acid which were identical with those obtained by X-rays and β-particles.

In addition, formation of other oxidizing species has been postulated upon irradiation of concentrated sulfuric acid and concentrated phosphoric acid. For example, Daniels and collaborators[20] found small quantities of peroxymono- and peroxydisulfuric acids. Since the yield of those peroxyacids is very low, we believe that the contribution to the oxidation of tetraphenylporphine as compared to that due to hydroxyl and perhydroxyl radicals will be only a small fraction.

Acknowledgments.—The authors wish to thank Drs. M. John Boyd and Joseph N. Seitchik for their courtesy in extending to them the use of the facilities of their laboratories at Hahnemann Medical College.

PHILADELPHIA 4, PENNA.

(20) M. Daniels, J. Lyons and J. Weiss, *J. Chem. Soc.*, 4388 (1957).

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

The Acidity Function, H_0, and Ion-pair Association Constants in Acetic Acid–Water Mixtures

BY KENNETH B. WIBERG AND ROBERT J. EVANS

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The acidity function has been determined for perchloric acid in acetic acid–water mixtures. The data allow the calculation of H_0 for solutions between 0.015 and 0.300 M in perchloric acid for any acetic acid–water mixture having from 10–95% acetic acid by weight. The ion-pair association constants for sodium perchlorate in 95 and 91% acetic acid have been determined using conductometric data. The values of K_a are 1900 and 220, respectively.

In connection with current studies of the mechanisms of chromic acid oxidation in acetic acid-water mixtures it became necessary to obtain data on the effect of the medium on the protonating power of an acid, which may be described by the Hammett acidity function, H_0.[1] It also was desired to have some idea of the magnitude of the ion-pair association constants in these solutions. These quantities have been measured and the results are given below.

The acidity function was measured in the usual fashion, that of determining spectrophotometrically the ratio of conjugate acid to the base using a colored base. For 95 and 91% acetic acid, *o*-nitroaniline was used, and for the other solvent mixtures, and also the lower acid concentrations in 91% acetic acid, *p*-nitroaniline was used. The value 0.99 was taken as the pK_a of *p*-nitroaniline[1] and in order to obtain consistent results in 91% acetic acid, the value -0.57 was taken as the pK_a of *o*-nitroaniline.

Since the values obtained were to be used in connection with kinetic studies, the formal ionic strength of the solution was maintained constant (0.300 M) by the addition of sodium perchlorate. Thus the H_0 values measured here are not exactly comparable to those usually obtained. Perchloric acid was taken as the acid since it is a monobasic acid and appears to be completely ionized (although largely in the form of ion pairs) in glacial acetic acid.[2] The results are given in Table I, and a plot of $-\log\ [H^+]$ against H_0 is given in Fig. 1.

TABLE I

ACIDITY FUNCTION FOR PERCHLORIC ACID IN ACETIC ACID–WATER MIXTURES

$[HClO_4]$	$-\log$ $[H^+]$	H_0 95%	91%	85%	51%	40%	25%	10%
0.300	0.52	−1.43	−0.84	−0.34	0.61	0.64	0.61	0.53
.225	.65	−1.20	− .66	− .18	.72	.77	.75	.65
.150	.82	−0.96	− .46	.03	.92	.95	.93	.82
.075	1.12	− .71	− .12	.36	1.22	1.25	1.24	1.11
.045	1.35	− .48	.10	.59	1.43	1.46	1.44	1.33
.030	1.52	− .21	.28	.76	1.59	1.60	1.58	1.50
.015	1.82	.11	.54	1.03	1.81	1.79	1.81	1.73

From 10–51% acetic acid, a linear relationship is found with a slope of 1.08, neglecting the point for the lowest acid concentration. This concentration is in error because of the "autoprotolysis" of the acetic acid, which contributes a small additional hydrogen ion concentration. The last point is the only one which would be seriously affected by this effect. If the difference between the acidity predicted from the slope and the amount of acid which was added is assumed to be the contribution from the acetic acid, the "autoprotolysis" constant may be calculated to be $5 \pm 1 \times 10^{-6}$ for this range of solvent composition.

In solutions containing a larger proportion of acetic acid, some curvature is noted in the plots, and this becomes particularly noticeable with 95% acetic acid. The average slopes are still close to unity indicating that the difference between H_0 and $-\log\ [H^+]$ is primarily due to a change in the proton level, and suggesting that the ratio of activity coefficients of the indicator base and its conjugate acid is essentially constant and probably close to unity. Thus, in this case, the acidity function is largely a measure of the activity of hydrogen ions.

The nature of the effect of water concentration on H_0 may be seen in a plot of the average $-\log\ [H^+] - H_0$ for each solution against the logarithm of the molality of water (Fig. 2). For the range of $\log M_{H_2O}$ from 0.5 to 1.2, an essentially linear relationship is obtained with a slope of 2.1. A simple interpretation would be that the reaction may be represented as

$$H_3O^+\cdot H_2O + B \rightleftharpoons BH^+ + 2H_2O$$

(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267; F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 1 (1957).

(2) T. L. Smith and J. H. Elliot, THIS JOURNAL, **75**, 3566 (1953).

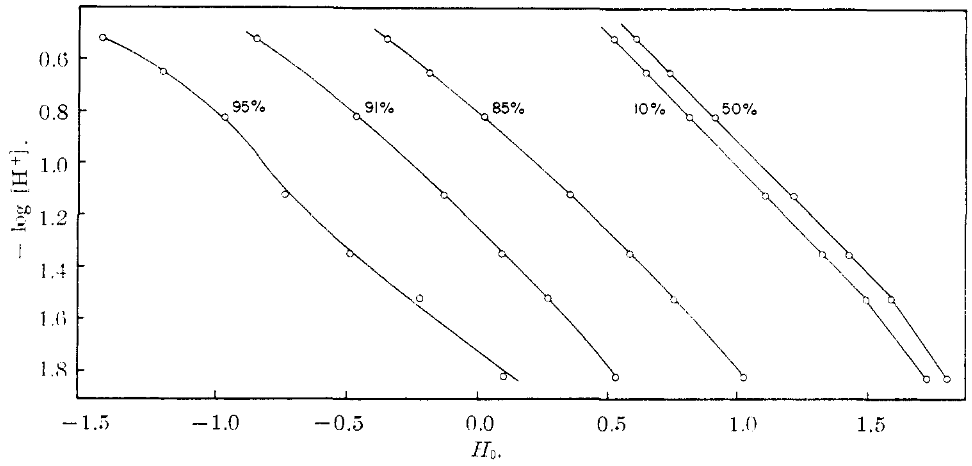

Fig. 1.—A comparison of $-\log$ [H^+] with H_0 for perchloric acid in acetic acid–water mixtures.

for which the equilibrium constant would be

$$K = \frac{[BH][H_2O]^2}{[H_3O^+\cdot H_2O][B]}$$

thus giving a second power dependence on the water concentration. Of course, the proton may be hydrated to a considerably higher degree, but all that is necessary is that the average number of molecules of water associated with the proton be two greater than the average number of molecules of water associated with the conjugate base. It is of course assumed that the pK_a of the indicator base is not changed by the change in solvent. If it were possible to take this into account, the slope of the curve might be changed somewhat, but the conclusion would not be significantly altered.

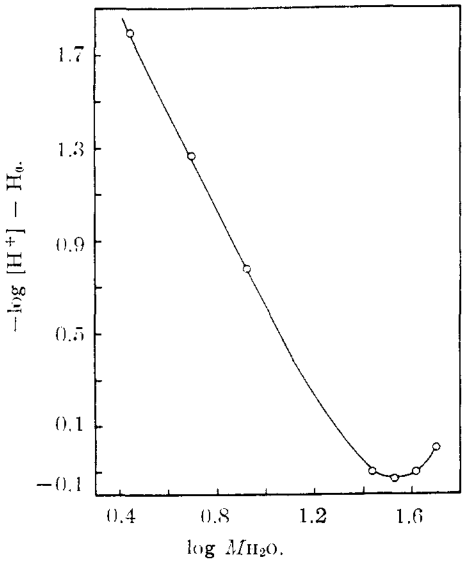

Fig. 2.—Effect of water concentration on the difference between H_0 and $-$ log [H^+].

The initial decrease in $-\log$ [H^+] $-H_0$ as the acetic acid concentration in the solvent is increased indicates that another factor is operating. This is probably the decrease in the activity coefficient with the decrease in dielectric constant caused by the addition of acetic acid to the solvent. It is difficult to estimate how large this effect will be since the ionic strength used here is too large to permit the application of the Debye–Hückel equation. However, since the logarithm of the activity coefficient is a function of $1/D^{3/2}$, it is apparent that a considerable decrease in the activity coefficient would be expected.

The activity coefficient of hydrogen ions would be expected to continue to decrease as the acetic acid concentration is increased, and therefore it is evident that the slope obtained for the straight part of the curve in Fig. 1 must contain an indeterminable contribution from the change in activity coefficient. This would act to increase the true slope. Another complication, as will be shown below, is that ion-pairs become important in solutions having less than 10% water, and when the ionic species are largely in the form of ion-pairs the value of H_0 is no longer a function of the activity of hydrogen ions but rather of the activity of ion-pairs containing a proton.

It was also desired to obtain some information on the magnitude of the ion-pair association constants of a typical salt in acetic acid–water mixtures. The most straightforward way of obtaining this is to examine conductometric data using the equations of Fuoss and Kraus,[3] or of Shedlovsky.[4] This presents some difficulties in the present case since acetic acid is appreciably ionized in these solutions and one does not know to how large an extent the addition of an inert salt will affect the degree of ionization. This makes it necessary to use data for higher concentrations of solute than would otherwise be desirable. Another difficulty is that the dielectric constants for acetic acid–water mixtures are not known, and indeed it is very difficult to obtain data for such solutions because of their high conductivity and consequently low Q for a tuned circuit having such a low resistance across the condenser.

A third factor is that the activity coefficients should be evaluated using the total ionic concentration which includes as unknown contribution from the ionization of acetic acid. In the present case the latter contribution was neglected.

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(3) R. M. Fuoss and C. A. Kraus, This Journal, **55**, 476 (1933); R. M. Fuoss, *ibid.*, **57**, 488 (1935).

(4) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

Although these considerations indicated that the results of a study of the conductance of a salt in these mixtures would not be as precise as in other studies, the possible value of such data seemed sufficient to make this investigation desirable. The dielectric constant values which were needed were estimated based on the data on the dielectric constants of mixtures of water with methanol, ethanol and acetone.[5] The values used were D = 8.5 (95%), 11 (91%) and 15 (85%). The conductance data for sodium perchlorate in 95 and 91% acetic acid are given in Table II.

The data were treated using Shedlovsky's equation[4]

$$\frac{1}{\Lambda_c S_z} = \frac{1}{\Lambda_0} + \frac{Kc\Lambda f_{\pm}^2 S_z}{\Lambda_0^2}$$

where K is the association constant, Λ_0 is the limiting equivalent conductance determined by successive application of the equation, $f_{\pm}^2$ is the square of the mean ionic activity coefficients, and S_z is a correction factor. Plots of $1/\Lambda_c S_z$ against $c\Lambda f_{\pm}^2 S_z$ for the two solutions are shown in Figs. 3 and 4. The slope is K/Λ_0^2 and the intercept is $1/\Lambda_0$. The values for the association constant and the limiting conductance are 1.9×10^3 and 28 for 95% acetic acid and 2.2×10^2 and 32 for 91% acetic acid. The data for 85% acetic acid were considerably less precise, but indicated the association constant was quite small. These values may be compared with the ion pair association constant for perchloric acid in glacial acetic acid, 1.1×10^6.[2]

One must use care in thinking about these association constants for they are defined as thermodynamic constants and include activity coefficients. The latter become quite small for reasonable concentrations ($10^{-3}M$) in these solutions, and thus one must take this into account if one wishes the concentration of ions rather than their activities. To facilitate a comparison of the two values, the fraction of the sodium perchlorate which is in the form of free ions (α) is given for each concentration in Table II. These values of α are corrected for the change in the equivalent conductance of the ions with changing concentration. From these data one may conclude that for solutions containing less than about 10% water, and for concentrations commonly used in kinetic studies, ionic species might best be considered as being in the form of ion-pairs.

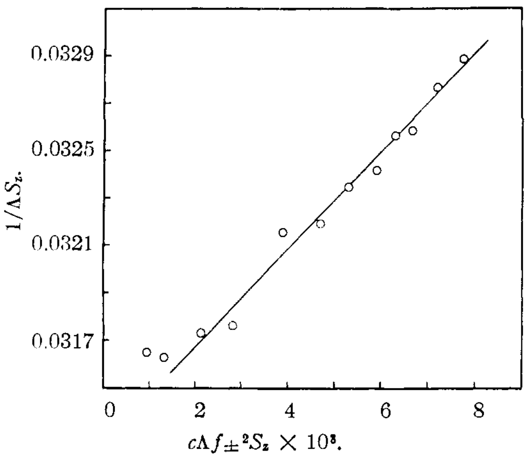

Fig. 3.—Shedlovsky plot for sodium perchlorate in 91% acetic acid.

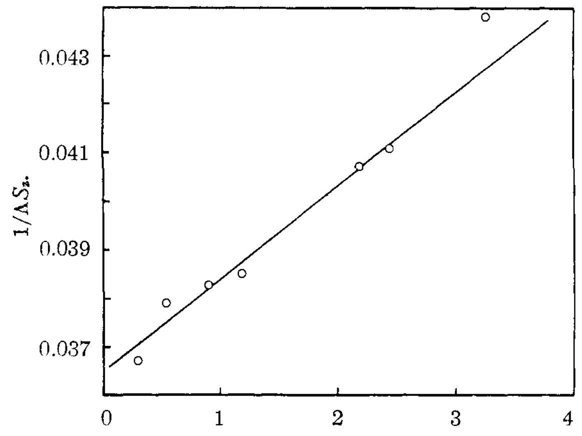

Fig. 4.—Shedlovsky plot for sodium perchlorate in 95% acetic acid.

TABLE II

CONDUCTANCE OF SODIUM PERCHLORATE IN ACETIC ACID–WATER MIXTURES

95% acetic acid				91% acetic acid			
$c \times 10^4$	$(\kappa - \kappa_0) \times 10^7$	Λc	α	$c \times 10^7$	$(\kappa - \kappa_0) \times 10^1$	Λc	α
0.141	3.72	26.3	0.98	0.952	28.3	29.7	0.99
.280	7.02	25.1	.94	1.188	35.0	29.5	.99
.549	13.39	24.4	.93	1.773	51.4	29.0	.99
.808	19.33	23.9	.93	2.35	67.3	28.6	.98
2.25	48.43	21.5	.88	3.58	99.1	27.7	.97
2.80	59.00	21.1	.87	4.76	129.5	27.2	.97
5.69	106.9	18.8	.81	5.94	158.6	26.7	.97
11.33	187.0	16.5	.76	7.11	187.0	26.3	.96
16.93	257.0	15.2	.73	8.28	214.5	25.9	.96
				9.45	241.9	25.6	.96
				11.76	294.0	25.0	.95
				14.63	357.0	24.4	.95
				17.48	416.0	23.8	.95

A rough estimate of the "autoprotolysis" constants for acetic acid in its mixtures with water may be made from the conductance of these mixtures (Table III). Table III also gives the concentration of sodium perchlorate for which $\kappa - \kappa_0$ equals κ_0. If the limiting conductance of acetic acid were approximately equal to that of sodium perchlorate, then these concentrations of ions are roughly equivalent to the concentrations of ions produced by the "autoprotolysis" of acetic acid since the fraction ionized is almost unity. The squares of these concentrations then give an estimate of the constants. These are not thermodynamic constants and must be multiplied by the square of the mean activity coefficients in order to obtain the latter. The values represent a maximum value for the constant since the equivalent conductance of acetic acid is probably somewhat greater than that for sodium perchlorate.

The observed change in the constant with decreasing water content is expected since the molality of water is decreasing, and since the decrease in the

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(5) G. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

TABLE III

CONDUCTANCE OF ACETIC ACID–WATER MIXTURES

Acetic acid, %	κ_0	Equiv. [$NaClO_4$]	K
100			2.5×10^{-13}[6]
95	4.67×10^{-6}	2.0×10^{-4}	4.0×10^{-8}
91	1.11×10^{-5}	4.0×10^{-4}	1.6×10^{-7}
85	4.50×10^{-5}	15.4×10^{-4}	2.4×10^{-6}

TABLE IV

H_0 DETERMINATION IN 85% ACETIC ACID

[p-Nitroaniline] × 10^5	[$HClO_4$]	Optical density 380 mμ	378 mμ	376 mμ	374 mμ	372 mμ	370 mμ	[BH^+]/[B]	H_0
48.5	0.300	0.321	0.327	0.331	0.335	0.339	0.340	21.5	−0.34
48.5	.225	.448	.453	.460	.463	.465	.467	14.7	− .18
24.3	.150	.339	.344	.348	.349	.350	.352	9.03	.03
14.6	.075	.384	.387	.392	.394	.395	.394	4.23	.36
9.70	.045	.377	.382	.385	.385	.386	.385	2.52	.59
9.70	.030	.494	.500	.504	.505	.506	.505	1.66	.76
9.70	.015	.694	.701	.708	.709	.710	.707	0.902	1.03
4.85	0.3 *M* NaOAc	.657	.666	.669	.670	.671	.669		
4.85	BH^+	.0026	.0031	.0034	.0034	.0036	.0038		

dielectric constant will make the formation of ions relatively less favorable.

Acknowledgment.—We wish to thank the National Science Foundation for their support of this work.

Experimental

H_0 Measurements.—The spectrophotometric data were obtained using a Beckman DU spectrometer and 1-cm. cells. The acetic acid was purified by distillation from chromic acid under reduced pressure. The acetic acid water mixtures were made up by weight. A set of typical data is shown in Table IV.

Conductance Measurements.—The conductance was measured using a Leeds and Northrup Jones bridge, and a cell of the design suggested by Jones.[7] The cell constant was determined using a potassium chloride solution, and had a value of 0.2195.

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[6] I. M. Kolthoff and A. Willman, THIS JOURNAL, **56**, 1007 (1934).

[7] G. Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

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

The Kinetics of the Chromic Acid Oxidation of Benzaldehyde

BY KENNETH B. WIBERG AND THEODORE MILL[1]

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The kinetics of the chromic acid oxidation of benzaldehyde has been found to have the rate law: $V = k[RCHO][HCrO_4^-]h_0$. The reaction was found to have a deuterium isotope effect of 4.3, and manganous ion was found to markedly decrease the rate of reaction. Electron-withdrawing groups were found to accelerate the reaction. These data suggest that a mechanism which is analogous to that for the permanganate oxidation of benzaldehyde may be operative.

Introduction

In a previous investigation,[2] the mechanism of the permanganate oxidation of benzaldehyde was studied. The possibility of a similarity in reaction between permanganate and chromic acid has prompted an investigation of the oxidation of benzaldehyde by the latter reagent. This reaction has been studied by Lucchi,[3] but his results are not sufficiently detailed to be a basis for the formulation of a mechanism for the reaction.

The reaction between benzaldehyde and chromic acid proceeds very slowly in water solution. However, in acetic acid–water mixtures the reaction proceeds at a reasonable rate. The increased solubility of benzaldehyde in this medium is also a convenience. The reaction was studied in 91% (by weight) acetic acid since this mixture gave a convenient rate of reaction and is similar to mixtures commonly used in synthetic work.

Experimental

Reagents.—Benzaldehyde was purified immediately before use by two successive distillations in a nitrogen atmosphere. In some cases the benzaldehyde was purified *via* the bisulfite addition compound, but in no case was any difference in rate observed using material purified by the two methods. The solid aldehydes, *p*-chlorobenzaldehyde, *p*-nitrobenzaldehyde and *m*-nitrobenzaldehyde were recrystallized from an ethanol–water mixture and then sublimed twice at 2 mm. pressure at a temperature slightly above their melting points. The liquid aldehydes were distilled under reduced pressure shortly before they were used. Benzaldehyde-d_1 was prepared as described previously.[4]

All of the solid inorganic reagents were reagent grade and were converted to the anhydrous form before making up solutions. Chromium trioxide was recrystallized from water before use. The perchloric acid was obtained as a 71% solution and was a reagent grade. The acetic acid was purified by heating reagent grade material with potassium dichromate and sulfuric acid followed by distillation under reduced pressure. When it was distilled at atmospheric pressure it was found to obtain a small amount of a

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[1] Taken from a thesis submitted by T. Mill to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree, 1957.

[2] K. B. Wiberg and R. Stewart, THIS JOURNAL, **77**, 1786 (1955).

[3] E. Lucchi, *Bull. sci. facolta chim. ind. Bologna*, **I**, 208, 318 (1940); **II**, 165, 175 (1941); *Gazz. chim. ital.*, **71**, 729, 752 (1941).

[4] K. B. Wiberg, THIS JOURNAL, **76**, 5371 (1954).