Kinetic Salt Effects on the Hydrolysis of Benzaldehyde Dimethyl Acetal[1,2]

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The rates of acid-catalyzed hydrolysis of benzaldehyde dimethyl acetal in water at 25 °C show linear responses to the molar concentrations of neutral electrolytes. For the alkali metal perchlorates the rates follow the form $k = k_0 + b$[salt] in the range of 0–0.1 M salt. At about 0.1 M salt the slopes decrease but again are linear to at least 2 M salt. The rate enhancement shows specific cation effects and in the order $Li^+ < Na^+ < K^+ < NH_4^+$. The effect depends upon charge density of the cation since the kinetic salt slope correlates linearly with the cube of the ionic radius. Similar effects are seen for the alkaline-earth perchlorates and the rates increase in the order $Mg^{2+} < Ca^{2+} < Sr^{2+}$. Interestingly barium does not fit with these salts but does fit with the alkali metal perchlorates. There is also a specific anion effect and for the sodium salts the rates increase in the order $NO_3^- < Cl^- < Br^- < ClO_4^-$. Again the effect is one of charge density and the kinetic salt slope correlates linearly with the pK_b of the anion.

The hydrolysis of acetals has occupied a central position in the history of chemical kinetics and mechanism studies.[3,4] One of the problems of acetal hydrolysis which continues to be studied is the nature of the transition state and how it is affected by various environmental factors.[4] A critical environmental factor which is not understood is the rate of acceleration produced by the presence of neutral electrolytes.

Early studies in the literature report finding linear relationships between rate constants and salt concentration for acetal hydrolyses[5,6] and for sucrose hydrolysis.[7,8] More recent studies[9-11] report that neutral salts have a linear relationship for the logarithm of the rate constants and the concentration of the salt for the acetal hydrolysis. Reasons for the dramatic differences in these results have not been discussed to our knowledge.

Recently we reported that dimethyl acetal formation for para-substituted benzaldehydes in 95% methanol–5% water has a linear rate response to the molar concentration of sodium perchlorate.[12] The rates follow the general form

$$k_{H_3^+O} = k_0 + b[\text{salt}] \qquad (1)$$

For the benzaldehydes studied, the rates are more sensitive to salt concentration the greater is the electron donating capability of the para substituent. Because it was possible that the effects observed were due to a methanol–water–salt interaction rather than a salt–reactant interaction, we extended our salt study to the hydrolysis of benzaldehyde dimethyl acetal in water. For this system we observed a specific cation effect for the alkali metal perchlorates with the rates of hydrolysis following eq 1 and the slopes increasing in the order $Li^+ < Na^+ < K^+$. Inasmuch as these studies in water were restricted to salt concentrations of less than 0.1 M one could not be completely sure that the rate effects observed to be linear in salt concentration with k might not be treated equally as well by a ln k vs. salt concentration over a wider range of concentrations. For that reason we expanded our study to concentrations as high as 2 M for alkali metal perchlorates and to include alkaline-earth metal perchlorates. We have also studied specific anion effects with sodium salts.

Experimental Section[13]

Benzaldehyde Dimethyl Acetal. This acetal was prepared from benzaldehyde and trimethyl orthoformate as previously described,[14] bp 68–69 °C (5 Torr), $n^{25}D$ 1.4910.

Salt Solutions. The reagent grade salts used in this study were purified by three recrystallizations from water and dried in a vacuum oven for 2 days. The dried salts were analyzed for residual water content by the Karl Fischer method and stored in a desiccator. All of the salts except $LiClO_4$, $Mg(ClO_4)_2 \cdot 6H_2O$, and $Ca(ClO_4)_2$ contained significantly less than 0.1% water and were used as pure. For the salts

containing more than 0.1% water the weight of salt was corrected to ensure the proper molarity of salt solution. Solubilities permitting, salt solutions of 0.1, 1.0, 2.0, and 4.0 M were prepared in volumetric flasks. These salt solutions were diluted to give the necessary final salt concentration for the kinetic runs. The pH of each aqueous salt solution was checked at several concentrations between 0.01 and 0.2 M to ensure the absence of excess acid or base in the salts.

Catalyst Solution. This solution was prepared by adding 1 ml (pipet) of concentrated perchloric acid to 1 l. of distilled water and diluted to give a solution of $10^{-3}–10^{-4}$ M $HClO_4$. This solution was used in the kinetic runs.

Measurement of Rates. The rate at which benzaldehyde appeared was followed at 281 nm with a Beckman DU spectrophotometer. The special cell holder and temperature regulation system has been described in detail.[14,15]

Into each of three 50-ml volumetric flasks there was added 4 ml (pipet) of the perchloric acid solution and sufficient salt solution to give the correct salt molarity after final dilution. One of the flasks was diluted to the mark with water and part of the solution placed in the reference cell of the spectrophotometer. The other two flasks were thermally equilibrated in the constant temperature bath. A solution of benzaldehyde dimethyl acetal was prepared (about 5×10^{-3} M) in water and 5 ml of this solution was added to the reaction flask which was then diluted to the mark and a portion transferred to a cell compartment of the spectrophotometer. Absorbance readings were taken to at least 60% reaction and the infinite absorbance reading after at least 10 half-lives. In all cases the value of A_∞ agreed within 1% or better with the calculated value based upon 100% hydrolysis of the amount of added acetal. After the first run was started a second acetal solution was prepared and a duplicate kinetic run made. Quadruplicate runs were made in all cases.

For kinetic salt studies made in methanol–water[12] the rates were sufficiently slow that we could use about 10^{-3} M perchloric acid and obtain reproducible kinetics using $[H_3^+O] = [HClO_4]$. When the solvent was changed to water the rates were over an order of magnitude greater than in methanol–water. To have adequate operating time for accurate analytical measurements the concentration of the acid was reduced by a factor of about 10 and for these cases we could not obtain reproducible kinetics because of uncertainties in the concentration of perchloric acid. For this reason a pH meter was used to obtain the hydronium ion concentration and this enabled us to obtain reproducible kinetics.

pH Measurements. At the completion of each kinetic run the pH of the reference solution and of the two reaction solutions were measured. All pH values were measured with a Corning Model 10 pH meter equipped with an Orion double junction electrode, Model 90-02-00, and an Orion glass electrode, Model 91-01-00. The solution for the inner chamber of the reference electrode was Orion filling solution 90-00-02. The outer chamber was filled with a 10% solution of ammonium nitrate which was changed daily. The pH meter was standardized before each series of measurements with a buffer solution of pH 4.00 (Coleman certified buffer tablets). The electrodes were washed to remove buffer, excess water was removed, and the pH was measured for the solutions. In all cases the pH values were stable within 1–2 min and remained stable for 1 h or longer.

The influence of salts on the pH values was checked by measurements of pH of standard acid solutions to which various amounts of salts had been added. These results are shown in Tables I and II.

Table I. Perchloric Acid–Sodium Perchlorate Concentrations and pH[a]

[HClO$_2$]	[NaClO$_4$]	pH calcd	pH obsd
1.043×10^{-2}	0.000	1.98	2.05
1.043×10^{-2}	1.100	1.98	1.95
1.043×10^{-3}	0.000	2.98	2.99
1.043×10^{-3}	1.100	2.98	2.95
1.043×10^{-4}	0.000	3.98	3.98
1.043×10^{-4}	1.100	3.98	3.99

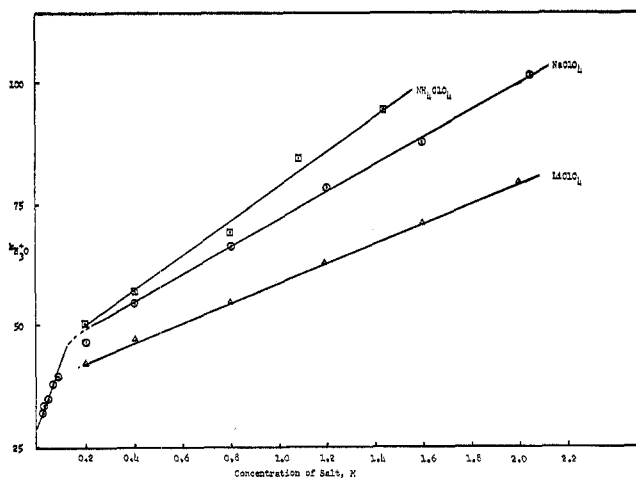[a] All readings are averages of duplicate values.

Figure 1. Linear plots of rate constants, $k_{H_3^+O}$, vs. salt concentration of NH$_4$ClO$_4$, NaClO$_4$, and LiClO$_4$ for the hydrolysis of benzaldehyde dimethyl acetal in water at 25.39 °C. The lines were fitted by least squares.

Results and Discussion

The rate of acid-catalyzed hydrolysis of benzaldehyde dimethyl acetal in water at 25.39 °C is markedly influenced by neutral electrolytes. The rate law in the absence of salt is $k_{obsd} = k_{H_3^+O}[H_3^+O]$. All rate constants reported in the presence of salt have been corrected for [H$_3^+$O] as determined with a pH meter. The rate constants were reproducible to about ±1% or better.

The results obtained for the alkali metal salts are summarized in Table III. The alkali metal and ammonium perchlorate results are shown on the left side of the table and the results for sodium chloride, sodium bromide, and sodium nitrate on the right side of the table.

As we reported earlier,[12] the rate constants show a linear response to salt molarity for KClO$_4$, NaClO$_4$, and LiClO$_4$ and this study has now been expanded to include NH$_4$ClO$_4$, NaCl, NaBr, and NaNO$_3$. These salt effects are described by eq 1 for the salt concentration in the range of from zero to about 0.1 M. The slope, b, is specific for each salt and is a direct measure of the rate acceleration produced by that salt. These slope values are given for each salt in Table III along with the intercept and the normalized slope of $q = b/k_0$.

In the salt concentration of about 0.1 M the rate constant–salt concentration slopes undergo a marked decrease but again are linear to at least 2 M salt following the expression

$$k'_{H_3O} = k'_0 + b'[\text{salt}] \tag{2}$$

which is of the same form as eq 1. These values of b' again are specific for each salt as are the q' values. The values of $k_{H_3^+O}$, b', k'_0, and q' are summarized in Table III.

Figure 1 shows a plot of k_{H_3O} vs. [salt] for sodium perchlorate over the entire concentration range and for lithium per-
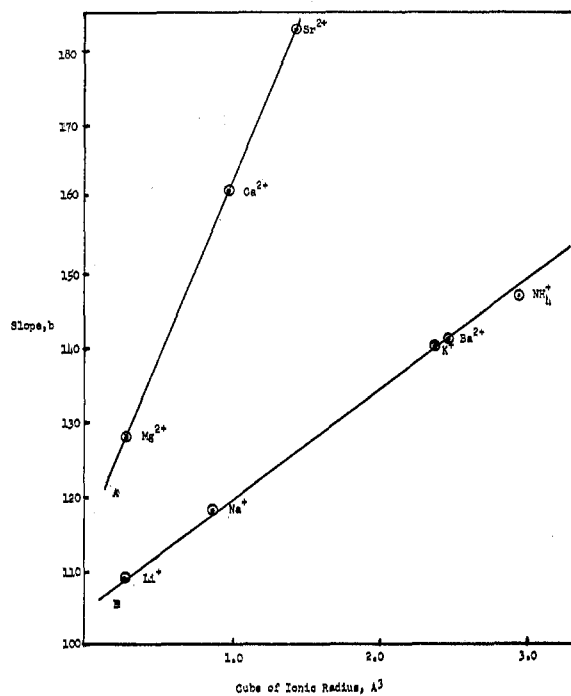

Figure 2. Kinetic salt effect slope vs. the cube of the cation radius for the hydrolysis of benzaldehyde dimethyl acetal in water at 25 °C. All salts were perchlorates and the catalyst was perchloric acid. Line A is for the alkaline earth metal perchlorates and line B is for the alkali metal perchlorates. The lines were placed by least squares.

chlorate and ammonium perchlorate for the higher concentration range only. These are representative results and the other salts show equally good linear plots.

For the perchlorate salts, the rates increase in the order Li$^+$ < Na$^+$ < K$^+$ < NH$_4^+$ for both concentration ranges. The effect appears to be one of charge density of the cation since plots of the slope terms vs. the cube of the ionic radii are linear and for the lower concentration ranges this result is shown as line B, Figure 2. For the univalent cations, all of the values fall on a single line which also includes Ba^{2+}. The cation having the largest volume or the lowest charge density exerts the greatest accelerating effect on the rate.

On the other hand, for a series of sodium salts with various anions the rates increase in the order NO$_3^-$ < Cl$^-$ < Br$^-$ < ClO$_4^-$. Again it appears to be a charge density effect as a simple relationship exists between the slope terms and pK_b of the anions. For the lower salt range a plot has been made for $q(b/k_0)$ and pK_b of the anions and is shown as line A of Figure 3. The data covers about 8 orders of magnitude in pK_b and extrapolate to near zero over an additional 16 orders of magnitude. We have shown that this remarkable and simple linear free energy plot for the kinetic salt effect for the hydrolysis of benzaldehyde dimethyl acetal is applicable also to the data of Bronsted and Grove[5] for the hydrolysis of dimethyl acetal. This correlation is line B of Figure 3.

The results for the alkaline earth metal perchlorates are summarized in Table IV. Again these salts follow the catalytic salt expression, eq 1, as for the alkali metal salts with a change in slope at about 0.1 M and then follow eq 2. The slopes, b, for these salts are plotted against the cube of the ionic radii as line A in Figure 2. The values for Mg^{2+}, Ca^{2+}, and Sr^{2+} conform to a straight line but the Ba^{2+} value is significantly off the line. The Ba^{2+} value is on the line for the alkali metal perchlorates, a fact for which we have no rational explanation.

We are convinced that the salt effects reported here are real and are not artifacts of our experimental procedure. However, if the effects are real then there are certain conflicts of our

Table II. Influence of Concentration of Salt on pH of Perchloric Acid Solutions[a]

Calcd pH 2.84		Calcd pH 3.98		Calcd pH 3.98		Calcd pH 3.98	
$[NaClO_4]$	pH obsd	$[NaClO_4]$	pH obsd	$[NaCl]$	pH obsd	$[Ca(ClO_4)_2]$	pH obsd
0.00	2.85	0.00	3.98	0.00	4.00	0.00	4.03
0.010	2.85	0.498	4.01	0.0125	4.02	0.0190	4.05
0.030	2.86	0.900	3.99	0.0482	4.03	0.0610	4.08
0.050	2.86	1.200	3.97	0.288	3.99	0.0998	4.08
0.080	2.85	1.499	3.99	0.480	3.91	0.200	4.11
0.167	2.86			0.715	3.86	0.500	4.10
0.300	2.84						
0.500	2.81						
1.000	2.76						

[a] All readings are averages of duplicate values.

Table III. Influence of Concentration on the Rate of Hydrolysis of Benzaldehyde Dimethyl Acetal[a]

Salt molarity	$k_{H_3^+O}$,[b] M^{-1} s^{-1} for						
	$LiClO_4$	$NaClO_4$	$KClO_4$	NH_4ClO_4	$NaCl$	$NaBr$	$NaNO_3$
A. Lower Salt Concentration							
0.00	29.5	29.5	29.5	29.5	29.5	29.5	29.5
0.008		31.7[d]					
0.02	30.7	32.8	32.9	33.1	31.7	31.9[d]	30.9
0.04	33.8	34.1	36.5	36.4	33.8	33.9	33.4
0.06		37.8		39.0	35.6	36.7	35.2
0.08	38.0	39.4	40.8	41.2[c]	37.8	38.6	36.1
Slope b	109.3	118.3	140.2	148.8	102.0	114.2	87.1
Intercept k_0	29.2	29.5	30.0	30.0	29.6	29.5	29.5
$q = b/k_0$	3.75	4.01	4.67	4.86	3.45	3.87	2.96
B. Higher Salt Concentration							
0.20	41.0	45.6[c]		49.4	41.7[c]	41.6	
0.40	46.9[c]	54.3		55.5	43.5	43.5	
0.80	54.2	66.2[c]		67.9	52.0	54.8	
1.08				83.6			
1.20	62.1	78.0[c]			56.5	61.4	
1.44				93.8			
1.60	70.6[c]	87.4			60.5	68.2	
2.00	78.9	99.3			69.2[c]	79.3[c]	
Slope b'	20.6	29.5		36.9	14.9	20.0	
Intercept k'_0	37.7	41.8		41.1	38.6	38.0	
$q' = b'/k_0'$	0.55	0.71	010.90	0.39	0.53		

[a] The hydrolysis was conducted in water at 25.39 °C with $\simeq 10^{-5}$ M perchloric acid catalyst. All values of acidity were determined by pH meter. Each value reported is the average of quadruplicate results except where noted. All values are least-squares values. [b] This value is the hydrolytic rate constant corrected to 1 M H_3^+O based upon the measured pH value. [c] Average of triplicate results. [d] Average of duplicate results.

results with those obtained by the regular approaches to salt effects, particularly for kinetic studies of the hydrolysis of acetals.

Most workers use the prepared concentrations of acid as the values for the hydronium ion concentration and then presume that all salt effects are rationalized by the Debye–Huckel correction to the activity coefficients of the reactants and transition state. For concentrations of acids of 10^{-3} M or greater one can reliably prepare standard solutions but we were unable to do so for 10^{-5} M acid solutions as indicated by nonreproducible rate constants. For this reason pH measurements were used to obtain the concentrations of hydronium ion and by which reproducible rate constants were obtained. As one expects, the presence of neutral salt may affect the measured pH values. However, there are also salt effects on the activity coefficients of the reactants and the transition state as well as salt effects on the dielectric constant. By using a measured pH one may obtain a close approximation to $a_{H_3^+O}$ and thus at least one complication due to salt effects is minimized.

For our work the values of the pH which were used in the rate experiments were not compared to known values of the acid concentration (unmeasured). Subsequent to completion of the kinetic studies we attempted a calibration of our pH scale as a function of salt concentration and acid concentration.[16] The values of the pH which were calculated and those which were measured were identical within experimental error for dilute perchloric acid having neutral salts at 0.2–0.3 M or lower (see Table II). It is only for significant concentrations of acid (10^{-3} M or greater) that we observed a decrease in pH with increasing salt concentration but then only at higher salt concentrations (0.3 M or higher; see Tables I and II). Inasmuch as all of our rate measurements were made in aqueous acid with a hydronium ion concentration of from about 1×10^{-5} to 8×10^{-5} M, the measured hydronium ion concentrations are likely very close to the actual values for even the highest salt concentrations used. However, even if the salt does in any case increase the acidity of the solution, the pH meter sees the increase and this effect is corrected for in the rate expression.
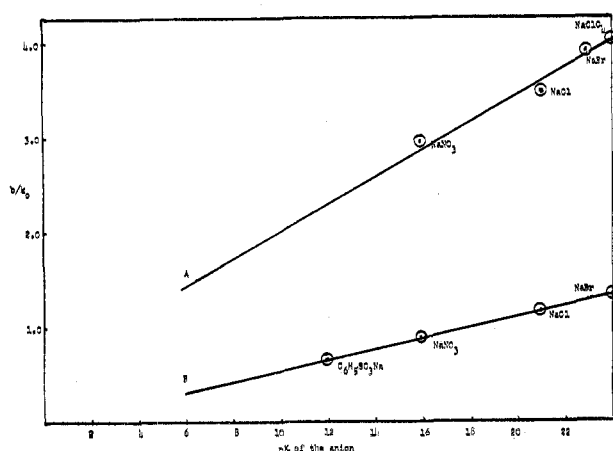
Figure 3. The influence of the basicity of anion of the salt on the rate of the acid-catalyzed hydrolysis of acetals in water at 25 °C. Line A is the data of this work for the hydrolysis of benzaldehyde dimethyl acetal. Line B is the data of Bronsted and Grove[5] for the hydrolysis of acetaldehyde dimethyl acetal. The lines were placed by least squares.

We find it necessary to use a double junction electrode for pH measurements above about 0.3–0.4 M salt.[17] For perchlorate salts this is imperative because of precipitation of $KClO_4$ at the junctions (from KCl in the reference electrode) but even for other salt solutions the double junction electrode works much better. Without the double junction electrode, the pH readings were erratic and nonreproducible for several hours even with the solutions protected from the atmosphere. We also find it necessary to recrystallize the salts (even the highest quality, reagent grade salts) because acid or base impurities can change the acidity of the reaction solutions, particularly since our acid catalyst is used at a very low concentration ($\sim 10^{-5}$ M). Failure to purify the salt magnifies the rate enhancement or inhibition depending upon whether the salt contains a trace of excess acid or base.

Studies by others on cation effects often report a reverse effect for the alkali metal salts to what we have observed (some see $K^+ < Na^+ < Li^+$ while we see $Li^+ < Na^+ < K^+$). In those cases where we have found such a reverse order from ours, the authors used a strong mineral acid at a significant concentration (0.1–1.0 M). The relatively high concentration of mineral acid is a significant electrolyte concentration to which is added the concentration of the neutral electrolyte. Thus the interaction of the mixed electrolyte may influence the ordering of the cation effect.

Our analyses of some recent data[10,11] show that their results are accommodated by some salts giving nicely linear plots for ln k vs. [salt] but not all. This same effect is observed for earlier results in the literature.[6–8] The work of Bronsted and Grove[5] for the hydrolysis of dimethyl acetal in the presence of salts is nicely correlated by a k vs. [salt] relationship.

It appears to us that there is no theoretical basis upon which to apply kinetic salt effects to reactions of this type (acetal hydrolysis) in water. The evidence calling to question the validity of the Debye–Huckel–Bronsted approach for the rationalization of specific salt effects is substantial,[18] at least for electrolytes used at real concentrations. Most workers who study salt effects on ion–molecular reactions use the Bronsted equation in spite of the fact that it predicts no salt effect for such systems ($Z_A Z_B = 0$). Furthermore, the equation is applied for salt concentrations far beyond its theoretical range which can be no more than about 0.1 M salt based upon the Debye–Huckel approximation. One of the more confusing aspects of work which attempts to interpret ion–molecule reactions by the Bronsted equation is that they usually observe specific salt effects for ln k vs. [salt] yet the Bronsted

Table IV. Influence of Concentration of Alkaline Earth Perchlorates on the Rate of Hydrolysis of Benzaldehyde Dimethyl Acetal[a]

| Salt molarity	k_2,[b] M^{-1} s^{-1} for			
	$Mg(ClO_4)_2$	$Ca(ClO_4)_2$	$Ba(ClO_4)_2$	$Sr(ClO_4)_2$
A. Lower Salt Concentration				
0.00	29.5	29.5	29.5	29.5
0.01		34.6		
0.02	34.5	37.0	34.8	35.0[d]
0.04	35.8	40.1	37.9	39.4[d]
0.06	38.2[c]			41.2[d]
0.08	40.5	44.1	41.6	44.3[d]
0.10		48.1		49.2[d]
Slope b	128.0	161.5	141.1	183.1
Intercept k_0	30.6	32.2	30.9	30.6
$q = b/k_0$	4.2	5.0	4.6	6.0
B. Higher Salt Concentration				
0.12		49.8		
0.16		51.9		
0.20	44.5		49.1[d]	
0.40	51.7	59.4	56.3	
0.60	55.8[d]	69.5	65.3	
0.80	63.6[c]	78.6	77.1	
Slope b'	30.6	41.7	46.5	
Intercept k_0'	38.6	44.5	38.7	
$q' = b'/k_0'$	0.79	0.94	1.20	

[a] The hydrolysis was conducted in water at 25.39 °C with $\sim 10^{-4}$ M perchloric acid catalyst. All values of acidity were determined by a pH meter. Each value reported is the average k of quadruplicate least-squares results except where noted. All values are least-squares values. [b] These values are the hydrolytic rate constants corrected to 1 M H_3^+O based upon the measured pH value. [c] Average of triplicate results. [d] Average of duplicate results.

equation predicts nonspecific effects.[18] Finally, we would note that change in slope of the k vs. [salt] plots at about 0.1 M salt appears to be an unreported effect. We do not think the effect is one of a fundamental change in the properties of the solution since we know of no solvent–electrolyte effects which undergo maxima or minima at about 0.1 M salt. At this point we have no experimental or theoretical leads to explain the effect which we have seen for every salt studied (except for $KClO_4$, which was limited by its low solubility).

The kinetic salt effects we observed are specific and cannot be interpreted simply in terms of activity coefficient changes.[18,19] The effects consistently fit eq 1 which is exactly of the form Winstein[20] found and exploited for the solvolyses of arenesulfonates in less polar solvents such as acetic acid. We do not believe that Perrin's model[21] is applicable to these acetal systems since his model assumes ion pairs for less polar solvents and requires the Debye–Huckel limitation of very dilute solutions. While the effects of salts on the kinetics of neutral molecule reactions are not understood, there are reports of their existence from the earliest days of organized chemistry to the present time.[22] Mechanism studies other than those due to Winstein's works on solvolyses have not properly taken neutral electrolytes into account.

One can readily postulate models to rationalize the specification and anion effects which are observed. For example, one could propose a direct interaction of the anion with the transition state. In this way the anion stabilizes the transition state while the cation as a counterion offsets the anion effect. However, one probably should not consider the ion effect to operate with unhydrated species and for this reason the

suggestion made by Olson and Tong[19] is attractive. Their proposal is that the anion serves to orient water molecules toward the positively charged transition state as well as serving to stabilize the developing transition state. An example could be
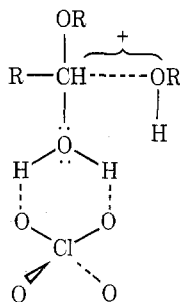
and this model can be used to explain very well the observed rate effects based on charge densities of the anion and the countercation. This explanation would require a direct involvement of the solvent in the transition state for acetal hydrolysis. All independent criteria developed for this system indicate that the solvent is not involved in the transition state,[4] but by no means has a final answer been found to this question. We do not at this time strongly advocate such a model since the explanation is essentially ad hoc in nature and is not quantitatively related to the fundamental properties of the solution or the solvent. We will not dwell upon this aspect of the results for this reason and because we are convinced that a great deal of experimental work must be performed for this and other systems as well as learning more about dielectric constants–salt effects[23] before one can hope to develop a sound theory for kinetic salt effects.

References and Notes

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(2) Taken in part from the M.S. Theses of D. B. Dennison and G. A. Gettys and the B.S. Thesis of D. Shepard, Department of Chemistry, Furman University.

(3) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution", 2d ed, Oxford University Press, London, 1947, p 1.

(4) E. H. Cordes and H. G. Bull, *Chem. Rev.*, **74**, 581 (1974).

(5) J. N. Bronsted and C. Grove, *J. Am. Chem. Soc.*, **52**, 1394 (1930).

(6) L. C. Riesch and M. Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935). Their data for the HCl-catalyzed hydrolysis of diethyl acetal does not follow a simple log *k* vs. salt plot but rather a more complicated hyperbolic relationship specific for each salt. We find their data sensibly linear for *k* vs. [salt] up to 1 M.

(7) C. F. Kautz and A. L. Robinson, *J. Am. Chem. Soc.*, **50**, 1022 (1928). We find their data to give essentially a linear plot of *k* vs. [salt] for LiCl, NaCl, KCl, and BaCl$_2$ even though they preferred a log *k* vs. [salt].

(8) J. N. Pearce and M. E. Thomas, *J. Phys. Chem.*, **42**, 455 (1938).

(9) F. A. Long and D. McIntyre, *J. Am. Chem. Soc.*, **76**, 3243 (1954).

(10) C. A. Bunton and J. D. Reinheimer, *J. Phys. Chem.*, **74**, 4457 (1970).

(11) H. G. Bull, K. Koehler, T. C. Pletcher, J. J. Ortiz, and E. H. Cordes, *J. Am. Chem. Soc.*, **93**, 3002 (1971).

(12) T. S. Davis, G. A. Gettys, and D. G. Kubler, *J. Org. Chem.*, **41**, note in this issue.

(13) All volumetric glassware was calibrated and all volumes reported are corrected.

(14) T. S. Davis, P. D. Feil, D. G. Kubler, and D. J. Wells, Jr., *J. Org. Chem.*, **40**, 1478 (1975).

(15) P. D. Feil, D. G. Kubler, and D. J. Wells, Jr., *Anal. Chem.*, **41**, 1908 (1969).

(16) We appreciate the suggestions of Professor E. Grunwald, Brandeis University, regarding the calibration of the pH measurement.

(17) We are grateful for advice from Professor R. G. Bates, University of Florida, on how to solve this problem.

(18) L. P. Hammett, "Physical Organic Chemistry", 2d ed, McGraw-Hill, New York, N.Y., 1970, Chapter 7, p 187.

(19) A. R. Olson and L. K. J. Tong, *J. Am. Chem. Soc.*, **66**, 1555 (1944).

(20) E. L. Allred and S. Winstein, *J. Am. Chem. Soc.*, **89**, 4012 (1967).

(21) C. L. Perrin and J. Pressing, *J. Am. Chem. Soc.*, **93**, 5705 (1971).

(22) Spohr, *Z. Phys. Chem. (Leipzig)*, **2**, 195 (1888); Lowenthal and Lenssen, *J. Prakt. Chem.*, **85**, 324 (1862); L. E. Bowe, *J. Phys. Chem.*, **32**, 291 (1927); P. Salomaa, A. K. Kankaapera, and M. Hahti, *J. Am. Chem. Soc.*, **93**, 2084 (1971), are some typical references.

(23) J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).