^+ (17) + HD \qquad k_{3a} \qquad (3a)$$
$$= CH_2D_2^+ (18) + H_2 \qquad k_{3b} \qquad (3b)$$
$$CH_5^+ + D_2 = CH_4D^+ (18) + HD \qquad k_{4a} \qquad (4a)$$
$$= CH_3D_2^+ (19) + H_2 \qquad k_{4b} \qquad (4b)$$

Reaction 1 was the predominant reaction involving CH_4^+, even at low relative CH_4 pressures. The ratio I_{18}/I_{17}, after correcting for $^{13}CH_5^+$, varied linearly with D_2 pressure (Fig. 1, curve A) and inversely with CH_4 pressure. These dependences on pressure require that the mass 18 species be formed from 2a or 3b, since 4a requires a different dependence of I_{18}/I_{17} on CH_4 pressure. From a kinetic analysis we found

$$I_{18}/I_{17} = (k_{2a} + k_{3b})(D_2)/k_1(CH_4) \qquad (5)$$

and in two separate experiments we obtained identical values of 3.0×10^{-12} cc./molecule-sec. for $(k_{2a} + k_{3b})$ from the D_2 dependence of the ratio I_{18}/I_{17}, and 1.6×10^{-12} cc./molecule-sec. from the CH_4 dependence. We were unable to resolve the $^{13}CH_5^+-^{12}CH_4D^+-^{12}CH_2D_2^+$ triplet, but we could easily distinguish any H_2O^+ at mass 18. This low value of 3×10^{-12} cc./molecule-sec. or 1×10^{-17} cm.^{2} for the sum of cross sections of 2a and 3b is in good agreement with the earlier observation of Lampe and Field[7] of a cross section not greater than 2×10^{-17} cm.^{2} for the reaction of $(CH_4 + D_2)^+$.

In similar experiments with mixtures of CH_4 and H_2 we obtained from the very slight increase in the I_{17}/I_{16} ratio with hydrogen pressure values of $0-7 \times 10^{-12}$ cc./molecule-sec. for k_6

$$CH_4^+ + H_2 = CH_5^+ + H \qquad k_6 \qquad (6)$$
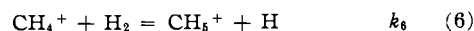
The lower precision in this case than with D_2 was the result of the difficulties in determining the very small increase in mass 17 from 6 compared to the very large amount of mass 17 from 1.

Since we observed only a very small amount of mass 19 greater than the ^{13}C isotope of mass 18, we could set an upper limit of 1×10^{-13} cc./molecule-sec. for the rate constant of 2b or 4b. We did not find any evidence for the formation of mass 19 or 20 (CHD_3^+ or CD_4^+) from CH_4^+ by reactions second order in D_2.

Since the ratio I_{17}/I_{16} increased slightly with an increase in D_2 pressure, we concluded that there was a small contribution of direct exchange between CH_4^+

(1) Supported in part by Project Squid under Contract No. Nonr-3623(S-18).

(2) (a) T. H. Pratt and R. Wolfgang, J. Am. Chem. Soc., **83**, 10 (1961); (b) S. Wexler, ibid., **85**, 272 (1963).

(3) F. H. Field, ibid., **83**, 1523 (1961).

(4) F. H. Field, J. L. Franklin, and M. S. B. Munson, ibid., **85**, 3575 (1963).

(5) (a) F. H. Field and M. S. B. Munson, Paper presented at 11th ASTM Conference on Mass Spectrometry, San Francisco, Calif., May, 1963; (b) D. P. Stevenson and D. O. Schissler, J. Chem. Phys., **23**, 1353 (1955).

(6) F. W. Lampe, J. L. Franklin, and F. H. Field, "Progress in Reaction Kinetics," Vol. 1, Pergamon Press, London, 1961, pp. 69–103.

(7) F. W. Lampe and F. H. Field, J. Am. Chem. Soc., **81**, 3242 (1959).

and D_2 according to 3a and we obtained values of 7 and 12×10^{-12} cc./molecule-sec. for k_{3a}. If the $(CH_4D_2^+)$ complex persisted long enough for randomization of the hydrogen atoms to occur, then one would expect k_{3b}/k_{3a} to be about 3/4. Experimental difficulties prevented our studying mixtures of CD_4 and H_2 with an electron energy too low for the formation of CD_3^+ or H_2^+ which would have distinguished between $CD_2H_2^+$ and CD_4H^+ (the analogs of CH_4D^+ and $CH_2D_2^+$ in the CH_4–D_2 system). Since, however, the mixtures of CH_4 and H_2 gave indications of the formation of CH_5^+ with a rate constant of the order of $(k_{2a} + k_{3b})$, we assumed that the mass 18 is CH_4D^+ formed from 2a. Even if the mass 18 were $CH_2D_2^+$ formed from 3b, the ratio k_{3b}/k_{3a} would be only 1/4 which is sufficiently different from 3/4 to suggest that randomization of the $(CH_4D_2^+)$ complex does not occur. Similarly, the absence of mass 19, $CH_3D_2^+$, also implies no randomization in the $(CH_4D_2^+)$ complex. The complex between CH_4^+ and D_2 may then be considered as a loose complex somewhat similar to that between $(CH_4$ and $CD_4)^+$, for which very little exchange was noted.[8]

Reactions of CH_3^+, H_2^+, H_3^+.—Although we were able to reduce the ionizing electron energy low enough to eliminate all of the primary ions except CH_4^+, we were unable to control the electron energy sufficiently well to be able to study the reactions of CH_3^+ in the absence of H_2^+ or H_3^+. From studies on mixtures of constant $[CH_4]$ with varying amounts of H_2 with 70-e.v. electrons we noted an increase in the ratio $(I_{15} + I_{29})/(I_{16} + I_{17})$, the ratio of total (CH_3^+) to total (CH_4^+), with increasing H_2 pressure. We concluded that 7a is faster than 7b

$$H_2^+ \ (or \ H_3^+) + CH_4$$
$$= CH_3^+ + H_2 + H \ (or \ 2H_2) \quad k_{7a} \quad (7a)$$
$$= CH_4^+ + H_2 \ (or \ H_2 + H) \quad k_{7b} \quad (7b)$$
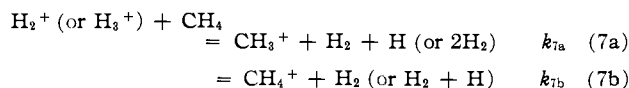
We have shown that the reaction of CH_4^+ with H_2 or D_2 is very slow and can be neglected. We would like to know whether 7b occurs at all. The ion C^+ cannot be formed from CH_4 by dissociative charge exchange of hydrogen because of energy considerations. Further, the reaction

$$C^+ + H_2 = CH^+ + H$$
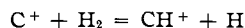
is endothermic[9] and hence will not occur at the conditions of our experiments; C^+ and H_2 might react by a third-order process but, if this occurs, it is very slow; C^+, therefore, can be taken as independent of hydrogen concentration. We observed that the ratio I_{12}/I_{16} was substantially independent of hydrogen concentration. Therefore we conclude that CH_4^+ is not formed by 7b. Thus the increase in $(I_{15} + I_{29})/(I_{16} + I_{17})$ with hydrogen addition must be attributed to 7a. The data are rather badly scattered, but suggest that H_2^+ rather than H_3^+ is the reactant in 7a with a rate of the order of many ion–molecule reactions.

In these same experiments the ratio I_{17}/I_{16} increased with increasing hydrogen pressure, although the effect is small. Since CH_4^+ reacts only very slightly with hydrogen, this implied that some mass 17, CH_5^+, was formed by a process of a different kind. This process appears to be second order in H_2 and could be either

$$CH_3^+ + 2H_2 = CH_5^+ + H_2 \quad (8)$$

or

$$H_3^+ + CH_4 = CH_5^+ + H_2 \quad (9)$$
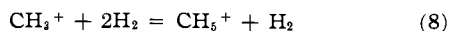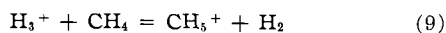
(8) C. D. Wagner, P. A. Wadsworth, and D. P. Stevenson, *J. Chem. Phys.*, **28**, 517 (1958).

(9) $\Delta H_f(C^+) = \Delta H_f(C) + I(C) = 170 + 260 = 430$ kcal./mole. $D(CH) = 80$ kcal./mole (G. Herzberg, "Spectra of Diatomic Molecules," D. van Nostrand Co. Inc., New York, N. Y., 1950). $I(CH) = 256$ kcal./mole giving $\Delta H_f(CH^+) = 400$ kcal./mole.
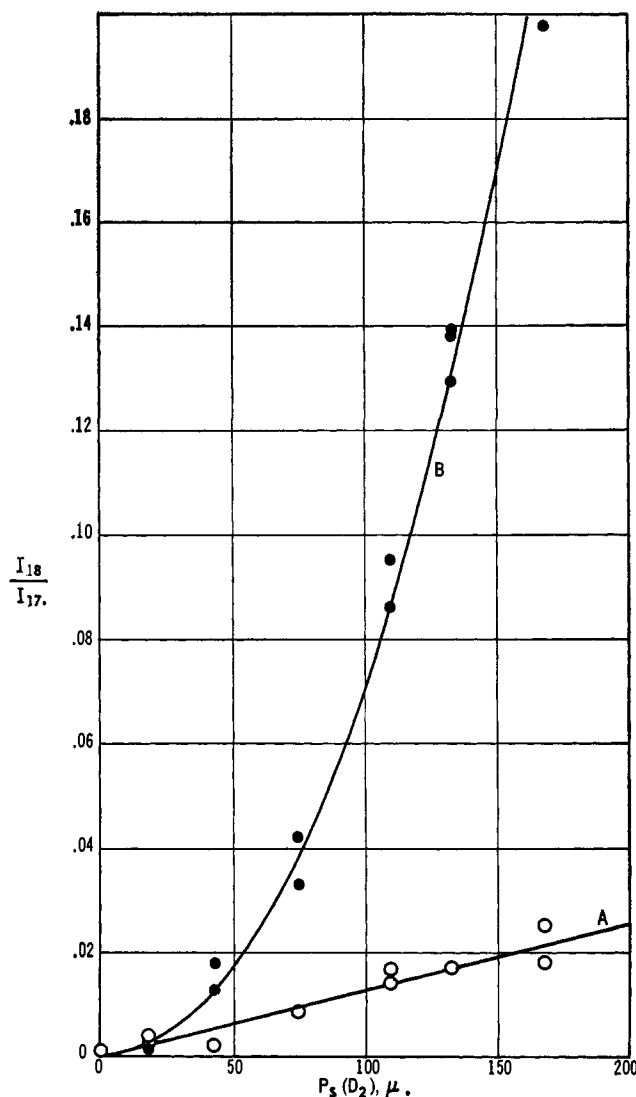
Fig. 1.—Variation of I_{18}/I_{17} with D_2 pressure; I_{18} corrected for 1.1% ^{13}C; $P(CH_4) = 23 \mu$: A, e.v. $\cong 12.5$ v. (no CH_3^+ or H_2^+); B, e.v. $\cong 15$ v. ($CH_3^+ + H_2^+$ present).

Equation 8 cannot be involved since this would produce $CH_3D_2^+$ with D_2 and we observe essentially no mass 19 in the experiments with CH_4 and D_2. The kinetics are, however, too complicated and the data too badly scattered to warrant an estimate of a rate constant.

The results of the experiments with CH_4 and D_2 using 70-e.v. electrons indicate that the situation is greatly complicated by exchange reactions. In addition to appreciable amounts of mass 18 (as high as 10–20% of mass 17) appreciable amounts of ions of masses 30, 31, and 32 are observed (I_{30}/I_{29} is as high as 0.4 at high D_2 pressures) and the ratios of the other ions show some marked variations.

The ratio I_{30}/I_{29} ($C_2H_4D^+/C_2H_5^+$) increased linearly with an increase in D_2 pressure and was substantially independent of methane pressure. The ratio I_{31}/I_{30} ($C_2H_3D_2^+/C_2H_4D^+$) also increased with increasing D_2 pressure, suggesting that the D-atoms are generally inserted one at a time into the ethyl ions, but the nonzero intercept of I_{31}/I_{30} against pressure suggests that substitution of two deuterium atoms per collision also occurs. The ratio I_{32}/I_{30} ($C_2H_2D_3^+/C_2H_4D^+$) also increased with increasing D_2 pressure as it must since three deuterium atoms cannot be brought into the complex on one collision. Trace amounts of mass 33 were also seen. Figure 2 shows plots of the ratios of ethyl ions as a function of D_2 pressure. From plots of ratios
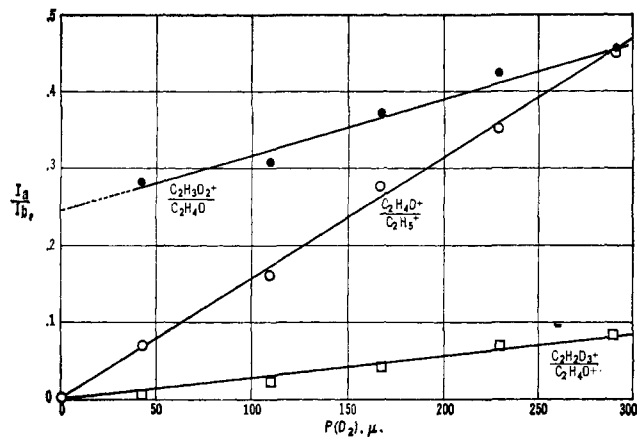
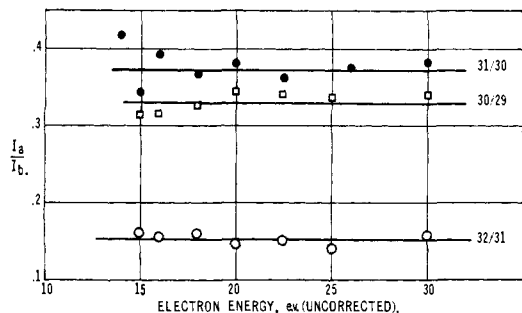Fig. 2.—Ratios of deuterated ethyl ions as function of D_2 pressure. e.v. = 70, $P(CH_4)$ = 97 μ.

Fig. 3.—Ratio of ethyl ions as a function of electron energy; $P(D_2)$ = 110 μ, $P(CH_4)$ = 23 μ.

of ion intensities as a function of electron voltage it appears that $C_2H_5^+$, $C_2H_4D^+$, $C_2H_3D_2^+$, and $C_2H_2D_3^+$ come from methyl ion (see Fig. 3).

The occurrence of dissociative charge exchange in the CH_4–H_2 system caused an increase in the ratio $(I_{15} + I_{29})/(I_{16} + I_{17})$. For CH_4–D_2 this same ratio (although it now includes some different ionic species) decreased with an increase in D_2 pressure. Further, the ratio I_{18}/I_{17}, which was first order in D_2 at low electron energies when only CH_4^+ was present, was second order in D_2 in the experiments with higher energy electrons, as well as present in much higher relative concentrations (see Fig. 1).

These data suggest that appreciable deuterium exchange occurs with CH_3^+. The lack of any significant increase in $(CH_3^+ + C_2H_5^+)$ suggests that the dissociative charge exchange reaction leading to CH_3^+ in the CH_4–H_2 system, 7a, is an ion–molecule reaction which for D_2^+ (or perhaps D_3^+) yields deuterated methyl ions. If this reaction involves D_2^+, the $(CH_4D_2^+)$ complex, which has a higher energy than the same complex formed from CH_4^+ and D_2, allows randomization of H and D atoms even though the $(CH_4D_2^+)$ complex from CH_4^+ does not. From the decrease in $\ln I_{15}/I_{12}^{10}$ with an increase in D_2 pressure and assuming that no appreciable amounts of CH_3^+ were formed from dissociative charge exchange, we obtained values of 1.5 and 1.1 $\times$ 10^{-10} cc./molecule-sec. for k_{11}. The formation of appreciable amounts of CH_3^+ by dissociative charge exchange of D_2^+ (or D_3^+) would mean that the actual value of k_{11} is greater than these calculated values.

(10) C^+ neither reacts with nor is formed from ions of H_2 (or D_2) and one may use I_{12} as a measure of the quantity $(P_i^+)_0$ for the various primary ions whose disappearance is determined by the pseudo-first-order equation, $\ln (P_i^+)/(P_i^+)_0 = -k(D_2)t_i$, since $(P_i^+)_0 \propto$ total intensity of CH_4 fragments $\propto I_{12}$. For the same reasons I_{16} in CH_4–H_2 mixtures and I_{20} in CD_4–H_2 mixtures may be used as "normalizing ions."
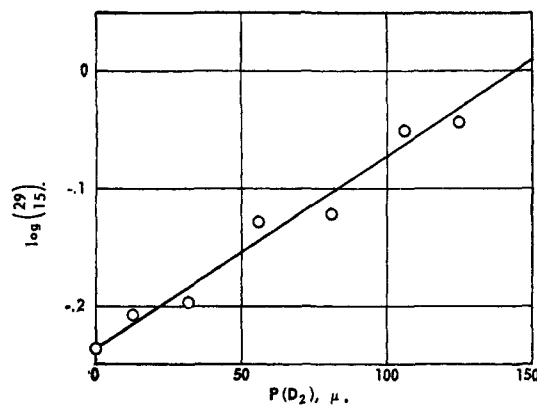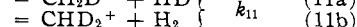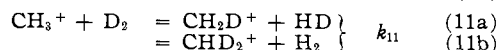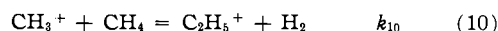

Fig. 4.—log $(C_2H_5^+/CH_3^+)$ vs. D_2 pressure; $P(CH_4)$ = 23 μ.

$$CH_3^+ + CH_4 = C_2H_5^+ + H_2 \qquad k_{10} \qquad (10)$$

$$CH_3^+ + D_2 \begin{array}{l} = CH_2D^+ + HD \\ = CHD_2^+ + H_2 \end{array} \Bigg\} \quad k_{11} \qquad \begin{array}{l} (11a) \\ (11b) \end{array}$$

It is also possible that the deuterated ethyl ions could be formed by exchange reactions of ethyl ions with D_2, and this mechanism would predict that the ratio $(C_2H_5^+)/(CH_3^+)$ would decrease with increasing D_2 pressure. If, however, one assumes that 10 and 11 occur and that CH_3^+ produced by dissociative charge exchange is negligible, one obtains

$$(C_2H_5^+)/(CH_3^+) = k_{10}(CH_4)[\exp(k_{10}(CH_4) + k_{11}(D_2))t - 1]/[k_{10}(CH_4) + k_{11}(D_2)] \quad (12)$$

Then $\ln (C_2H_5^+)/(CH_3^+)$ should increase approximately linearly with D_2 pressure, as is shown in Fig. 4. From the slope of the curve in Fig. 4 we obtained an approximate value of 2.4 $\times$ 10^{-10} cc./molecule-sec. for k_{11}. The agreement is satisfactory. Although Wexler[2] noted no evidence for exchange reactions of $C_2H_5^+$ with D_2 and indeed saw the same type of phenomena which we report here, he did not consider the exchange reactions of CH_3^+ seriously and in his proposed mechanism for tritium exchange postulated the direct exchange of $C_2H_5^+$ with T_2.

The mass 18 is obviously formed by a different process in these experiments from those with only CH_4^+ present. Either 13 or 14 or both must be occurring

$$D_2^+ + CH_4 = CH_4D^+ + D_2 \qquad (13)$$

$$CH_3^+ + 2D_2 = CD_3^+ + H_2 + HD \qquad (14)$$
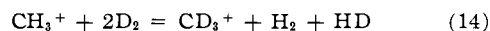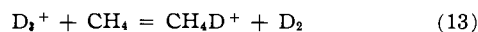
Equation 13 must be occurring since its analog in the CH_4–H_2 system was observed and the very pronounced second-order dependence in this case strengthens the assignment of 9. High resolution studies on the CH_4–D_2 system indicated that the mass 18 peak was a doublet. This phenomenon is clearly shown in Fig. 5 for mass 19 which was separated into a $(H_3O^+ + HDO^+)$ peak and a poorly resolved hydrocarbon doublet. From the relative separations, we concluded that the hydrocarbon doublet at mass 19 must be $^{13}CDH_4^+$– $^{13}CD_3^+$. In studies on mixtures of CD_4 and H_2, both CH_3^+ (m/e 15) and CD_4H^+ (m/e 21) were formed by processes second order in H_2 as would be expected if both reactions 13 and 14 are involved in the CH_4–D_2 system. (The electron energy was controlled so that contributions of CHD^+ to mass 15 were negligible.)

From studies on mixtures of CD_4 and H_2 one can confirm the exchange reactions we have noted from the increase in the relative intensities of the odd mass ions with increasing H_2 pressure. Since there is no interference of masses, the ratio I_{12}/I_{20} (C^+/CD_4^+) is anal-

ogous to the ratio I_{12}/I_{16} in the CH_4–H_2 system. Since the ratio I_{12}/I_{20} is also substantially independent of H_2 pressure, we may use I_{20} for normalizing. From the decrease in log (I_{18}/I_{20}) as a function of H_2 pressure we obtained rate constants for 15 directly, again assuming negligible dissociative charge exchange to CD_3^+

$$CD_3^+ + H_2 = CD_2H^+ + HD \quad \} \quad k_{15} \quad (15a)$$
$$ = CDH_2^+ + D_2 \quad \} \quad \phantom{k_{15}} \quad (15b)$$
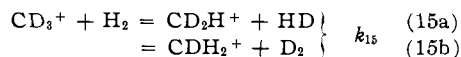
The values of 2.2, 2.4, and 1.2 $\times$ 10^{-12} cc./molecule-sec. for k_{15} are in very good agreement with the value of 1.7 $\times$ 10^{-10} cc./molecule-sec. for k_{11}.

Because of the reactions second order in H_2 or D_2 which also produce CD_2H^+ and CDH_2^+, together with the fact that both are produced by reactions of CH_2^+ or CD_2^+, we were unable to make any reliable estimate as to the relative amounts of the two products formed by 11 and 15. Some mass 5 is observed in the CH_4–D_2 system and the ratio I_5/I_{16} varies approximately linearly with CH_4 pressure and inversely with D_2 pressure. Analogously, mass 4 is observed in the CD_4–H_2 system. For

$$(D_2 + CH_4)^+ = D_2H^+ + CH_3 \quad k_{16} \quad (16)$$
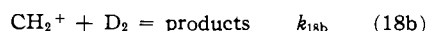$$(H_2 + CD_4)^+ = H_2D^+ + CD_3 \quad k_{17} \quad (17)$$
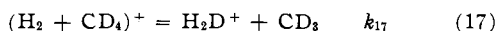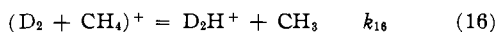
we obtained values of 2.4 $\times$ 10^{-11} cc./molecule-sec. for k_{16} and 3.8 $\times$ 10^{-11} cc./molecule-sec. for k_{17} calculated on the assumption that the reactant is H_2^+ or D_2^+ even though there is some uncertainty as to whether the charged entity is hydrogen or methane.

To recapitulate the reactions of CH_3^+, H_2^+, and H_3^+ ions in methane–hydrogen systems we find: (1) Attack of hydrogen molecular ions produces methyl ions which, where D–H exchange can occur, will be extensively exchanged. (2) Extensive exchange reactions of methyl ions with hydrogen. The exchanged methyls account for most, if not all, of the exchanged ethyl ions, which are also observed. (3) H_3^+ (D_3^+) reacts with methane to give CH_5^+ (CH_4D^+). (4) H_2^+ (D_2^+) probably attacks methane to produce small amounts of H_3^+ (D_2H^+).

Reactions of CH_2^+, CH^+.—From plots of log (I_{14}/I_{16}) and log (I_{13}/I_{16}) as functions of H_2 pressure we obtained rate constants for the reactions

$$CH_2^+ + H_2 = CH_3^+ + H \quad k_{18a} \quad (18a)$$
$$CH^+ + H_2 = CH_2^+ + H \quad k_{19a} \quad (19a)$$
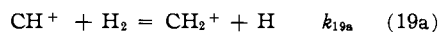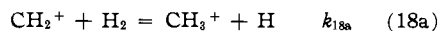
assuming that CH_2^+ is not formed appreciably from dissociative charge exchange. The CH_2^+ formed by reaction of CH^+ was small compared to the total CH_2^+ and would not materially alter the rate constants. We obtained values of 2.4, 2.3, and 2.3 $\times$ 10^{-10} cc./molecule-sec. for k_{18a} and 3.3, 8.5, and 5.8 $\times$ 10^{-10} cc./molecule-sec. for k_{19a} at CH_4 pressures of 97, 23, and 13 μ, respectively. For the reactions of CH_2^+ and CH^+ with D_2

$$CH_2^+ + D_2 = \text{products} \quad k_{18b} \quad (18b)$$
$$CH^+ + D_2 = \text{products} \quad k_{19b} \quad (19b)$$

we obtained values of 2.4 and 3.9 $\times$ 10^{-10} cc./molecule-sec. for k_{18b} and 4.5 and 5.2 $\times$ 10^{-10} cc./molecule-sec. for k_{19b}. (These values were obtained from plots of log (I_{14}/I_{12}) and log (I_{13}/I_{12}) as functions of D_2 pressure since mass 16 includes CH_4^+, CH_2D^+, and CD_2^+.) From the variation of log (I_{14}/I_{20}) as a function of hydrogen pressure in CD_4–H_2 mixtures we obtained values of 2.7 and 4.4 $\times$ 10^{-10} cc./molecule-sec. for the rate constant for the reaction of CD^+ with H_2.
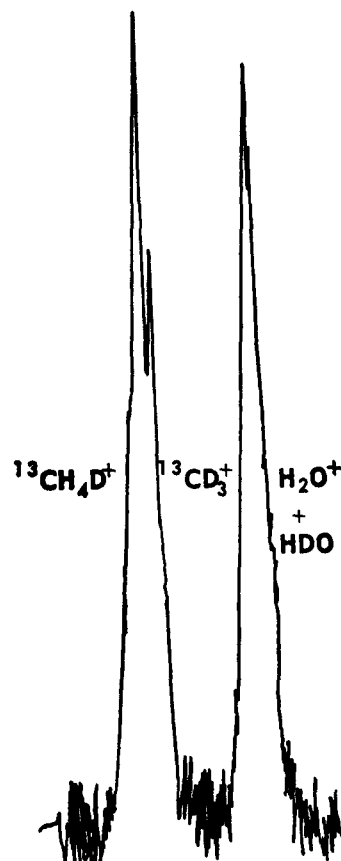

Fig. 5.—Mass 19 under high resolution; $P(CH_4) \cong 45 \mu$, $P(D_2) \cong 135 \mu$.

Discussion

Table I lists rate constants for the reactions in the "methane–hydrogen" systems. These are not precise enough to allow us to say anything about an isotope effect except that no gross effect exists. Nor

Table I

Ionic Reactions in "Methane–Hydrogen" Systems

Reaction	k, cc./molecule-sec.
$CH_4^+ + D_2 \rightarrow CH_4D^+$	2.5×10^{-12}
$CH_4^+ + H_2 \rightarrow CH_5^+$	0–7×10^{-12}
$CH_4^+ + D_2 \rightarrow CH_3D_2^+$	$\leqslant 1 \times 10^{-13}$
$CH_4^+ + D_2 \rightarrow CH_3D^+$	9.5×10^{-12}
$CH_3^+ + D_2 \rightarrow \begin{cases} CH_2D^+ \\ CHD_2^+ \end{cases}$	1.7×10^{-10}
$CD_3^+ + H_2 \rightarrow \begin{cases} CD_2H^+ \\ CH_2D^+ \end{cases}$	1.6×10^{-10}
$CH_2^+ + H_2 \rightarrow CH_3^+$	2.3×10^{-10}
$CH_2^+ + D_2 \rightarrow$	3.1×10^{-10}
$CH^+ + H_2 \rightarrow CH_2^+$	5.8×10^{-10}
$CH^+ + D_2 \rightarrow$	4.9×10^{-10}
$CD^+ + H_2 \rightarrow$	3.5×10^{-10}
$H_2^+ + CD_4 \rightarrow H_2D^+$	3.8×10^{-11} (?)
$D_2^+ + CH_4 \rightarrow D_2H^+$	2.4×10^{-11} (?)

do the reactions of CH^+ and CD^+ appear to be sufficiently faster when exchange can occur than when it cannot to warrant any statement concerning atom-exchange reactions of these ions. (The amount of CH^+

produced in the CD_4–H_2 experiments is less than a third of the decrease in CD^+.)

The rate constants for reaction of CH_3^+, CH_2^+, and CH^+ with D_2 are about one-fourth of the rate constants for the reaction of these ions with CH_4.[4] If the rate constants are proportional to $(\alpha/\mu)^{1/2}$, the polarizability of the molecule divided by the reduced mass of the complex,[11] then the rate constant for the reaction of CH_2^+ with H_2 would be equal to the rate constant for CH_2^+ with CH_4. (The differences in reduced mass balance the differences in polarizability.) The observed ratio of rate constants is very different from this calculated value and is actually about the same as the ratio of the polarizabilities of H_2 and CH_4.

Pratt and Wolfgang[2a] in their paper suggest exchange between CH_5^+ and T_2 to give CH_4T^+ followed by proton exchange with CH_4 to give the neutral CH_3T. Accord-

(11) H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

ing to our data this exchange reaction of CH_5^+ with D_2 does not occur or if it does occur its rate constant must be less than 10^{-12} cc./molecule-sec. Similarly, direct reaction between CH_4^+ and D_2 to give CH_4D^+ was observed to have a very small cross section, similar to the direct atom-exchange reaction. Some CH_4T^+ could presumably be formed by the reaction of T_3^+ with CH_4 which we observed between D_3^+ and H_3^+ and CH_4, but we found that very rapid exchange occurs in CH_3^+ and its product $C_2H_5^+$ as did Wexler[2b] (Wexler did not observe the disappearance of CH_3^+ and formation of CH_2D^+ from the reaction of CH_3^+ with D_2 as we report; he merely observed the presence of the substituted ethyl ions.) It seems reasonable to us that the exchange should proceed through the methyl and ethyl ions and their neutralization products.

The Monte Carlo Integration of Rate Equations[1]

BY L. J. SCHAAD

The difficult problem of analytic integration of rate equations can be circumvented by constructing a digital computer model of the reacting system. Concentration–time curves, accurate to 1 or 2%, are obtained directly from the model for all components of the system.

Introduction

One often accepts or rejects a proposed reaction mechanism by comparing experimental concentration–time data with those predicted by that proposed mechanism. It is easy enough to write down differential equations governing the model mechanism, but unfortunately their integration to give the desired concentration–time curves is usually difficult. In even the relatively simple case

$$A \xrightarrow{k_1} B+C \xrightarrow{k_2} D \qquad (1)$$
$$A \xrightarrow{k_3} D$$
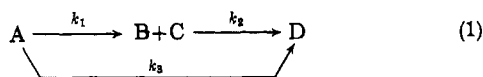
Pearson, King, and Langer[2] have shown that integration of the rate equations

$$d[A]/dt = -k_1[A] - k_3[A]$$
$$d[B]/dt = d[C]/dt = k_1[A] - k_2[B][C] \qquad (2)$$
$$d[D]/dt = k_3[A] + k_2[B][C]$$

gives

$$[B] = [A]_0 \frac{k_1}{k_1 + k_3} (\tau/K)^{1/2} \frac{iJ_1(2i\sqrt{\tau K}) - \beta H_1{}^1(2i\sqrt{\tau K})}{J_0(2i\sqrt{\tau K}) + i\beta H_0{}^1(2i\sqrt{\tau K})} \qquad (3)$$

where

$$\tau = e^{-(k_1 + k_3)t}, \quad K = k_1 k_2 [A]_0/(k_1 + k_3)^2,$$
$$\beta = iJ_1(2i\sqrt{K})/H_1{}^1(2i\sqrt{K})$$

and J's and H's are Bessel functions. For mechanisms even slightly more complex, integration in closed analytical form is impossible.

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., November, 1962.

(2) R. G. Pearson, L. C. King, and S. H. Langer, *J. Am. Chem. Soc.*, **73**, 4149 (1951).

A method is therefore presented here which avoids this integration. A digital computer is used to set up a statistical (*i.e.*, Monte Carlo[3]) model of the reacting system from which concentration–time curves are obtained directly. This is described first in general to show the scope of the method and then in detail for mechanism 1.

Monte Carlo Integration of a First-Order Rate Equation.—Consider, to take an example, the uncatalyzed thermal decomposition of H_2O_2. Here the first-order rate equation

$$d[H_2O_2]/dt = k[H_2O_2]$$

can easily be integrated to give

$$\log [H_2O_2] = (a\ constant) - kt$$

To construct a Monte Carlo model of this reaction, a portion of computer storage is set aside to represent the reaction flask, and an H_2O_2 molecule is represented in the computer by the digit 1. Decomposition is indicated by replacing these 1's by 0's. To start the reaction, the flask is filled with H_2O_2 by loading 1's into the computer storage. Suppose there are 1000 1's in storage at the start of the reaction. Each is in a particular location and hence each can be distinguished as the 0th, 1st, . . . 999th molecule. The remaining part of storage is used to generate a random number between 0 and 999. If the number 215 (say) is generated, the 215th H_2O_2 molecule is reacted by replacing the 1 representing it by a 0. Another random number is generated and the reaction continued. If 215 is generated again, a 0 will be replaced by another 0 giving in effect no reaction. This is repeated some specified number of times; then H_2O_2 is "titrated" by counting the number of 1's remaining

(3) A. S. Householder, G. E. Forsythe, and H. H. Germond, "Monte Carlo Method," National Bureau of Standards, Applied Mathematics Series 12 (1951).