give rise to many capillary spaces of variable diameter in which water can be retained, even at very low relative humidity. Some of the sodium laurate apparently is not a part of the fibrous structure but is present as granules 100–200 Å. in diameter irregularly spaced along the fiber.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Acid Hydrolysis of Methyl Acetate in Dioxane–Water Mixtures

BY HERBERT S. HARNED AND ARTHUR M. ROSS, JR.[1]

The exhaustive study of the properties of hydrochloric acid in dioxane–water mixtures, made in this Laboratory,[2] has invited further research upon the catalytic activity of this acid in these media. For this purpose, the acid-catalyzed hydrolysis of a simple ester (methyl acetate) has been selected. Dioxane is apparently an inert solvent, and is, at the same time, completely miscible with water. The use of dioxane–water mixtures as media, therefore, gives a wide variation in water concentration as well as drastic changes in dielectric constant, ranging from 80 in water to 2 in pure dioxane.

In addition to the velocity measurements, the activity coefficient of the ester was determined by measurement of its vapor pressure over these mixtures at 25°. These data, together with the known vapor pressures of water in dioxane–water mixtures, and the properties of hydrochloric acid are sufficient to calculate all factors of the Brönsted[3] equation for reaction velocities with the obvious and necessary exception of the activity coefficient of the "fugitive" complex. This material will form a comprehensive body of evidence upon which certain aspects of the theory may be discussed.

Reaction Velocity Measurements.—The velocity measurements were made by the usual method of titration with standard sodium hydroxide solution. A special reaction vessel designed to secure a minimum exposure of the reaction solution to the atmosphere at the time of sampling was employed. All chemicals were carefully purified.

In order to express the results on different concentration scales, density measurements were required. These were executed in 30-cc. density bottles at the completion of a run. Several experiments showed that the density change during reaction was entirely negligible. This was proved by placing the initial reaction mixture in a 200-cc. bulb surmounted by a 2-mm. capillary. Once thermal equilibrium had been attained, no motion of the meniscus in the capillary could be observed.

The hydrolysis is of the first order with respect to ester in aqueous solutions. Our results show that it remains of first order throughout the range of dioxane strengths. The calculation of the velocity constant from the buret readings was made by the method of Guggenheim[4] which avoids the use of an infinity reading. Two sets of readings were taken such that each member of the second set is made at a fixed and constant time interval after each corresponding member of the first set. Using the first order velocity equations, we obtain

$$\ln (R_{t+T} - R_t) = \ln \Delta R = -k_t + \text{constant} \quad (1)$$

where T is the constant time interval, R_{t+T} and R_t are the buret readings at the times indicated and k is the velocity constant. By plotting $\ln \Delta R$ against t, k may be obtained.

In practice these readings were made in two groups of seven to eight, about an hour elapsing between successive readings within a set. The first set was made well before, the second well after, the "half-life" of the reaction. At 25° this meant a difference of a full day for the 0.1 M mixtures, and overnight for the 0.2 M mixtures. About half these intervals were required for the same acid strengths at 35°.

A detailed discussion of errors seems unnecessary. The measurements in water were found to be reproducible to within less than 1% and

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[1] This communication contains part of the material of a dissertation presented by Arthur M. Ross, Jr., to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1939.

[2] Harned, Morrison, Walker, Donelson and Calmon, THIS JOURNAL, **61**, 49 (1939). This communication contains a bibliography of the other contributions to this subject.

[3] *Z. physik. Chem.*, **102**, 169 (1922); *Chem. Rev.*, **5**, 231 (1928).

[4] Guggenheim, *Phil. Mag.*, [7], **2**, 538 (1926).

checked the measurement of Lamble and Lewis[5] with 0.1 N hydrochloric acid to well within this error. Reproducibility is not so good in the mixtures rich in dioxane; but the whole situation should be covered by taking the maximum error as 2%.

The Vapor Pressure Measurements.—The activity coefficient of methyl acetate relative to that in pure water may readily be determined by vapor pressure measurements. This is evident from the equations for the chemical potential of methyl acetate in the vapor phase:

$$\mu_e = \mu_e^0(T) + RT \ln p_e \quad (2)$$

and in the solution phase

$$\mu_e' = \mu_e^{0\prime}(T,p) + RT \ln N_e f_e \quad (3)$$

where p_e is the pressure of the ester in the gaseous phase, and N_e and f_e its mole fraction and activity coefficient in the liquid phase. In the latter equation, it is to be noted that $\mu_e^{0\prime}(T,p)$ is so written to indicate that it is referred to a *given* medium (generally pure water) and does not depend upon the particular solution under investigation. At equilibrium $\mu_e = \mu_e'$, and, therefore

$$\ln (p_e/N_e f_e) = \frac{\mu_e^{0\prime} - \mu_e^0}{RT} \quad (4)$$

or for the relative activity coefficients at constant temperature

$$f_e = g(p_e/N_e) \quad (5)$$

where g is the same for all media.

We have determined the activity coefficient f_e by a differential method, measuring the increase in total pressure when successive portions of methyl acetate are added to a given mixture of dioxane and water.

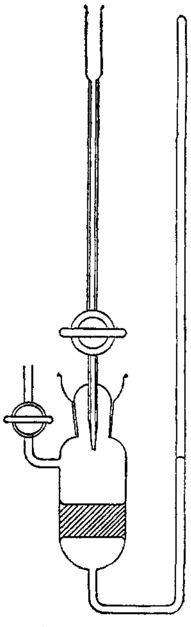

Fig. 1.—Vapor pressure apparatus: manometer and micro-buret.

The design of the vapor pressure apparatus is shown in Fig. 1. The well of a carefully filled mercury manometer consisted of a 300-cc. solution bulb; this had a side-arm closed off by a stopcock through which it could be evacuated. Its mouth was a ground glass joint into which fitted the microburet used for adding the methyl acetate. The latter consisted of about 30 cm. of heavy-walled Pyrex capillary which was carefully calibrated (with respect to a graduation mark) by weighing successive portions of mercury delivered from it. At its upper end it was widened into a 10-mm. tube more than sufficient in size to hold the ester for one run; and at its terminal end it bore a carefully ground stopcock of the mercury seal type and a fine dropping-tip, the whole being integral with the joint connecting it to the manometer vessel. The manometer, mounted in a brass frame, was rocked mechanically in a vertical waterbath equipped with a plate glass front through which the motion of the menisci could be observed with a cathetometer reading to 0.05 mm. The thermostatic control was ±0.01°.

The solution under investigation was run into the manometer bulb at 25° out of a calibrated 50-cc. pipet. The microburet was previously filled in the following manner. A quantity of mercury sufficient to fill the capillary down to the tip was introduced. Into the wide upper part about 3 cc. of methyl acetate was placed; mercury was then drawn through the stopcock until about 10 cm. of the capillary was full of ester. Mercury from a dropper was added at the top and more mercury withdrawn at the tip until the ester, trapped between two threads of mercury, had run nearly to the stopcock. In this way ester was never permitted to lie in contact with the stopcock, and no difficulty was experienced with dissolving grease.

With the joint well greased, the microburet was fixed to the manometer, and the bulb was then evacuated until the pressure fell to approximately the vapor pressure of the dioxane–water mixture. At incipient boiling the stopcock was closed to prevent loss of contents, and the solution in the bulb was warmed gently to hasten the equilibrium of permanent gases distributed between the two phases. Although no effort was made to remove such gases completely, they were invariably found to be present in such small amounts that the addition of 1 cc. of mercury had no observable effect on the total pressure. This test was made at the beginning of each run. In order to calculate a correction for gases dissolved in the ester itself, a blank was run, in which portions of ester were added to equilibrated ester in the manometer. No appreciable pressure change was found, which indicated that the original material was sufficiently gas-free to neglect this correction.

The thread of ester trapped between two threads of mercury was measured by the cathetometer, appropriate corrections being applied for the capillary calibration and the curvature of the two confining menisci. This curvature was found to be nearly constant throughout the use of the apparatus, so that a constant correction factor was adequate. It was also found that the mercury meniscus in the vacuum side of the manometer tube remained sufficiently constant in curvature. Moreover, the depth of the solution in the vessel increased negligibly during the run (less than one-third of a cc. of ester was added in all, corresponding to a maximum final ester concentration of 0.09 mole per liter), so that two readings sufficed to determine the total pressure.

Knowing the amount and composition of the solution in the bulb and the amounts of ester added, it was possible to plot p_e against N_e. About four points were determined in each run, and through these it was found possible to draw a straight line which each point fitted to within 0.5%.

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[5] Lamble and Lewis, *J. Chem. Soc.*, **105**, 2330 (1912).

The slope p_e *versus* N_e is the Henry's law constant, from which the relative activity coefficients of the ester could be computed.

Experimental Rate Constants

TABLE I

FIRST ORDER RATE CONSTANTS

X = wt. % dioxane; N_{HCl}, m_{HCl}, and c_{HCl} equal mole fraction, molality and volume concentrations of HCl.

X	N_{HCl}	m_{HCl}	c_{HCl}	$k \times 10^5$
I. Approximately 0.1 M HCl, t = 25°				
0	0.00178	0.0993	0.0974	63.8
10	.00195	.1000	.0989	68.9
19.7	.00212	.0996	.0993	68.9
20	.00215	.1009	.1011	69.4
30	.00237	.1009	.1011	67.5
44.4	.00274	.0991	.1000	60.4
45	.00272	.1013	.1023	60.4
60.1	.00330	.0962	.0982	48.9
70	.00389	.0964	.0982	41.5
75	.00442	.1000	.1022	43.6
80.3	.00458	.0982	.0943	37.3
86.0	.00515	.0912	.0926	38.9
90.0	.00628	.1003	.1034	45.9
II. Approximately 0.2 M HCl, t = 25°				
0	0.00358	0.201	0.196	128.5
10	.00389	.200	.198	135
20	.00426	.200	.200	139
30	.00470	.200	.201	135
45	.00555	.200	.203	122
60.1	.00683	.201	.204	106
70	.00801	.200	.204	89.4
75	.00878	.200	.204	84.1
80.3	.00958	.196	.199	80.4
86.0	.0112	.200	.203	84.9
90	.0124	.199	.203	91.1
III. Approximately 0.1 M HCl, t = 35.3°				
0.0	0.00207	0.116	0.1147	194
9.1	.00196	.101	.1011	175
19.9	.00223	.105	.1056	179
29.7	.00233	.0993	.0993	165
40	.00289	.110	.1122	170
49.3	.00275	.0935	.0943	129
59.8	.00352	.103	.1060	132
68.9	.00394	.0997	.1020	110
73.7	.00427	.0991	.1000	103
79.7	.00537	.110	.1123	113
83.4	.00527	.0996	.1018	100
89.9	.00690	.105	.1069	126

Table I contains values of the velocity constants corresponding to approximately 0.1 and 0.2 M catalyst, respectively, at 25° and also values for 0.1 M hydrochloric acid at 35.3°. These were computed from the Guggenheim slopes[4] by least squaring the experimental points to a straight line. Before this was done, rough plots of ln ΔR against t [Equation (1)] were made in order to reject obviously erroneous results. Each of the rate constants is an average of two determinations. Duplicate results were required to check within 2%. Runs which did not yield straight lines were rejected. Considerable difficulty was experienced in reproducing results in mixtures rich in dioxane for reasons which remain obscure.

Following prevalent usage the unimolecular rate constant is calculated from natural logarithms with time in minutes. The catalyst concentration is given in mole fractions, molalities and volume concentrations. The latter were calculated from the densities previously mentioned.

Henry's Law Constants for Methyl Acetate.—The results of the vapor pressure measurements are given in Table II. The relative activity coefficients, referred to pure water, in the three customary concentration units are also given.

TABLE II

HENRY'S LAW CONSTANTS AND RELATIVE ACTIVITY COEFFICIENTS OF METHYL ACETATE IN DIOXANE–WATER MIXTURES AT 25°

X = weight of dioxane; f_e, γ_e, and y_e are the relative activity coefficients on the mole fraction, molality and volume concentration scales, respectively; p_e in mm. Hg.

X	P_e/N_e	X	f_e	γ_e	y_e
0.0	5040	0	1.000	1.000	1.000
19.9	3674	10	0.867	0.940	0.940
30.2	3040	20	.726	.874	.865
60.0	1224	30	.603	.796	.777
69.8	817	40	.452	.700	.674
79.8	546	50	.357	.586	.562
90.1	367	60	.242	.467	.457
100	246	70	.161	.368	.365
		80	.109	.297	.283
		90	.073	.258	.248

Effects of Solvent Composition, Catalyst Concentration upon Velocity Constants. Activation Energy

In Fig. 2, the variation of k/c_{HCl} with dioxane composition is shown. This plot shows a maximum at a 15% dioxane composition and a minimum at 80% dioxane. The plot of k/N_{HCl} is simpler as shown by Fig. 3, in which results at both 25 and 35° are plotted.

The most striking observation which can be made immediately is that to the first approximation k/N_{HCl} is independent of the acid concentration in all the solvent mixtures as shown by Table III. Since the solutions are moderately dilute, the same proportionality is also valid when the acid concentration is expressed in molalities or normalities.

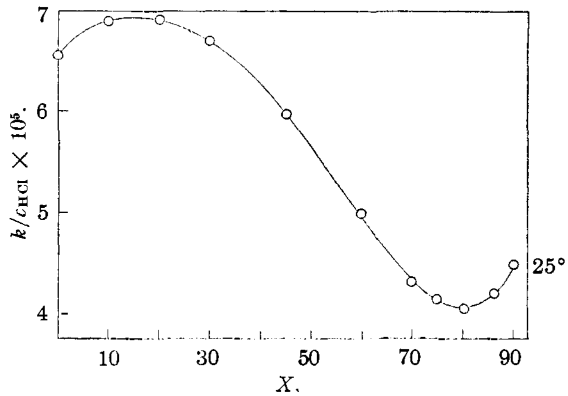

Fig. 2.—Plot of k/c_{HCl} against weight per cent. of dioxane at 25°.

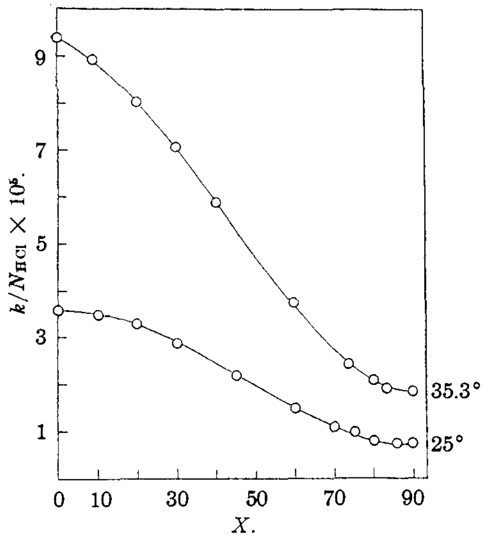

Fig. 3.—Plots of k/N_{HCl} against weight per cent. of dioxane at 25 and 35.3°.

It would seem at first glance that this proportionality of k to c_{HCl} would indicate definitely just which species are catalytically active. In dioxane-rich medium, the ions associate to form ion pairs and therefore the relative amounts of hydronium ion and associated ions should vary with acid concentration. The equilibria involved may be represented by

$$H_3O^+ + Cl^- \rightleftarrows [H_3O^+ \ldots Cl^-]^\circ \rightleftarrows HCl + H_2O$$

Up to 90% dioxane solutions, the association is of the ion pair type and only in the very high percentage dioxane solutions is there indication that un-ionized HCl is present in appreciable amount. If the catalytic activities of the hydronium ion, hydronium chloride and HCl molecule are identical, then strict proportionality between k and c_{HCl} would occur. Neglecting the possible effect of small amounts of HCl, the evidence, particularly in the 86 and 90% dioxane solutions, indicates that both the hydronium ion and the hydronium chloride ion pair are effective catalysts. This, however, is not entirely conclusive in the moderately concentrated dioxane solutions (45 to 82%) because, owing to the nature of the activity coefficient function, the degree of dissociation, α, given by

$$\frac{\alpha^2 m}{1 - \alpha} = \frac{K_a}{y_{\pm}^2} \qquad (6)$$

does not vary greatly between 0.1 and 0.2 M acid. This is shown in Table IV, where α is calculated from the dissociation constants[6] and the activity coefficients.[7]

TABLE III

ILLUSTRATING CONSTANCY OF k/N_{HCl} IN A GIVEN SOLVENT

X	0.1 M HCl k/N_{HCl}	0.2 M HCl k/N_{HCl}
0	0.358	0.359
10	.353	.347
20	.323	.326
30	.285	.287
45	.214	.220
60.1	.148	.155
70	.107	.112
75	.0979	.0958
80.3	.0815	.0839
86	.0755	.0758
90	.0731	.0735

TABLE IV

DEGREE OF DISSOCIATION OF HYDROCHLORIC ACID IN DIOXANE–WATER MIXTURES

X	K_a	γ(0.1 M)	γ(0.2 M)	α(0.1 M)	α(0.2 M)
45	0.3	0.55	0.50	0.90	0.88
70	.008	.21	.81	.72	.66
82	.0002	.063	.052	.50	.45

For computing the activation energy, k/N_{HCl} was used since N_{HCl} is independent of the temperature. The integrated form of the Arrhenius equation

$$E_A = R\frac{T_1T_2}{T_2 - T_1}\ln\frac{k_{(T_2)}}{k_{(T_1)}} \qquad (7)$$

was used and values of the velocity constants read

TABLE V

ACTIVATION ENERGY IN CALORIES

X	E_A	X	E_A
0	17,100	50	15,600
10	16,500	60	15,500
20	16,100	70	15,500
30	16,000	80	15,400
40	15,800	90	16,500

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[6] Owen and Waters, THIS JOURNAL, **60**, 2371 (1938).

[7] Harned and Donelson, *ibid.*, **60**, 2128 (1938); Harned, Donelson and Calmon, *ibid.*, **60**, 2133 (1938); Harned, Walker and Calmon, *ibid.*, **61**, 44 (1939).

off the smooth curves in Fig. 3. The results, given in Table V, show that as a first approximation E_A is independent of the solvent composition.

Application of the Brönsted Equation

The application of the Brönsted[8] reaction velocity equation, which has been shown by Eyring[9] to result from transition state theory, to the data on the dioxane–water medium effect leads to interesting results. Assuming that the reaction velocity constant is of the first order with respect to ester, water and the hydrogen ion, the Brönsted equation becomes

$$k = k^0 m_{\mathrm{H}} a_{\mathrm{H_2O}} \frac{\gamma_e \gamma_{\mathrm{H}}}{\gamma^*} \qquad (8)$$

where γ^* is the activity coefficient of the transition complex, k is the observed velocity constant, and k^0 involves equilibrium constants for compound and intermediate complex formation. Evidence that the reaction is of the first order with respect to water has been obtained recently by Friedman and Elmore,[10] who studied the hydrolysis of methyl acetate in acetone containing just enough water to react with the ester. We assume that $\gamma_{\mathrm{H}} = \gamma_{\mathrm{HCl}}$ so that

$$k = k^0 m_{\mathrm{HCl}} a_{\mathrm{H_2O}} \frac{\gamma_e \gamma_{\mathrm{HCl}}}{\gamma^*} \qquad (9)$$

Since we have at our disposal all the quantities in Equation (9) except γ^*, this quantity may be calculated. For the activity of water we employed the partial vapor pressure measurements of Hovorka, Schaeffer and Dreisbach.[11] Electromotive force measurements of the cell

H_2 | HCl (m), Dioxane (X), H_2O (Y) | AgCl – Ag

by Harned, *et al.*[12] in 0, 20, 45, 70 and 82% dioxane solutions were used to compute the activity coefficient (mean) of hydrochloric acid in these mixtures relative to its value in water. For the rates and the ester activity coefficient, the results in Tables I and II were employed. We have assumed that the presence of the catalyzing acid does not appreciably affect the partial vapor pressure of the water or ester in the reaction mixtures and have used the values of $a_{\mathrm{H_2O}}$ and γ_e obtained in the acid free solvents. For facility in using the electromotive force data, we have employed the molality scale. Moreover, all activity coefficients have been referred to unity in water at a given acid concentration. The values of γ^* in Table VI were calculated from smooth curves of the reaction rates, vapor pressures and electromotive force measurements. The table also includes the relative activity coefficients of the acid and the water molecule.

TABLE VI

THE ACTIVITY COEFFICIENTS OF THE TRANSITION STATE COMPLEX

X	$k^a/m_{\mathrm{HCl}} p_{\mathrm{H_2O}} \gamma_e$	$\gamma_{\mathrm{HCl}}{}^a$	$\gamma_{\mathrm{H_2O}}$	γ^{*a}
0	1.00	1.00	1.00	1.00
10	1.13	1.13	1.10	1.00
20	1.27	1.28	1.23	1.00
30	1.38	1.50	1.37	1.09
45	1.58	2.03	1.70	1.29
60.1	2.00	3.20	2.22	1.60
70	2.23	5.14	2.82	2.31
75	2.40	6.89	3.31	2.87
80.3	2.72	9.60	4.01	3.53

[a] Relative to unity in water.

The comparative plots of the logarithms of these quantities against the weight per cent. of dioxane are shown in Fig. 4. The coefficients, γ_{HCl}, γ^* and $\gamma_{\mathrm{H_2O}}$ increase with dioxane concentration while γ_e decreases. In comparison with γ_{HCl}, the behavior of γ^* is quite reasonable. It is a monatone decreasing function of the dielectric constant and is seen to be similar in form to γ_{HCl}.

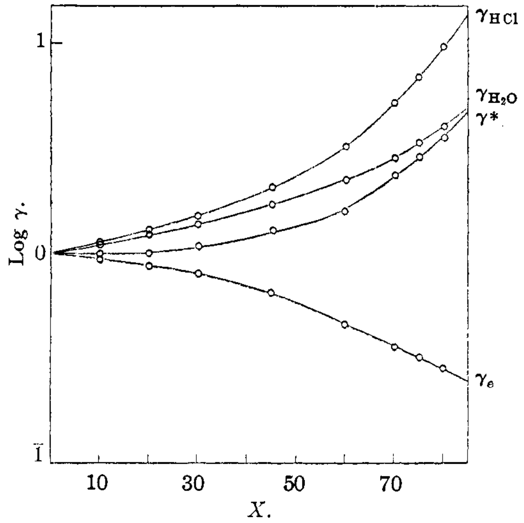

Fig. 4.—Plots of the logarithms of the activity coefficients, γ_{HCl}, γ^*, $\gamma_{\mathrm{H_2O}}$ and γ_e against weight per cent. dioxane at 25°.

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[8] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1927); *Chem. Rev.*, **5**, 231 (1928).

[9] Eyring, *J. Chem. Phys.*, **3**, 107 (1935); Wynne-Jones and Eyring, *ibid.*, **3**, 492 (1935).

[10] Friedman and Elmore, THIS JOURNAL, **63**, 864 (1941).

[11] Hovorka, Schaeffer and Dreisbach, *ibid.*, **58**, 226 (1936); (correction), **59**, 2753 (1937).

[12] Harned and Ehlers, *ibid.*, **55**, 2179 (1933); Harned and Donelson, *ibid.*, **60**, 339, 2128 (1938); Harned, Donelson and Calmon, *ibid.*, **60**, 2133 (1938); Harned and Walker, *ibid.*, **61**, 48 (1939).

Although the equation of Born[13] which includes only the coulombic interactions fails in its application to the transfer of electrolytes in these solvent media, it requires an increase in activity coefficient with decreasing dielectric constant. It also requires that the activity coefficient be smaller when the ionic radius is large. This latter condition is satisfied since the radius of the positive ion in the transition complex would certainly be greater than that of the hydronium ion. We note, however, that γ_{H_2O} is of the same magnitude as γ_{HCl} which indicates that a large part of any of these effects may be intermolecular.

Our finding (Table III) that k is proportional to m_{HCl} guarantees that to a first approximation γ^* behaves correctly with varying acid concentration. If we write

$$\gamma^* = \left[k_0\frac{m_{HCl}}{k}\right]p_{H_2O}\gamma_e\gamma_{HCl} \qquad (10)$$

we see that the term in brackets is, for a given solvent, independent of concentration at high dilution. Moreover, p_{H_2O} changes by only 1 part in 30,000 in going from 0 to 0.1 M HCl, and γ_e by less than 5% if Glasstone's[14] solubility data be used for the estimate. Then at low concentration γ^* is actually proportional to γ_{HCl} as theory would demand.

An interesting result of these calculations is illustrated in Fig. 5 in which γ^* is plotted against the weight per cent. of dioxane on the activity coefficient of hydrochloric acid scale (*versus* γ_{HCl}). The graph is nearly linear and is seen to differ greatly in form from the similar plot for γ_{H_2O}.

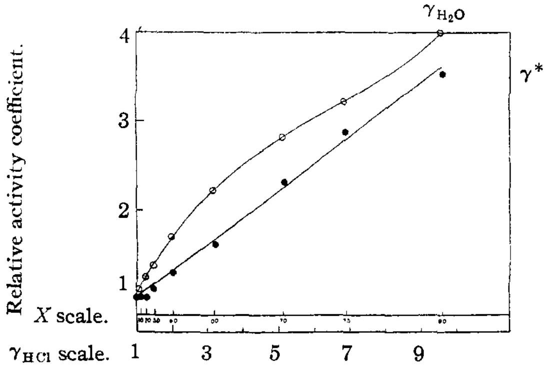

Fig. 5.—Plot of the relative activity coefficient of the transition complex, γ^*, against that of hydrochloric acid, or against weight per cent. of dioxane on the γ_{HCl} scale. Similar plot for γ_{H_2O}.

A calculation of the salt effect upon the catalytic hydrolysis of ethyl acetate yields a similar result. From Robinson's[15] velocity measurements with 0.1 M hydrochloric acid as catalyst in lithium and sodium chloride, Glasstone's solubilities of ethyl acetate in salt solutions, and the vapor pressure measurements of Pearce and Nelson,[16] and Pearce and Snow,[17] γ^* in potassium, sodium and lithium chloride solutions has been computed by equation (10). These results are plotted against the salt molality in Fig. 6, which also includes plots of γ_{HCl} in these solutions derived from the electromotive forces.[18] Velocity measurements were not available at salt concentrations below 1 M. It is at once apparent that all these plots are similar in form in the concentrated solutions. Moreover, the order of effectiveness of salts in decreasing γ^* (Li > Na > K) is the same as for γ_{HCl}. Finally, plots of γ^* *versus* γ_{HCl} (*viz.*, molality of salt on the γ_{HCl} scale) are straight in the concentrated solutions. This result is similar to that shown in Fig. 5.

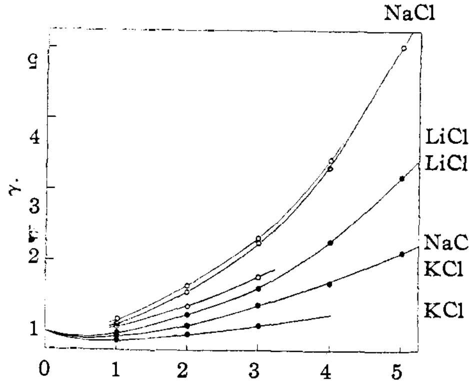

Fig. 6.—Plots of γ^* and γ_{HCl} in lithium, sodium and potassium chloride solutions: ○, γ^*; ●, γ_{HCl}.

The activity coefficient of the neutral ester in these salt solutions differs from that of γ^*. For example, plots of log γ^* against salt concentrations are linear from 1 to 5 M. A similar graph for log γ_e in lithium chloride solutions shows marked curvature.

In general these results indicate that γ^* possesses properties similar to those of γ_{HCl} and differs from the behavior of neutral molecules. Since the

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[13] Born, *Z. Physik*, **1**, 45 (1920); see Harned and Calmon, THIS JOURNAL, **61**, 1491 (1939).

[14] Glasstone and Pound, *J. Chem. Soc.*, **127**, 2660 (1925); Glasstone, Dimond and Jones, *ibid.*, **128**, 2935 (1925).

[15] Robinson, *Trans. Faraday Soc.*, **26**, 217 (1930).

[16] Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932); **55**, 3075 (1933).

[17] Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

[18] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); Harned and Copson, *ibid.*, **55**, 2206 (1933); Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

situation is very complicated and involves assumptions concerning the mechanism of the reaction, the above considerations should be regarded as giving qualitative support to the Brönsted theory and not as proving the validity of the Brönsted equation.

Summary

1. Reaction velocity measurements of the hydrolysis of methyl acetate, catalyzed by 0.1 and 0.2 M hydrochloric acid at 25 and 35° in dioxane–water mixtures covering a range of concentration of dioxane from 0 to 90% by weight have been made.

2. The relative activity coefficient of methyl acetate in these dioxane–water mixtures has been determined by vapor pressure measurements.

3. The reaction velocity constant was found to be proportional to the acid concentration in all mixtures in moderately dilute acid solution.

4. As a first approximation, the activation energy was found to be independent of the solvent composition.

5. From Brönsted's equation, the activity coefficient of the transition complex was computed and found to vary with solvent composition in a manner similar to the variation of the activity coefficient of hydrochloric acid in these mixtures. A similar result was found for the variation of these quantities in salt solutions. These conclusions are evidence for the validity of the Brönsted theory.

NEW HAVEN, CONN. RECEIVED MARCH 13, 1941

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

The Relative Strengths of Acids and Bases

BY E. C. LINGAFELTER

In presenting a generalized theory of acids and bases, Lewis(1) has suggested that it is impossible to arrange acids or bases in a single monotonic order of strength, which would hold for neutralizations by all bases or acids under all conditions. Luder, in his recent review on the electronic theory of acids and bases,(2) implies that such an order should be possible. However, if we consider the various factors which affect the strength of the bond between an acid and a base, it is evident that such an order should not be possible.

Luder states that "according to Lewis' theory, the strength of an acid corresponds to its tendency to accept an electron-pair from a base. The strength of a base corresponds to its tendency to donate an electron-pair to an acid." More correct statements would be: (a) The strength of an acid corresponds to the strength of the bond which it can form with a base, or (b) the strength of an acid corresponds to the decrease in free energy upon formation of a bond with a base.

The interatomic forces in such an acid–base neutralization compound involve not only the bonding forces of the covalent bond, but also electrostatic forces which depend upon the magnitude and separation of charges, and the presence or absence of dipole moments in either acid or base.

Pauling(3) has pointed out the variation in the strengths of bonding orbitals of different types. Since the factors contributing to bond strength can vary more or less independently, the relative strengths of a series of bases may depend on the particular acid used in making the comparison. That this is the case, can be shown by a brief consideration of some equilibrium constants.

The equilibrium constant

$$K = \frac{\text{(neutralization compound)}}{\text{(acid) (base)}}$$

is a measure of the strength of the acid or base. In Table I are given the equilibrium constants at 25°(4) for the reactions

$H^+ + \text{base} = \text{neutralization compound}$
$Ag^+ + 2(\text{base}) = \text{neutralization compound}$, and others.

Thus, using H^+ for our reference acid, we find: $CN^- \sim NH_3 > SO_3^=$ while for Ag^+: $CN^- > SO_3^= > NH_3$. The difference is even more striking if we consider the effect of the charges of the bases.

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(1) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(2) Luder, *Chem. Rev.*, **27**, 547 (1940).

(3) Linus Pauling, "The Nature of the Chemical Bond," Chap. III, Cornell University Press, Ithaca, N. Y., 1939.

(4) Equilibrium constants for the metal-complexes and for HCN, NH_4^+ and HSO_3^- are taken from Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938. The relative strengths of HCl, HBr, and HI are from Hantzsch and Weissberger, *Z. physik. Chem.*, **125**, 251 (1927).