[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL & REFINING COMPANY]

Reaction of Gaseous Ions. VII. Methane–Hydrogen and the Proton Affinities of Methane and Ethane

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Upper limits to the cross-sections of gaseous ion reactions between methane and hydrogen are assigned. Upper and lower limits for the proton affinities of methane and ethane are estimated from existing knowledge of ion–molecule reactions that have been observed.

In a previous communication concerning the formation of protonated methane,[1] we reported that we were unable to find any evidence of CD_4H^+ ion formation in ionized mixtures of tetradeuteromethane and hydrogen. Since the absence of reaction seemed so unusual and since recently Tal'roze and Frankevich[2,3] have reported contradictory results, we have made a more detailed investigation of the system, the results and conclusions of which we report in this paper.

Experimental

The experiments were carried out with methane–deuterium and tetradeuteromethane–hydrogen mixtures in a Consolidated Electrodynamics Corporation (CEC) Model 21-620 cycloidal focusing mass spectrometer and a Westinghouse Type LV mass spectrometer. The ionization chamber of the CEC instrument was calibrated for pressure using total ionization cross-sections for 75 v. electrons.[4] The ionization chamber of the LV instrument was calibrated for pressure using the previously measured cross-sections of the ion–molecule reactions producing $C_4H_7^+$ and $C_4H_8^+$ ions in ethylene.[5] In the case of the CEC spectrometer, the relationship between ionization chamber concentration in molecules-cm.$^{-3}$, $[N]$, and inlet reservoir pressure in mm., P_R, is

$$[N]_{CEC} = (73 + 2.8P_R) \times 10^{11}\, P_R \qquad (1)$$

while for the LV spectrometer the relationship with manifold pressure in mm., P_M, is

$$[N]_{LV} = (410 + 0.78P_M) \times 10^{8}\, P_M \qquad (2)$$

Pressures in both gas handling systems were measured with mercury manometers.

The pertinent ionization chamber conditions for the experiments carried out in the CEC were: electron current = 2.0 microamperes; ion repeller = 1.0 v. (corresponding to an electric field strength of 10 v./cm.); temperature = 150°. The corresponding experimental conditions in the LV were: electron current = 3.0 microamperes; ion repeller = 2.6 v. (corresponding to an electric field of 5.7 v./cm.); temperature = *ca.* 260°. The experimental techniques and procedures for the measurement of secondary ions have been described previously.[5]

Phillips Research Grade methane (minimum purity 99.58%) and tetradeuteromethane (minimum purity 95%) obtained from Tracerlab, Inc., were used as received. Hydrogen from the Matheson Company and deuterium from the Stuart Oxygen Company were used without further purification.

Results

Tetradeuteromethane–Hydrogen Mixtures.—In Fig. 1 we present the results of experiments carried out in the LV spectrometer in which the partial pressure of tetradeuteromethane, $P_M(CD_4)$, was held at about 40 mm. while the partial pressure of hydrogen was varied from zero to 420 mm. The open circles in Fig. 1 represent the ratio I_{21}/I_{20} as a function of the hydrogen partial pressure, $P_M(H_2)$. Superimposed on this plot are the results of a set of experiments in which the tetradeuteromethane pressure was varied from 50 to 400 mm. The triangles in Fig. 1 represent the ratio of I_{22} to I_{20} as a function of $P_M(CD_4)$. Since the ratio of the slopes of the lines is a measure of the relative amounts of bimolecular reaction occurring, it is apparent that the cross-sections of reactions producing CD_4H^+, namely

$$H_2^+ + CD_4 \longrightarrow CD_4H^+ + H \qquad (3)$$

$$CD_4^+ + H_2 \longrightarrow CD_4H^+ + H \qquad (4)$$

must be much smaller than the cross-section of

$$CD_4^+ + CD_4 \longrightarrow CD_5^+ + CD_3 \qquad (5)$$

Identical experiments in the CEC yielded completely equivalent results.

Methane–Deuterium Studies.—Studies identical to those just described were carried out with this system in both the CEC and LV mass spectrometers. In this system the product formed by an ionic reaction between methane and deuterium would be the CH_4D^+ ion having a mass of 18, and the necessary impurity and background corrections result in more scatter of I_{18}/I_{16} than was found with the I_{21}/I_{20} values in the tetradeuteromethane–hydrogen system. Nevertheless equivalent results were found.

Figure 2 shows the results of experiments with the CEC spectrometer in which the reservoir pressure of methane, $P_R(CH_4)$, was held essentially constant at about 1.2 mm. while $P_R(D_2)$ was varied from 1 to 18 mm. The open circles, representing I_{18}/I_{16} as a function of $[D_2]$, show no upward trend. On the other hand, I_{17}/I_{16} increases linearly with $[CH_4]$ in the same concentration range showing that the ionization chamber pressures are sufficiently high to observe easily ion–molecule reactions. Identical results on this system were obtained in the LV spectrometer.

One is thus forced to conclude that the cross-sections of the reactions

$$D_2^+ + CH_4 \longrightarrow CH_4D^+ + D \qquad (6)$$

$$CH_4^+ + D_2 \longrightarrow CH_4D^+ + D \qquad (7)$$

must be very small relative to the cross-section of

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (8)$$

In Table I the results on both systems obtained from both mass spectrometers are summarized.

As a matter of interest in this same general connection, we have been unable to find any evidence for the exothermic reaction

$$D_2^+ + CH_4 \longrightarrow D_2H^+ + CH_3 \qquad (9)$$

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

[2] V. L. Tal'roze and E. L. Frankevich, *ibid.*, **80**, 2344 (1958).

[3] E. L. Frankevich and V. L. Tal'roze, *Doklady Akad. Nauk SSSR*, **119**, 1174 (1958).

[4] F. W. Lampe, J. L. Franklin and F. H. Field, THIS JOURNAL, **79**, 6129 (1957).

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

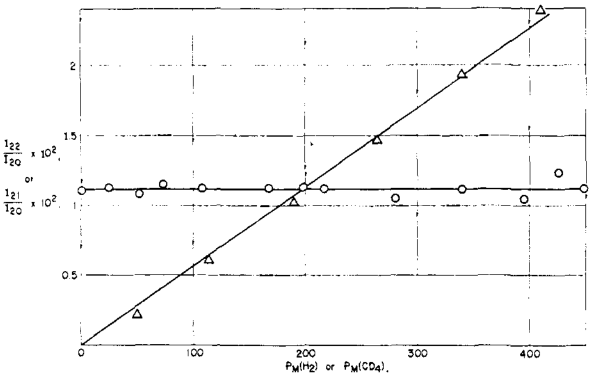

Fig. 1.—CD_4–H_2 system in LV mass spectrometer: O, $I_{21}/I_{20} \times 10^2$; Δ, $I_{22}/I_{20} \times 10^2$.

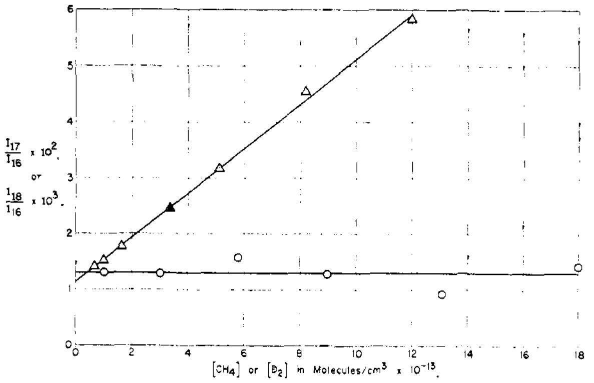

Fig. 2.—CH_4-D_2 system in CEC mass spectrometer: O, $I_{18}/I_{16} \times 10^3$; Δ, $I_{17}/I_{16} \times 10^2$.

TABLE I

ABSENCE OF PROTONATED METHANE FORMATION IN METHANE–HYDROGEN MIXTURES

Mass spectrometer	System	Pressure range (mm.) "Methane"	Pressure range (mm.) "Hydrogen"	$\frac{I_{18}}{I_{16}} \times 10^3$	$\frac{I_{21}}{I_{20}} \times 10^2$
CEC	CD_4–H_2	1.5–2.5	0–8.5	....	0.898 ± 0.005
LV	CD_4–H_2	40 ± 10	0–420	....	1.12 ± 0.03
CEC	CH_4–D_2	1.2 ± 0.2	0–16.7	1.30 ± 0.13	....
LV	CH_4–D_2	40 ± 10	0–310	0.92 ± 0.16	....

over pressure ranges in which the reaction

$$D_2^+ + D_2 \longrightarrow D_3^+ + D \qquad (10)$$

and (8) are easily detectable.

Discussion

Reaction Cross-sections.—It is apparent from Figs. 1 and 2 that ionic reactions between "methane" and "hydrogen" to produce the isotopic analogs of CH_5^+ are not occurring to an extent that is within our experimental sensitivity to detect. Moreover, this absence of detectable reaction exists over a pressure range in which we can readily observe the CH_5^+ ion formation from methane alone. Such an apparent absence does not, however, permit us to say that the reactions do not occur. The failure to observe a given reaction permits one only to assign an upper limit to its cross-section.

Let us assume that, in the CD_4–H_2 system, CD_4H^+ can be formed by (3) and (4) while, in the CH_4–D_2 system, CH_4D^+ can be formed by (6) and (7). Then it can be shown easily that in these systems, respectively

$$\Delta\left(\frac{I_{21}}{I_{20}}\right) = \left(\sigma_4 + \frac{f_{H_2}Q_{H_2}}{f_{CD_4}Q_{CD_4}}\,\sigma_3\right)[H_2]d \qquad (11)$$

and

$$\Delta\left(\frac{I_{18}}{I_{16}}\right) = \left(\sigma_7 + \frac{f_{D_2}Q_{D_2}}{f_{CH_4}Q_{CH_4}}\,\sigma_6\right)[D_2]d \qquad (12)$$

where σ is the reaction cross-section, d is the distance from the center of the electron beam to the ion exit slit, Q is the total ionization cross-section, f_{H_2} is the fraction of ions of mass 2 in the primary mass spectrum of hydrogen and the other f's have analogous definitions. Taking values of f from the API Tables of Mass Spectra and of Q from our recent tabulation,[4] $f_{H_2}Q_{H_2}/f_{CD_4}Q_{CD_4}$ has the value 0.53 while $f_{D_2}Q_{D_2}/f_{CH_4}Q_{CH_4}$ is 0.56.

Making the reasonable assumption that we could detect a systematic increase in the ion–current ratio over the pressure range studied that exceeded twice the indicated uncertainties (Table I), and taking d to be 5×10^{-2} cm. in the CEC and 0.23 cm. in the LV, we are led to these upper limits for reaction cross-sections

$$(\sigma_4 + 0.53\sigma_3) < 2 \times 10^{-17}\ \text{cm.}^2$$
$$(\sigma_7 + 0.56\sigma_6) < 2 \times 10^{-17}\ \text{cm.}^2$$

Since we obtain the same result for both the CH_4–D_2 and the CD_4–H_2 systems, it is reasonable to conclude that the cross-sections of the completely protium analogs of (3), (4), (6) and (7) are also less than 2×10^{-17} cm.^{2}.

Proton Affinities of Methane and Ethane.—At the ionization chamber pressures generally obtaining in studies of ion–molecule reactions, any activation energy in excess of 1 or 2 kcal./mole would so decrease the chance of occurrence of a reactive collision that a corresponding reaction would not be observable. Thus the detection of an ion–molecule reaction permits one to conclude (within an uncertainty of 1 or 2 kcal./mole) that its heat of reaction is equal to or less than zero. Further, if the heats of formation of the reactants and neutral product(s) are known, the upper limit of the heat of formation of the ionic product can be calculated.

Contrary to one point of view,[2] however, this requirement of thermoneutrality or exothermicity is a necessary but not a sufficient condition for the observation of a given reaction. Thus the failure to detect a given reaction does not permit one to conclude without qualification that the reaction is endothermic. There may be other factors involved which result in failure to observe a reaction. One possibility is the occurrence of a more probable competitive reaction. An example of this is provided by the finding of Meisels, Hamill and Williams[6] that A^+ undergoes a dissociative charge transfer reaction with methane rather than the hydrogen atom abstraction which would be energetically equivalent to the established formation of AH^+ in argon–hydrogen mixtures.[7] Another possibility, which may account for the failure[2,3] to observe $C_2H_7^+$ and $C_3H_9^+$ ions in ethane–hydrogen

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[6] G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *J. Chem. Phys.*, **25**, 790 (1956).

[7] D. P. Stevenson and D. O. Schissler, *ibid.*, **23**, 1353 (1955).

and propane–hydrogen mixtures, respectively, is that of the very rapid further decomposition of a highly energetic product ion formed in a very exothermic reaction. An extreme example of this alternative is the complete failure so far to detect the dimer ion of the reactants.[1–3,5–8]

From all the reactions we have observed[1] that produce CH_5^+ (or its deuterated analog) we calculate $\Delta H_f(CH_5^+) \leq 234$ kcal./mole. Reactions 3 and 6 cannot, of course, be endothermic for this would mean that $\Delta H_f(CH_5^+) > 286$ kcal./mole which is an obvious inconsistency. Though we do not observe (4) and (7), we do not think it is because of energetic limitations, and furthermore Tal'roze and Frankevich[3] report evidence that (3), (4), (6), (7) do occur. However, neither we[8] nor others[3] have been able to detect the reaction

$$CH_4^+ + H_2O \longrightarrow CH_5^+ + OH \qquad (13)$$

which, if due to energetic limitations, permits the assignment of $\Delta H_f(CH_5^+) > 218$ kcal./mole. Expressing these energetic limits as proton affinities, *P*, we thus have

$$113 \text{ kcal./mole} < P(CH_4) < 129 \text{ kcal./mole}$$

in agreement with Tal'roze and Frankevich.[2,3]

For the reasons discussed above we do not believe that the failure to detect $C_2H_7^+$ ion in ethane–hydrogen mixtures permits the assignment of $P(C_2H_6) < 61$ kcal./mole.[2,3] Furthermore it seems unreasonably low when compared with the range found for methane. A more reasonable estimate can be made from the energetics of a well-established reaction occurring in methane,[5,9] namely

$$CH_3^+ + CH_4 \longrightarrow [C_2H_7^+] \longrightarrow C_2H_5^+ + H_2 \quad (14)$$

The reaction must proceed through the $C_2H_7^+$ ion and so it must have at least a transitory existence. Moreover, for the reaction to be observable $\Delta H_f(C_2H_7^+)$ must be less than $\Sigma\Delta H_f$(reactants) but greater than $\Sigma\Delta H_f$(products). Hence,[10] 224 kcal./mole $< \Delta H_f(C_2H_7^+) <$ 244 kcal./mole which expressed as limits for the proton affinity of ethane is

$$101 \text{ kcal./mole} < P(C_2H_6) < 121 \text{ kcal./mole}$$

It is of interest that a value of $\Delta H_f(C_2H_7) > 224$ enables one to answer the question as to why a reaction analogous to (8) and (10) does not occur in ethane. For the reaction

$$C_2H_6^+ + C_2H_6 \longrightarrow C_2H_7^+ + C_2H_5 \qquad (15)$$

$\Delta H > 20$ kcal./mole, and thus has an activation energy that surely precludes its observation. Moreover, the reaction

$$H_2^+ + C_2H_6 \longrightarrow C_2H_5^+ + H_2 + H \qquad (16)$$

for which $\Delta H < 60$ kcal./mole may be the reason for the failure to detect the $C_2H_7^+$ ion.[2,3] The heat of reaction of

$$H_2^+ + CH_4 \longrightarrow CH_3^+ + H_2 + H \qquad (17)$$

is $\Delta H < 24$ so that (17) may be responsible for our inability to detect (3), (4), (6) and (7). Although we did not observe an increase in CH_3^+ with hydrogen pressure, this might well be due to our sensitivity limitations in detecting small differences between relatively large numbers.

Acknowledgment.—We wish to thank Mr. B. L. Clark for his assistance with the experimental work reported in this paper.

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[8] F. W. Lampe, F. H. Field and J. L. Franklin, THIS JOURNAL, **79**, 6132 (1957).

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

[10] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. VIII.[2] X-Ray Diffraction and Polarographic Study of *t*-Butyl Peresters and Diacyl Peroxides of Aliphatic Monobasic Acids[3]

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Alternating series are obtained from long spacing and melting point data for the even and odd acyl chain members of diacyl peroxides and *t*-butyl peresters. The even membered diacyl peroxides have lower long spacing and higher melting point curves than the odd members. The even acyl chain membered *t*-butyl peresters have higher long spacing and melting point curves than the odd members. Long spacings have been redetermined for several acid anhydrides and reported for the first time for several *t*-butyl esters. Peroxide bond skew is revealed as a foreshortening of chain length. An exact computation of the O–O bond length in diacyl peroxides by a series comparison of the crystal data cannot be made because of uncertainties involving end packing and the degree to which the peroxide oxygen atoms are shielded as a result of skew by the attached carbonyl carbon atoms although a projected O–O group distance of 1.44 Å. has been derived. Half-wave potentials of −0.82 to −0.96 volt *vs.* S.C.E. for *t*-butyl peresters and −0.08 to −0.12 volt *vs.* S.C.E. for diacyl peroxides also have been obtained. Half-wave potentials for *t*-butyl peresters and diffusion current constants for diacyl peroxides decrease with chain ascension. The relations $i_d M^{1/2}$ = const. and $i_d M^{2/3}$ = const. are proposed to account equally well for the change of diffusion current constant with chain size in the diacyl peroxides. An order of decreasing bond strengths in peroxides based on half-wave potentials is di-*t*-butyl peroxide > *t*-butyl perester ≥ hydroperoxide > diacyl peroxide > peracid.

The availability of pure homologous diacyl peroxides and *t*-butyl peresters of long chain aliphatic monobasic acids, the preparation of which is described in a previous paper,[2] permitted a determination and study of their X-ray diffraction spectra (Tables I, II and III) and polarographic characteristics (Table IV). The results of these investigations are reported in this paper. Several acid an-

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[1] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Paper VII, *Anal. Chem.*, **30**, 385 (1958). Paper VI, THIS JOURNAL, **81**, 2364 (1959).

[3] Presented at the Fall Meeting of the American Chemical Society, Chicago, Illinois, September 7–12, 1958.

[4] Deceased.