Börnstein,[5] and we find that a linear relationship exists between these quantities, as is shown in Fig. 2. This relationship can be rationalized theoreti-
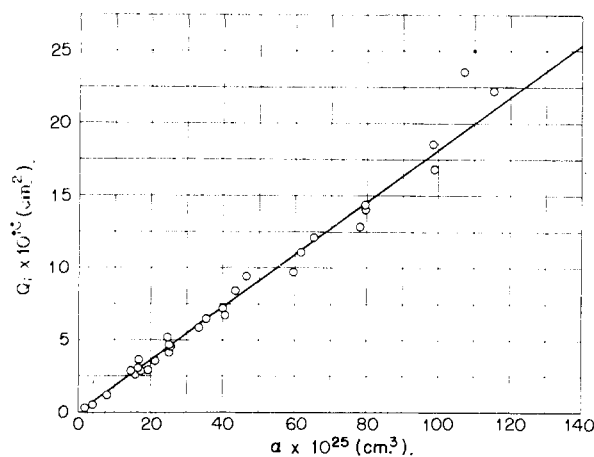

Fig. 2.—Total ionization cross section vs. polarizability.

cally as follows. From Slater[6] we write for the static polarizability of an atom

$$\alpha = \frac{2}{h} \sum_a \frac{|M_{ao}|^2}{\nu_{ao}^8} \tag{1}$$

where $|M_{ao}|$ is the aoth element of the dipole moment matrix and ν_{ao} is the frequency corre-

(5) Landolt-Börnstein. "Zahlenwerte und Functionen." 6 Auflage, "Atom und Molecularphysik," 3 Teil. Springer–Verlag. Berlin. 1950, pp. 510–517.

(6) J. C. Slater. "Quantum Theory of Matter." McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 388–396.

sponding to the transition between the states o (ground state) and a. An approximate expression for atomic ionization cross sections is[7]

$$Q^i_{nl} = \frac{2\pi e^4}{mv^2} \frac{c_{nl}}{|E_{nl}|} Z_{nl} \log \left(\frac{2mv^2}{C_{nl}} \right) \tag{2a}$$

$$c_{nl} = (Z^2_{eff}/n^2 a_6^2) \int |X_{nl.K}|^2 dK \tag{2b}$$

where the integration in equation 2b is carried out over the appropriate portion of the ionization continuum. The matrix element $|X_{nl.K}|$ will be proportional to the corresponding dipole moment matrix element $|M_{nl.K}|$, and to the extent that the variation in $\Sigma_a(M_{ao}^2/\nu_{ao})$ parallels that in $c_{nl}/|E_{nl}|$ in going from one atom to another, a linear relationship between polarizability and cross section should be observed. We expect that analogous expressions apply to molecules.

The empirical equation for the line in Fig. 2 is $Q_i = (1.80 \times 10^8)\alpha$ where Q_i is in cm.[2] and α in cm.[3]. The average deviation of the experimental cross sections plotted in Fig. 2 (30 compounds) from those calculated from the above equation is 8%. Thus this equation offers a means of estimating the cross section of a substance if its polarizability is known. Unlike the situation with the additivity concept, our data indicate that no restriction of similarity of compound type need be placed on this correlation.

Acknowledgment.—We wish to express our appreciation to Mr. B. L. Clark for carrying out the experimental work reported in this paper.

(7) N. F. Mott and H. S. W. Massey. "The Theory of Atomic Collisions." Oxford University Press. London. 1949. p. 247.

BAYTOWN, TEXAS

Reactions of Gaseous Ions. IV. Water

BY F. W. LAMPE, F. H. FIELD AND J. L. FRANKLIN

The gas phase reactions of H_2O and D_2O with H_2O, D_2O, CH_4 and H_2 have been investigated and the specific reaction rates and cross sections measured. Relative cross sections of the reactions of D_2O with C_2H_6, C_3H_8, cyclo-C_3H_6, and n-C_4H_{10} have been measured. The ionic reactants in the ethane and propane systems are $C_2H_6^+$ and $C_3H_8^+$, respectively; water ion is the ionic reactant in all other systems (ionic reactant in the methane systems not known). The reaction cross sections are compared with those predicted from the polarizability theory of ion–molecule reactions, and it is concluded that the theory does not account satisfactorily for the values observed. The significance of the experimental results to the radiation chemistry of water is discussed.

Introduction

As a continuation of investigations[1,2] into the reactions of gaseous ions, we report in this paper the results of detailed studies of ionic reactions of water with water, hydrogen and methane. Also, we present the results of briefer studies of the reactions and relative rates involved in the formation of gaseous hydronium ion from water and water, hydrogen, methane, ethane, propane, cyclopropane and n-butane.

The possibility that the formation of H_3O^+ in the ionization chamber of a mass spectrometer was due

(1) F. H. Field. J. L. Franklin and F. W. Lampe, THIS JOURNAL, 79, 2419 (1957).

(2) F. H. Field. J. L. Franklin and F. W. Lampe. ibid., 79, 2665 (1957).

to a secondary process was first recognized by Mann, Hustrulid and Tate.[3] Tal'roze and Lyubimova[4] reported the H_3O^+ ion to be formed by the reaction between the water molecule-ion and water and methane, but they presented no quantitative results such as specific reaction rates or reaction cross sections. In recent work directed toward obtaining the proton affinity of water, Tal'roze and Frankevich[5] have studied the formation of H_3O^+ in water and in mixtures of water and NH_3, H_2S, C_2H_2 and C_3H_8. No rate data are given.

(3) M. M. Mann, A. Hustrulid and J. T. Tate, Phys. Rev., 58, 340 (1940).

(4) V. L. Tal'roze and A. K. Lyubimova, Doklady Akad. Nauk S.S.S.R., 86, 909 (1952).

(5) V. L. Tal'roze and E. L. Frankevich, ibid., 111, 376 (1956).

Experimental

While the experimental methods employed in the detailed studies have been described previously,[1] additional precautions were necessary for the work with mixtures. In order to obtain reproducible and meaningful concentrations of the components of the mixture in the ionization chamber, we found it necessary to allow at least 30 minutes for mixing after the gases were introduced into the reservoir. This mixing time was arrived at by determining the minimum time of mixing required for the components of the mixture at given partial pressures to show characteristic peak heights equal to the peak heights for the pure compounds at total pressures equal to the given partial pressures.

In the studies of the relative rates of formation of hydronium ion, mixtures of D_2O and RH were prepared in convenient proportions in the mass spectrometer and the intensities of the D_2O^+ and HD_2O^+ ions measured. To provide a basis of comparison, the intensities of the D_3O^+ and D_2O^+ ions formed in D_2O were determined. The ionization chamber field strength was maintained at 10 v./cm.

In the study of reaction rates a Consolidated Electrodynamics Corporation (CEC) model 21-620 cycloidal focusing mass spectrometer was used. In the calibration of the ionization chamber for pressure, ionization cross sections[6] recently determined were used. Appearance potentials were measured with a Westinghouse type LV mass spectrometer.

The water used in these experiments was ordinary distilled water. The deuterium oxide was obtained from the Stuart Oxygen Co. and had a stated purity of 99.5%. The hydrocarbons were Phillips Research Grade, all having stated purities in excess of 99.5%. The hydrogen was obtained from the Matheson Co. and was used without further purification.

Results and Discussion

The reactions observed and the specific reaction rates and cross sections measured in the systems H_2O, D_2O, H_2O-CH_4, D_2O-CH_4, and D_2O-H_2 are shown in Table I.

TABLE I

GASEOUS ION REACTIONS IN WATER SYSTEMS

| Reaction	$\left(\dfrac{dV}{dx}\right)$ volts cm.	$f\sigma \times 10^{14}$ cm.²	$k \times 10^9$ cm.³/ mole- cules- sec.
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	10	0.95	1.26
$(H_2O + CH_4)^+ \rightarrow H_3O^+ + CH_3$	10	1.80	2.46
$D_2O^+ + D_2O \rightarrow D_3O^+ + OD$	10	1.02	1.19
$(D_2O + CH_4)^+ \rightarrow HD_2O^+ + CH_3$	10	1.48	1.99
$D_2O^+ + H_2 \rightarrow HD_2O^+ + H$	10	0.63	0.643
$D_2O^+ + D_2O \rightarrow D_3O^+ + OD$	0	2.46	2.19
$(D_2O + CH_4)^+ \rightarrow HD_2O^+ + CH_3$	0	3.55	3.36
$D_2O^+ + H_2 \rightarrow HD_2O^+ + H$	0	1.39	3.05

The various reactions occurring were deduced primarily from appearance potential measurements. The appearance potential of the H_3O^+ ion in water was found to be 12.5 v., which is in sufficiently good agreement with the electron-impact ionization potential of water (12.67 v.) to provide conclusive evidence that the reactant ion is H_2O^+. Identical findings are reported by Tal'roze and Frankevich.[5] Similarly, the D_2O^+ ion is involved in the formation of the HD_2O^+ ion in the D_2O-H_2 system, since the appearance potential of the HD_2O^+ ion was found to be 13.0 v., which is to be compared with the ionization potential of 12.9 v. found in our instrument for D_2O. Unfortunately, the ionization potentials of water and methane are so close (within about 0.5 v.) that appearance potentials cannot be used to establish the ionic reactant in the

(6) F. W. Lampe, J. L. Franklin and F. H. Field, THIS JOURNAL, 79, 6129 (1957).

water–methane system. The kinetic results given in Table I for this system are calculated assuming that the water ion reacts, but as will be shown below, not greatly differing results are obtained if it be assumed that methane ion reacts.

The specific reaction rates at 10 v./cm. listed in Table I were obtained from experiments in which the ion source concentrations were varied. In the H_2O-CH_4 system the H_3O^+ ion can be formed by the two reactions (taking water as the ionic reactant)

$$CH_4 + H_2O^+ \longrightarrow H_3O^+ + CH_3 \qquad (1)$$
$$H_2O + H_2O^+ \longrightarrow H_3O^+ + OH \qquad (2)$$
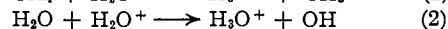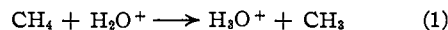
and the calculational formalism previously described[1] must be modified slightly. For these reactions we write

$$k_1(H_2O^+)(CH_4)\tau_{H_3O^+} + k_2(H_2O^+)(H_2O)\tau_{H_3O^+} = (H_3O^+) \qquad (3)$$

and

$$\frac{I_{H_3O^+}}{I_{H_2O^+} + I_{H_3O^+}} \frac{1}{(CH_4)} = k_1\tau_{H_2O^+} + \frac{(H_2O)}{(CH_4)} k_2\tau_{H_2O^+} \qquad (4)$$

It is seen that the slope of the plot (Fig. 1) of the left-hand-side of (4) vs. $(H_2O)/(CH_4)$ contains the rate constant for the water–water reaction and the
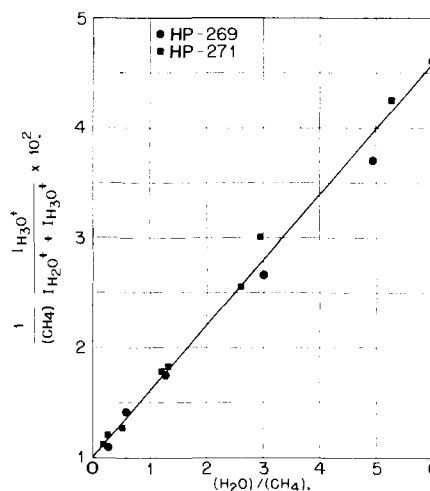

Fig. 1.—Formation of H_3O^+ in methane–water mixtures at 10 volts/cm. field strength.

intercept contains the rate constant for the methane–water reaction. It is of interest that the water–water rate constant obtained from the slope agrees satisfactorily with the value obtained from concentration studies on pure water. Obviously, the form of the plot can be inverted, that is, $\dfrac{I_{H_3O^+}}{I_{H_2O^+} + I_{H_3O^+}} \dfrac{1}{(H_2O)}$ can be plotted against $\dfrac{(CH_4)}{(H_2O)}$. It is found that rate constants obtained from the intercept using one method of plotting are in satisfactory agreement with rate constants obtained from the slope using the inverted method of plotting.

In the D_2O-CH_4 and the D_2O-H_2 systems the products of the homogeneous $(D_2O^+ + D_2O)$ and cross $(D_2O^+ + CH_4$ or $H_2)$ reactions are distinguishable, and the usual calculation can be used. A typical plot of $I_{HD_2O^+}/(I_{HD_2O^+} + I_{D_3O^+} + $

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TABLE II

I	II	III	IV	V	VI
			—Relative cross section—		
			For $D_2O^+ +$ $RH \rightarrow$ $HD_2O^+ + R$	For $RH^+ +$ $D_2O \rightarrow$ $HD_2O^+ + R$	Relative
Reaction	$A(HD_2O^+)$	I(Reactant)ᵃ	$HD_2O^+ + R$	$HD_2O^+ + R$	$\alpha^{1/2}$
$D_2O + D_2O^+ \rightarrow D_3O^+ + OD^b$	..	....	1.00		1.00
$H_2 + D_2O^+ \rightarrow HD_2O^+ + H$	12.9	$I(H_2) = 15.44$	0.57		0.74
$(CH_4 + D_2O)^+ \rightarrow HD_2O^+ + CH_3$	..	....	1.4	1.5	1.3
$C_2H_6^+ + D_2O \rightarrow HD_2O^+ + C_2H_5$	11.9 ± 0.1	$I(C_2H_6) = 11.65$	2.0	4.5	1.7
$C_4H_8^+ + D_2O \rightarrow HD_2O^+ + C_4H_7$	$11.5 \pm .1$	$I(C_4H_8) = 11.21$	2.0	4.5	2.1
Cyclo $C_4H_6 + D_2O^+ \rightarrow HD_2O^+ + C_4H_6$	$12.2 \pm .5$	$I(cycloC_4H_6) = 10.23$	0.39	0.34	2.0
$n\text{-}C_4H_{10} + D_2O^+ \rightarrow HD_2O^+ + C_4H_9$	$13.1 \pm .6$	$I(n\text{-}C_4H_{10}) = 10.8$	0.94	3.9	2.4

ᵃ Taken from Field and Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957. ᵇ Assumed by analogy with the known reaction $H_2O + H_2O^+ \rightarrow H_3O^+ + OH$.

$I_{D_2O^+})$ vs. the H_2 concentration is given in Fig. 2. Here also values of the homogeneous rate constant obtained from the mixture studies agree very well with the value for the $D_2O^+ + D_2O$ reaction obtained from studies on pure D_2O. This agreement leads us to think that our values for the cross reactions are correct.
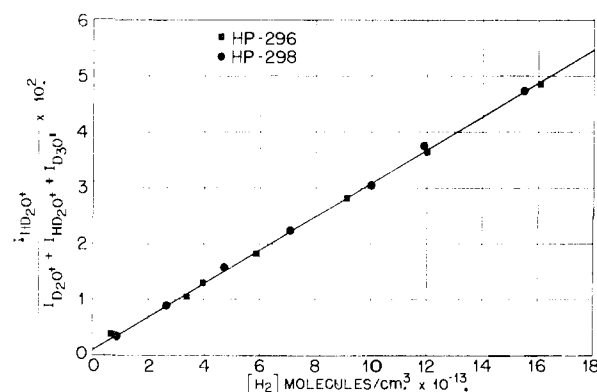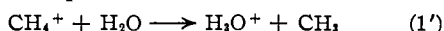

Fig. 2.—Formation of HD_2O^+ in D_2O-H_2 mixtures at 10 volts/cm. field strength.

If in the methane–water system CH_4^+ is the ionic reactant, eq. 1 becomes

$$CH_4^+ + H_2O \longrightarrow H_3O^+ + CH_3 \qquad (1')$$

and eq. 4 becomes

$$\frac{I_{H_3O^+}}{I_{H_3O^+} + I_{H_2O^+}} \frac{1}{(CH_4)} = \frac{k_1'b}{a} \tau_{CH_4^+} + k_2 \frac{(H_2O)}{(CH_4)} \tau_{H_2O^+} \qquad (4')$$

where $a = (H_2O^+)/(H_2O)$, $b = (CH_4^+)/(CH_4)$, and $b/a = Q_i(CH_4)p_{CH_4^+}/Q_i(H_2O)p_{H_2O^+}$ ($Q_i =$ ionization cross section, $p =$ fraction of parent ion in mass spectrum). From the ionization cross-sections[6] and mass spectra of methane and water, we calculate that $b/a = 0.94$. Also, $\tau_{CH_4^+} = \sqrt{16/18}\tau_{H_2O^+} = 0.94\tau_{H_2O}$. Thus, if in actuality CH_4^+ is the reactant the rate values for this system given in Table I are 12% low.

The reaction cross sections at zero field strength given in Table I have been obtained by extrapolation of the experimental cross sections measured at field strengths between 2 and 100 volts/cm. In previous work[1,2] we found that the variation of the reaction cross section is well described by the expression

$$f\sigma = \frac{1}{2} \left(\frac{m_1(m_1 + m_2)}{m_2} \right)^{1/2} \frac{\theta e \pi \alpha^{1/2}}{(3kT + eVd_0/3)} \qquad (5)$$

where θ is an arbitrary constant, d_0 is the distance from the electron beam to the ion-exit slit, α is the polarizability and V is the voltage gradient. The arbitrary constant θ is best determined from a plot of the experimental values of $f\sigma$ against $1/(3kT + eVd_0/3)$, and a plot of typical results found in the present work is given in Fig. 3. The good
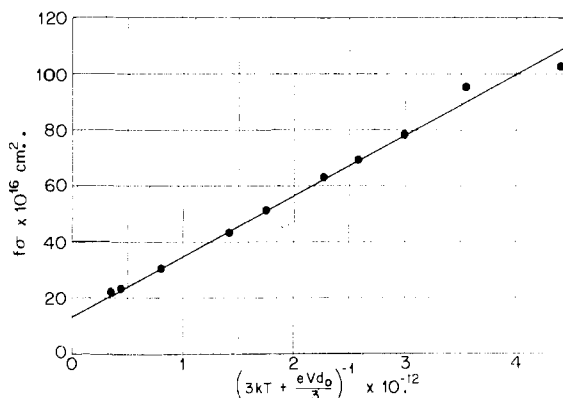

Fig. 3.—Reaction cross section for formation of HD_2O^+ in D_2O-H_2 mixtures as a function of field strength.

linearity observed is in accordance with eq. 5, but the plot does not pass through the origin as required by eq. 5. For the systems here considered eq. 5 must be replaced by

$$f\sigma = (f\sigma)_v + (f\sigma)_\infty \qquad (5')$$

where $(f\sigma)_v$ represents the right side of eq. 5 and $(f\sigma)_\infty$ is the limiting reaction cross section at infinite field strength. The reaction cross sections at zero field strength given in Table I are obtained from eq. 5' taking the arbitrary constants from plots such as that of Fig. 3. We do not understand why the previously studied reactions do not have a limiting reaction cross section at high field strengths, while those reported here do. We think that the behavior observed here is more to be expected. As we have come to expect of gaseous ionic reactions, the rates given in Table I are exceedingly large.

The results of the study of the relative rates of formation of the hydronium ion by the reaction of water with several hydrogen-containing substances are given in Table II. The reactions listed in column I are deduced from a comparison of the measured appearance potentials listed in column II with the ionization potentials listed in column III and with our measured value $I(D_2O) = 12.9$ v.

The uncertainties given in column II are average deviations from average of replicate measurements. From a similar comparison of appearance potentials, Tal'roze and Frankevich[5] postulate that $C_3H_8^+$ is the ionic reactant in the $H_2O-C_3H_8$ reaction, and thus our results for this reaction are confirmatory. The difference in the reactions with water of ethane and propane, on the one hand, and cyclopropane and n-butane, on the other hand, is somewhat surprising; but actually not enough is yet known about ionic reactions for one really to have reasonable expectations.

The relative reaction cross sections are listed in columns IV and V. Although we feel that the reactions listed in column I must be accepted as correct (excepting the unknown reaction between water and methane), it is still of interest to calculate for some of the reactions relative cross sections based on the alternative assumptions that D_2O^+ is the ionic reactant (column IV) or that RH^+ is the ionic reactant (column V). The cross sections are calculated from the following relations: for $D_2O^+ + RH \rightarrow HD_2O^+ + R$

$$\text{Rel. XS} = \frac{(f\sigma)RH}{(f\sigma)D_2O} = \frac{\frac{1}{(RH)}\left(\frac{I_{21}}{I_{20} + I_{21}}\right)_{RH}}{\frac{1}{(D_2O)}\left(\frac{I_{22}}{I_{20} + I_{22}}\right)_{D_2O}} \quad (6)$$

and for $RH^+ + D_2O \rightarrow HD_2O^+ + R$

$$\text{Rel. XS} = \frac{(f\sigma)RH^+}{(f\sigma)D_2O} = \frac{\frac{1}{(RH)}\left(\frac{I_{21}}{I_{20}}\right)_{RH^+} \frac{Q_{D_2O}p_{D_2O}}{Q_{RH}p_{RH}}}{\frac{1}{(D_2O)}\left(\frac{I_{22}}{I_{20} + I_{22}}\right)_{D_2O}} \quad (7)$$

where the Q's are ionization cross sections[6] and the p's are the fraction of the parent ions in the mass spectra of the various substances. Relative values of the square roots of the polarizabilities of the neutral reactants (always assuming that D_2O^+ is the ionic reactant) are listed in column VI. The values are given relative to that of D_2O, which is taken to be the same as that of H_2O.

The theory of ion–molecule reactions[1] predicts that the reaction cross section should vary with the square root of the polarizability of the molecule involved in the reaction. By comparing columns IV, V and VI (and keeping in mind that reactions involving neutral D_2O have a theoretical relative rate of 1.00), it is clear that the theory does not adequately account for the observed variations in rates. However, it should be noted that the values given in columns IV and VI are in good agreement through propane. Unfortunately, the values given in column IV for ethane and propane refer to what we think are the wrong reactions, and the significance of the agreement is questionable. Similar considerations apply to the nearly identical relative rates given in column V for ethane, propane and n-butane. Past results[1,2] convince us that the theory of ion–molecule reactions based upon polarizability accounts adequately for the order of magnitude of the reaction rates, but the present results show that unless some of the reactions occurring are not as we have written them, the fine details of the rates are determined by other, unknown factors.

The radiolysis of water has been one of the most extensively studied reactions in the field of radiation chemistry but it has generally been assumed that only free radical reactions are involved. However, we submit that the large reaction cross sections and specific reaction rates reported here force one to consider reactions of the H_2O^+ ion. Obviously, neutralization processes compete with possible reactions of the ion with molecules, and it is of interest to compare the rates of the two processes. The lifetime of H_2O^+ with respect to its reaction with H_2O is $1/k(H_2O)$, where k is the specific reaction rate of the ion–molecule reaction and may be taken (Table I) to be 2×10^{-9} cc./molecule sec. The concentration of water molecules may be taken as 3×10^{22} molecules/cm.[3]. The lifetime with respect to the ion–molecule reaction is then 1.6×10^{-14} seconds. This time is of the same order as the smallest estimates of the time (10^{-13} to 10^{-14} seconds) in which neutralization occurs in liquid water.[7] It is thus evident that the bimolecular reactions of the H_2O^+ must be considered in the radiolysis of water.

(7) A. H. Samuel and J. L. Magee, J. Chem. Phys., 21, 1080 (1953).