The liquid unsaturated acid, V, was not further examined, except in so far as one unsuccessful attempt at catalytic hydrogenation.

2-Methyl-2-phenylcyclopentylacetic Acid, VI.—The solid isomer of V was easily reduced in 95% yield to VI by shaking with hydrogen over Adams platinic oxide catalyst in acetic acid. The product boiled from 140 to 143° at 1 mm. An attempt to separate a pure isomer by fractional crystallization of the amides failed. The highest melting amide fraction melted from 90 to 92°.

Anal.[b] Calcd. for $C_{14}H_{18}O_2$: C, 77.1; H, 8.3. Found: C, 76.6, 76.5; H, 8.5, 8.6. Calcd. for $C_{14}H_{19}ON$: C, 77.4; H, 8.8; N, 6.5. Found: C, 77.4, 77.2; H, 8.6, 8.4; N, 6.5, 6.6.

4-Keto-1-methyl-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene, VII.—The acid chloride of VI was cyclized by stirring with a slight excess of aluminum chloride in benzene solution at 50 to 60° for forty-five minutes. The ketone, VII, b. p. 109–111° at 1 mm., was obtained in 90% yield. A part of the ketone isomer mixture was converted (quantitatively) into semicarbazones. On fractional recrystallization, a pure semicarbazone, m. p. 244–247° (dec.), was obtained. This was hydrolyzed to give a pure isomer, VII, which differed little in index of refraction and boiling point from the mixture of isomeric ketones, $n^{20}D$ (pure) 1.5650, (mixture) 1.5652. A 2,4-dinitrophenylhydrazone, m. p. 221.8–222.2° cor., of the pure ketone was prepared.

Anal.[b] Calcd. for $C_{15}H_{19}N_3O$: C, 70.0; H, 7.4; N, 16.3. Found: C, 70.2, 70.1; H, 7.1, 7.1; N, 16.4, 16.3. Calcd. for $C_{20}H_{20}N_4O_4$: C, 63.2; H, 5.3; N, 14.7. Found: C, 63.1, 63.1; H, 5.4, 5.4; N, 14.2. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.0. Found: for mixture of isomers, C, 83.6, 83.6; H, 7.9, 7.9. for pure isomer, C, 83.6, 83.5; H, 7.9, 7.9.

1-Methyl-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene, VIII.—A part of the pure ketone, VII (1.33 g.), was reduced by the modified Clemmensen method.[9] The pure hydrocarbon, VIII, was obtained in 70% yield as a colorless liquid, b. p. 128–132° at 11 mm., $n^{20}D$ 1.5472 (Kon[5] gives b. p. 128 at 12 mm., $n^{17.8}D$ 1.5479).

Anal.[b] Calcd. for $C_{14}H_{18}$: C, 90.3; H, 9.7. Found: C, 90.5, 90.3; H, 9.6, 9.7.

Summary

The synthesis of 4-keto-1-methyl-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene, VII, is described. Hydratroponitrile is alkylated with γ-iodobutyronitrile to yield the dinitrile of α-methyl-α-phenyladipic acid. Internal cyclization followed by hydrolysis and decarboxylation yields 2-methyl-2-phenylcyclopentanone. A two-carbon acid chain is introduced at the ketonic carbon by the usual procedure involving the Reformatsky reaction, dehydration, hydrolysis and reduction. Finally, the resulting acid is cyclized to the desired ketone by an intramolecular Friedel–Crafts reaction.

[9] Martin, THIS JOURNAL, 58, 1438 (1936).

COLUMBUS, OHIO RECEIVED MARCH 22, 1944

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Interpretation of the Effects of Salts on the Rates of Some Hydrolytic Reactions

BY A. R. OLSON AND L. K. J. TONG

In aqueous solutions, acetal, $CH_3CH(OC_2H_5)_2$, is stable enough at ordinary temperatures so that the "spontaneous" rate of hydrolysis to alcohol and aldehyde can be neglected.[1]

In the presence of hydrogen ions, the hydrolysis proceeds smoothly according to the first order equation

$$d \ln (A)/dt = \text{constant}$$

The addition of neutral salts to such an acid solution of acetal produces a change in the rate. It is this change which Brønsted[2] calls a "Medium Effect," and which he in the same article divides into a "primary kinetic salt effect" and a "secondary salt effect." The secondary effect influences the rate by changing the concentration of the hydrogen ions, *i. e.*, if a weak acid were present its dissociation in general would be changed by the addition of "inert" salts.

The primary salt effect involves the "kinetic activity factor" $\gamma_A\gamma_B/\gamma_X$ in the equation

$$R = kC_AC_B\,\frac{\gamma_A\gamma_B}{\gamma_X} \qquad (1)$$

for a reaction between A and B, where γ_A and γ_B are the activity coefficients of A and B, respectively, and γ_X the activity coefficient of some evanescent reaction complex. Setting $-\log \gamma = 0.5z^2\sqrt{\mu} + \beta\,\mu$ where z is the charge on a particle and μ is the ionic strength, the velocity equation (1) becomes

$$R = kC_AC_Be^{\mu(\beta_A + \beta_{H^+} - \beta_{X^+})}$$

for the acetal reaction. "This corresponds to a linear salt effect in the dilute range. As the β factor for the hydrogen ion is unusually large (and, therefore, larger than β_x) and for a non-charged molecule usually positive, we have reason to expect a positive salt effect in a hydrogen ion catalysis as actually found for such reactions."

The salt effects are indeed large—so large that we were led to believe that even if the above ideas are correct, some factors must be missing in the above rate expression, a conclusion to which Riesch and Kilpatrick[3] also came. These investigators, studying the hydrolysis of acetal in hydrochloric acid solution at 0°, concluded that "equation (1) is only approximately in agreement with experiment even in dilute solution."

We have, therefore, measured the rates of hydrolysis of acetal in a variety of solutions as well as those of dimethyl acetal and dipropyl formal. The latter react much more slowly than does

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[1] J. H. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 25, 59 (1929).

[2] J. N. Brønsted, *ibid.*, 24, 630 (1928).

[3] C. C. Riesch and M. Kilpatrick, *J. Phys. Chem.*, 39, 561 (1935).

acetal—the hydrolysis of the formal is so slow that it can be studied in 0.5 molar hydrochloric acid at 25°. In addition we have measured the rate of the base catalyzed decomposition of nitramide in some of the same solvents, and we have determined the activity coefficients of these reactants in many of the solutions.

Preparation and Purification of Materials.—The methods of preparation and purification of acetal and nitramide have been published.[4]

The dimethyl acetal and the dipropyl formal were prepared by permitting the alcohol and the aldehyde to react in the usual manner and then washing, drying and fractionating the product.

Rate Measurements.—The methods of following the rates of the acetal hydrolysis and the nitramide decomposition were discussed by Tong and Olson.[4] The dimethyl acetal procedures paralleled those for acetal. The formal reaction was so slow that it was carried out either in sealed or in stoppered flasks. The rate was then determined by analysis.

Determination of Activity Coefficients.—The activity coefficients of acetal and of dimethyl acetal usually were determined by obtaining their distributions between the saline solutions and benzene and then analyzing the separate phases by the bisulfite method. Sometimes it was more feasible to determine the distributions between water (or saturated benzoic acid solutions), and the saline solutions directly. In these cases air was bubbled back and forth in a closed system, the equilibrium being established through the vapor phase.

The analysis for acetal was conducted as follows:

Approximately 10 cc. of acetal was dissolved in 800 cc. of benzene. This was washed four times with equal volumes of very dilute sodium hydroxide, and then filtered through a cotton plug; 100 cc. of the benzene solution was then pipetted into 150 cc. of the aqueous salt solution, after both had separately been brought to the correct temperature and then shaken; 100 cc. of the aqueous phase then was removed, pipetted into a 400-cc. Erlenmeyer flask containing 10 cc. of 0.4 *N* sulfurous acid solution to which 1 cc. of 1 *N* hydrochloric acid had been added and allowed to stand overnight. The excess sulfurous acid then was titrated with 0.1 *N* triiodide solution to a starch end-point. Following this 20 cc. of a saturated sodium bicarbonate solution was added and the liberated sulfurous acid was titrated immediately with 0.01 *N* triiodide solution again using starch indicator. The first titration shows the excess of the sulfurous acid, the second the quantity of acetal. The concentration of acetal in the benzene phase was likewise determined by titration.

Dimethyl acetal and formal were analyzed for by the same method. Formal reacts slowly enough and it is sufficiently insoluble so that we could determine its solubility in the aqueous solutions. We then assumed that its activity coefficient was inversely proportional to its solubility.

In the nitramide distribution, carefully purified dibutyl ether was substituted for the benzene. To a mixture of 50 cc. of dibutyl ether and 30 cc. of saline solution in a separatory funnel, a small weighed amount of nitramide was added. The mixture was then shaken for about three minutes, the lower (aqueous) phase drawn off and 25 cc. of this pipetted into a closed reaction system into which 0.2 g. of sodium acetate could be dropped to decompose the nitramide. From the pressure readings extrapolated to allow for the slow decomposition of nitramide which occurred before the sodium acetate was added, the concentrations in the two phases were calculated. From the ratio of these concentrations, and the usual assumptions, the activity coefficients were obtained.

For many runs, it was convenient for us to use a solution which at all times was saturated with benzoic acid. The addition of salts to such solutions changes the concentration of hydrogen and benzoate ions. These changes have been calculated as shown in Table I. The data have been compiled from the work of various investigators by Dr. Leo Brewer of this Laboratory.

Table I

NaCl	(H‡)	NaCl	(H‡)
0.000	1.34×10^{-3}	0.40	1.58
.008	1.41	.50	1.56
.010	1.42	.60	1.53
.020	1.45	.75	1.48
.025	1.47	.80	1.47
.040	1.49	1.0	1.39
.050	1.50	1.2	1.32
.080	1.53	1.4	1.25
.100	1.54	1.5	1.21
.15	1.56	1.6	1.17
.20	1.58	2.0	1.03
.25	1.59	2.5	0.84
.30	1.59	2.75	.77
		3.0	.69

Experimental Data

Most of the data on the activity coefficients can be summarized by equations of the type $\log \gamma = K\mu$. In Table II we give the details.

Table II

Substance	Temp., °C.	Added electrolyte	Max. concn. of electrolyte	Method	*k*
Acetal	0	NaCl	2.78	Benzene distribution	0.302
Acetal	0	$NaNO_3$	3.43		.233
Acetal	0	$NaClO_4$	3.03		.225
Acetal	0	KCl	2.91		.300
Acetal	0	KNO_3	1.18		.220
Acetal	0	LiCl	2.68		.194
Acetal	0	$LiNO_3$	2.53		.130
Acetal	25	NaCl	2.36		.260
Acetal	25	KNO_3	2.00		.170
Acetal	25	NaCl	3.05	Vapor equilibrium	.260
Acetal	25	KNO_3	1.31		.170
Acetal	25	KAc	2.45		.102
Acetal	25	NaOH	2.15		.381
Dimethyl acetal	25	NaCl	2.56		.191
	25	NaCl	3.00	Benzene distribution	.191
Dipropyl formal	25	NaCl	2.00		.282
	25	HCl	0.50		.060
	25	KBr	2.00		.264
	25	KI	2.00		.121
	25	KCl	1.00		.279
Nitramide	25	NaCl	4.00	Dibutyl-ether distribution	.014
Nitramide	25	KCl	2.00		−.07

In addition the following data were taken which did not conform to equation $\log \gamma = Ku$.

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[4] L. K. J. Tong and A. R. Olson, This Journal, **63**, 3406 (1941); **65**, 1704 (1943).

TABLE III

Substance	Temp., °C.	Added electrolyte	Concn. of added electrolyte	Method	Log γ	γ
Acetal	25	NaBz	0.49	Vapor equilibrium	0.024	1.05
Acetal	25	NaBz	0.98		.026	1.06
Acetal	25	NaBz	1.50		.000	1.00
Acetal	25	NaBz	1.96		− .065	0.86

In Tables IV to VII, inclusive, we have collected the specific rate constants based on common logarithms for the hydrolyses and the decomposition reaction under various conditions. The units are moles per minute at unit concentration of hydrogen ion. In each case the run was followed almost to completion. When log A was plotted against t, the data could be represented very well by a straight line.

TABLE IV

THE SPECIFIC RATES, $\frac{r}{(H^+)} = k$, OF HYDROLYSIS OF ACETAL, DIMETHYL ACETAL AND DIPROPYL FORMAL, AND OF THE DECOMPOSITION OF NITRAMIDE IN SATURATED BENZOIC ACID SOLUTIONS CONTAINING THE SPECIFIED NaCl CONCENTRATIONS AT 25°

	Acetal		Dimethyl acetal		Dipropyl formal		Nitramide	
NaCl	$r \times 10^3$	$r/(H^+)$	$r \times 10^3$	$r/(H^+)$	$r \times 10^3$	$r/(H^+)$	$r \times 10^3$	$r/(Bz^-)$
0.000	46.0	34.3	9.60	7.16	3.64	2.72	0.84	0.627
.008			10.39	7.36	4.00	2.83		
.010								
.020			10.76	7.40	4.19	2.88		
.025							.85	.58
.040	53.0	35.6			4.40	2.95		
.050			11.71	7.78				
.080			12.4	8.10				
.100	63.0	40.9			5.19	3.36		
.150			13.8	8.83				
.20	67.6	42.7			5.81	3.68		
.25	70.6	44.3						
.30			15.8	9.96				
.40	76.2	48.2			7.39	4.67	.88	.56
.50	79.0	50.6						
.56			19.2	12.4				
.60	85.0	55.1						
.80	99.0	67.3	22.0	15.0				
1.00	105.6	76.3			10.78	7.74	.83	.60
1.20			26.8	20.3				
1.60			30.8	26.2				
2.00			35.0	34.0	17.4	16.9	.60	.58
2.50			41.1	48.9				
2.75			43.6	56.6				
3.00			47.7	69.1			.41	.59

TABLE V

THE SPECIFIC RATES, $\frac{r}{(H^+)} = k$, OF HYDROLYSIS OF ACETAL AND OF DECOMPOSITION OF NITRAMIDE AT 25° IN SOLUTIONS WHICH ARE KEPT SATURATED WITH BENZOIC ACID AND WHICH CONTAIN THE INDICATED CONCENTRATIONS OF SODIUM BENZOATE AND SODIUM CHLORIDE

SODIUM BENZOATE = 0.01066 M

	Acetal		Nitramide	
NaCl	$r \times 10^3$	$r/(H^+)$	$r \times 10^3$	$r/(Bz^-)$
0.00	6.65	35.7	6.48	0.597
.0229	7.72	38.2		
.040			6.47	.596
.20	10.67	47.2	6.51	.598
.40	12.97	56.4		
.60	14.03	65.0	6.56	.604
1.00	15.97	89.8	6.70	.618
1.40	16.85	117	6.55	.606
2.00	17.5	177	6.76	.629
3.00	16.72	376	6.92	.646

TABLE VI

SODIUM BENZOATE = 0.40 M

	Acetal		Nitramide	
NaCl	$r \times 10^3$	$r/(H^+)$	$r \times 10^3$	$r/(Bz^-)$
0.00	2.16	38.5	24.5	0.611
.20	3.02	48.2		
.40	3.54	56.6	24.4	.610
.60	3.84	66.3		
.80			24.2	.605
1.00	4.26	90.0	25.0	.625
1.50	4.58	129		
2.0			25.3	.635
2.10	4.69	200		
2.74	4.49	310		
4.00			25.8	.645

TABLE VII

THE SPECIFIC RATES OF HYDROLYSIS OF DIPROPYL FORMAL AT 25° IN SOLUTIONS HAVING THE INDICATED CONCENTRATIONS OF SPECIFIED SALTS AND HCl

NaCl	0.01 M HCl	0.05 M HCl	0.5 M HCl
	$k \times 10^3$		
0.00	2.82	3.04	4.62
.08	3.52	3.26	
.16			5.42
.20	3.81	3.88	
.40	4.60	4.87	
.48			7.12
.60	5.50	5.80	
.80	6.60		9.46
1.00	8.13	8.31	
1.20			13.04
1.60	12.86	13.06	
2.00	18.8	17.9	
1 M NaCl	8.13		
1 M KCl	7.34		
1 M KBr	9.88		
1 M KI	13.7		

Discussion

If we assume Brønsted's equation to be correct, we can set the specific rate constants which we have tabulated equal to $k'\gamma_A\gamma_{H^+}/\gamma_{X^+}$ for the hydrolysis reactions and to $k'\gamma_{Na}\gamma_{Bz^-}/\gamma_{X^-}$ for the nitramide decomposition. In the saturated benzoic acid solution the ionic strength is only 1×10^{-3} when the added salt is zero. The activity quotient, therefore, cannot differ much from unity. In Fig. 1 we have plotted k/k_0 and $k/k_0\gamma_A$ for the hydrolyses of acetal, dimethyl acetal, and dipropyl formal at 25° in saturated benzoic acid solutions containing sodium chloride as the added salt, against the concentration of the salt. k_0 is the specific rate when the sodium chloride concentration is zero. While for the sake of clarity only one curve was completed to the origin, the

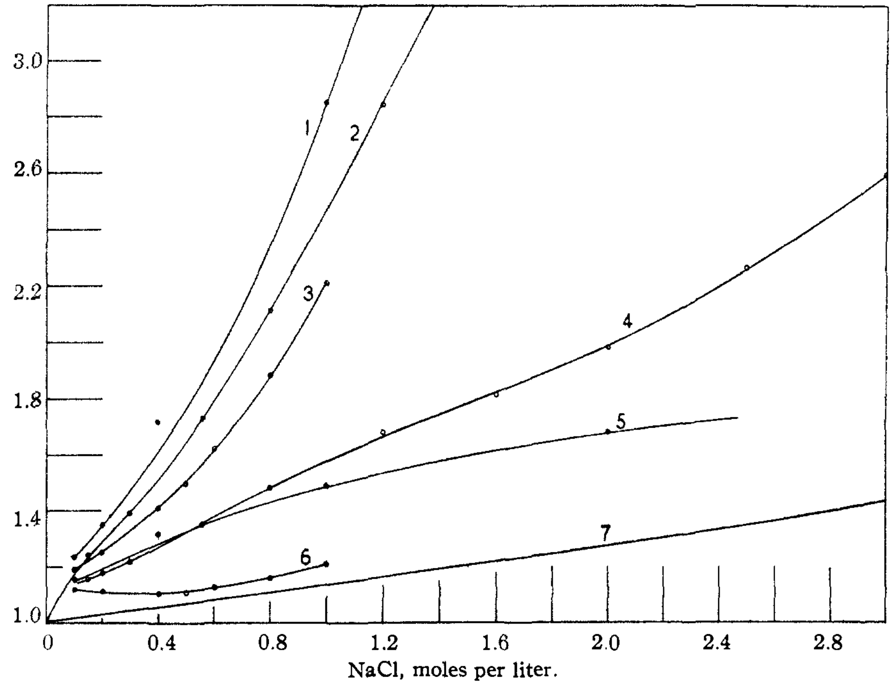

Fig. 1.—1, k/k_0 dipropyl formal; 2, k/k_0 dimethyl acetal; 3, k/k_0 diethyl acetal; 4, $k/k_0\gamma$ dimethyl acetal; 5, $k/k_0\gamma$ dipropyl formal; 6, $k/k_0\gamma$ diethyl acetal; 7, $\gamma\mathrm{Li}^+/\gamma\mathrm{K}^+$.

other curves resemble the one shown. The quantity $k/k_0\gamma_A$ should be equal to $\gamma_{H^+}/\gamma_{X^+}$.

When some of this material was presented at a symposium,[5] the statement was made from the floor, that $k/k_0\gamma_A$ did not differ from unity by more than $\gamma_{Li^+}/\gamma_{K^+}$ did under the same conditions. We have, therefore, calculated $\gamma_{Li^+}/\gamma_{K^+}$ for small quantities of these salts in the indicated sodium chloride solutions.[6] The data were taken from Robinson and Harned.[7] We have plotted these values as the lowest curve in Fig. 1. The lack of agreement is obvious. Erroneous as the statement was, it nevertheless serves a useful purpose in setting an upper limit to what we might expect from such a ratio of activity coefficients—a quantity which otherwise is limited only by wishful thinking. We are forced to conclude, therefore, that even if such a quotient of activity factors contributes to the rate, its contribution is small compared to the effect of some other factor or factors.

The rapid changes in the graph near the origin in Fig. 1 will be discussed in connection with the rates in hydrochloric acid solutions.

In the activity theory of reaction rates the velocity constant k can be expressed as $k_A = k_A' \gamma_A a_{H^+}$ for a first-order reaction catalyzed by hydrogen ion and for a first-order reaction catalyzed by benzoate ion $k_B = k_B'\gamma_B a_{Bz^-}$.

The ratios of the rates, measured in some salt solution, k_s, to the rate measured in some solution of very low ionic strength, k_0, becomes

$$\frac{1}{\gamma_A}\frac{(k_s)}{(k_0)_A} = \frac{(a_{H^+})_s}{(a_{H^+})_0}$$

and

$$\frac{1}{\gamma_B}\frac{(k_s)}{(k_0)_B} = \frac{(a_{Bz^-})_s}{(a_{Bz^-})_0}$$

In a saturated benzoic acid solution the product $a_{H^+}a_{Bz^-}$ is constant as a salt is added and therefore the product

$$\frac{1}{\gamma_A}\frac{(k_s)}{(k_0)_A}\,\frac{1}{\gamma_B}\frac{(k_s)}{(k_0)_B}$$

is a constant no matter how the individual ion activities change if this theory is correct.

In Fig. 2 we have plotted $(1/\gamma)(k_s/k_0)$ for dimethyl acetal and for nitramide as well as the product of these quantities, as sodium chloride is added to the solution at 25° which always is kept saturated with benzoic acid. The nitramide rate has been corrected for the spontaneous rate according to the data of Marlies and LaMer.[8] The graph of the product should be a horizontal line if the assumed mechanisms are correct and if the activity theory holds.

Figure 1 likewise shows the prominence that is accorded to a small change in a slow reaction when we plot the ratio of rates with or without a correction for the activity of the non-electrolyte. The change in the formal rate is only one-eighth of that of the acetal rate at 1 *M* sodium chloride, but the change in the ratio for formal is almost

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[5] A. C. S. Symposium, Buffalo, N. Y., Aug., 1942.

[6] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Harned, This Journal, **48**, 326 (1926).

[7] R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 442 (1941).

[8] C. H. Marlies and V. K. LaMer, This Journal, **57**, 1812 (1935).

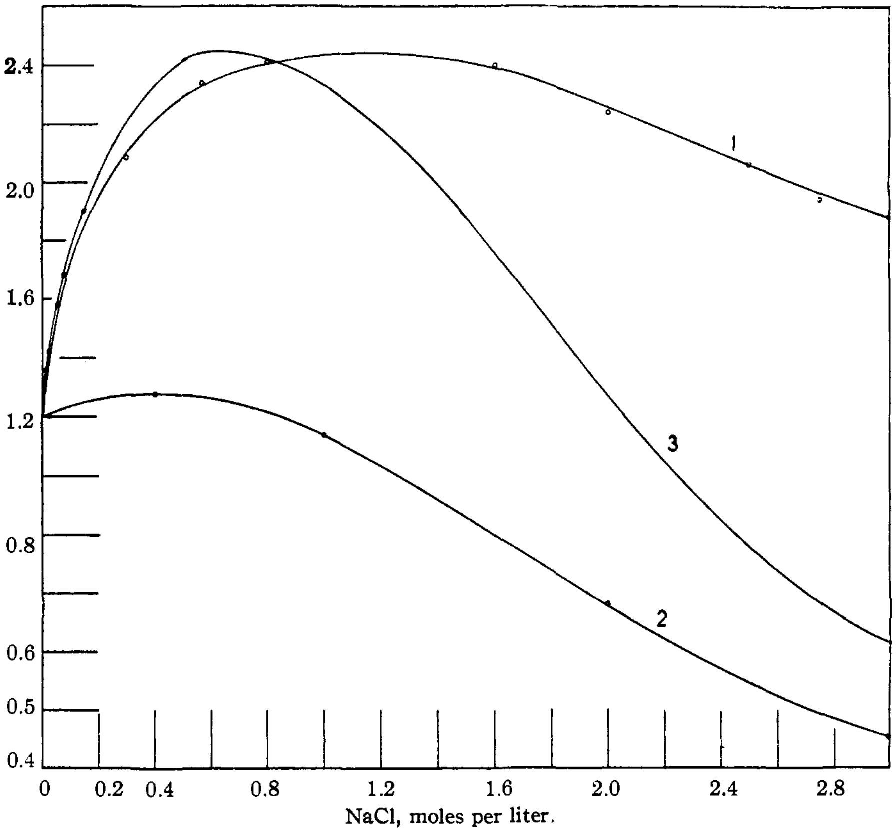

Fig. 2.—1, $\frac{1}{\gamma_A}\left(\frac{k_s}{k_0}\right)_A$; 2, $\frac{1}{\gamma_B}\left(\frac{k_s}{k_0}\right)_B$; 3, $\frac{1}{\gamma_A}\left(\frac{k_s}{k_0}\right)_A \times \frac{1}{\gamma_B}\left(\frac{k_s}{k_0}\right)_B$.

half again as much as that of the acetal ratio. We will, therefore, plot rate differences instead of rate quotients. For the same reaction in different salt solutions this change is equivalent merely to a change in the scale of plotting.

This change in graphing is based also on a conclusion which will be discussed in some detail below, *i. e.*, the main change in the observed rate of reaction on the addition of "inert" salts may be due to changes in the number and the character of the solution complexes of the substrate. The total number of complexes will not be changed by the addition of salt unless the substrate is subject to some association, but if the salt makes new types of solvation complexes possible, the number of each type will be changed by such an addition. If the specific rate of reaction of the new type is greater than that of the old, there will be an increase in observed rate, if it is less, there will be a decrease.

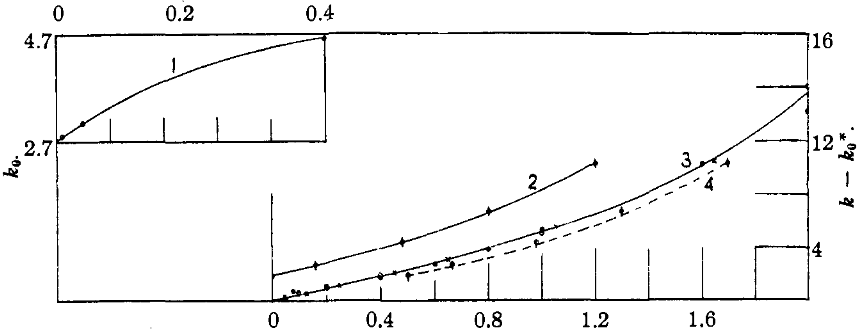

Fig. 3.—1, Variation of k_0 for dipropyl formal with concentration of HCl; 2, $k - k_0^*$ in 0.5 M HCl *vs.* concentration of NaCl; 3, $k - k_0^*$ in (a) satd. HBz + NaCl indicated by ○ (b) 0.01 M HCl + NaCl indicated by ● (c) 0.05 M HCl + NaCl indicated by × *vs.* total electrolyte concentration; 4, $k - k_0^*$ in 0.5 M HCl + NaCl *vs.* total electrolyte concentration.

The hydrolysis of dipropyl formal has been measured in saturated benzoic acid solutions and in 0.01, 0.05 and 0.50 M hydrochloric acid solutions at 25°. A glance at the specific rate constants in Table VII shows that value of the constant increases with the concentration of the hydrogen ion. In Fig. 3 this has been shown graphically. In Fig. 3 we likewise have plotted $k - k_0$ against the ionic strength for these reactions, where k_0 is the specific rate constant for the

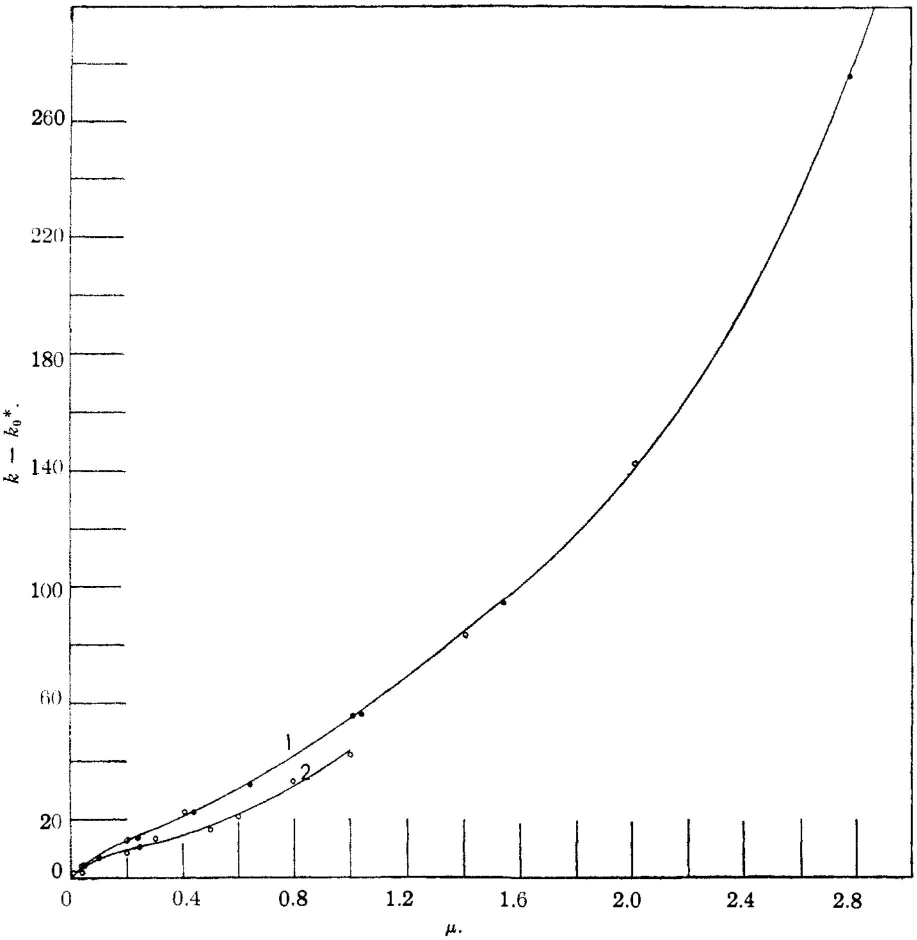

Fig. 4.—Variation of $k - k_0^*$ with μ for acetal. Solutions are saturated with HBz and contain NaCl + (a) 0.01066 M NaBz (open circles Curve 1), (b) 0.04 M NaBz (filled circles Curve 1), and (c) no NaBz (Curve 2).

0.0013 M hydrogen ion (saturated benzoic acid) solution. The agreement between the sets of data for the three low hydrogen ion solutions is excellent. If we plot against the sodium chloride concentration, this agreement between the three low acid concentrations will not be disturbed, but the 0.5 M run will be transferred to the upper curve. This in effect recognized the dual function of the hydrochloric acid, *i.e.*, as a catalyst and as an "inert" electrolyte. To get complete agreement between all the runs, it is necessary to assume that hydrochloric acid is only four-fifths as effective an electrolyte as is sodium chloride at these concentrations. At low concentration it seems to be much more effective. This appears to be the explanation of the hump in curves in Fig. 1 near the origin. Here we have allowed for the change in the hydrogen ion concentration with the ionic strength so far as its catalytic effect is concerned when we calculated the specific rate constants, but no allowance was made for the "salt effect" due to the increased ionization of benzoic acid.

In Fig. 4 we have plotted $k - k_0$ *vs.* μ for the rate of hydrolysis of acetal at 25° in saturated benzoic acid solution containing (a) no added sodium benzoate, (b) 0.01066 M sodium benzoate, and (c) 0.040 M sodium benzoate. Sodium chloride is the inert salt. k_0 is the specific rate in the saturated benzoic acid solution with no added benzoate or chloride. The agreement between curve b and curve c is remarkable when we recall that each point is obtained by taking the difference between two rather large numbers, each of which is obtained by dividing a measured rate by a small number. The lack of agreement between curve c and the others is not fully explained. It may be due to experimental difficulties with the very fast rates which obtain in unbuffered benzoic acid solutions.

The "hump" near the origin again is very noticeable. The agreement shown in these plots proves that all except the fastest acetal rates are proportional to the first power of the hydrogen ion concentration if its concentration is not high enough to contribute appreciably to an "electrolyte" effect.

Figure 5 shows the effect which the addition of

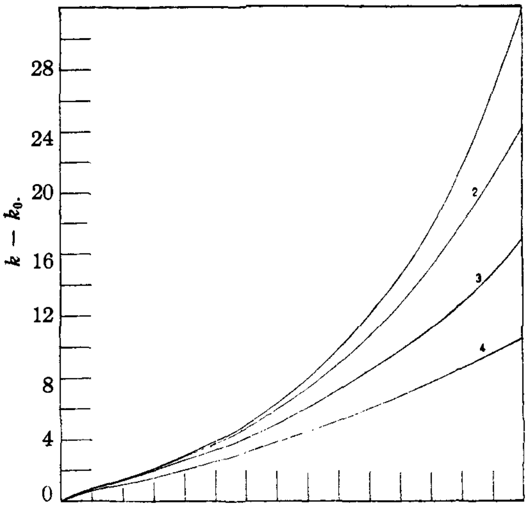

Fig. 5.—$k - k_0$ (for acetal) in 0.01 M HCl at 0° containing 1, LiCl; 2, NaCl; 3, KCl; 4, $NaNO_3$.

salts has on the rate of acetal hydrolysis in 0.01 M hydrochloric acid solutions at 0°. The rate data are taken from an article by Riesch and Kilpatrick.[3] In Fig. 6 we have plotted the same data as used in Fig. 5 except that we have divided the increase in the rate by the activity coefficient of acetal. The rate of hydrolysis is about 50% greater in 3 M sodium chloride solution than it is in 3 M potassium chloride solution; the activity coefficient of acetal is the same.

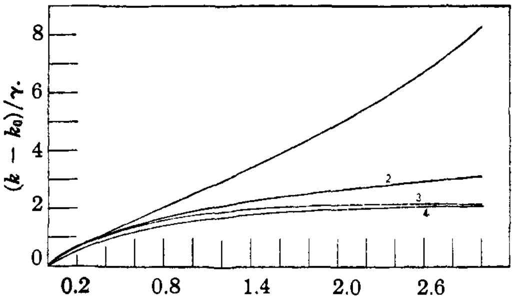

Fig. 6.—$(k - k_0)/\gamma$ (for acetal) in 0.01 M HCl at 0° containing 1, LiCl; 2, NaCl; 3, KCl; 4, $NaNO_3$.

Introducing the activity coefficient of acetal gives no clue as to why the rates in these solutions should differ. On the other hand, it does not obscure anything since the activity coefficient is the same in the two solutions. However, if we compare the rate in 3 M lithium chloride solution with that in 3 M sodium chloride solution we see that the division by γ_A multiplies a 20% difference by a factor greater than ten. It is obvious, therefore, that the rate does not involve the activity coefficient of the acetal, at least not in the simple way postulated by the Brønsted equation, *i.e.*, the mode of escape represented by the reaction is not proportional to the mode of escape measured by the vapor pressure of the acetal.

It is for reasons such as these that we proposed[5] to set the rate of a reaction proportional to the rate of diffusion of reaction domaines, the number and to some extent the reactivity of the domaines changing with the salt concentration and with the character of the salt. At that time we showed that it was possible to describe a number of rates by empirical equations of the type $R = (A - Be^{-f(\mu)})e^{-f'(\mu)}$ where the functions $f(\mu)$ and $f'(\mu)$ are simple power series limited to the first term or two. The accuracy in the most dilute solutions was not sufficient to include or exclude the term in $\mu^{1/2}$. It must be emphasized that these equations like the hyperbolic equations of Riesch and Kilpatrick are empirical and so they will not be discussed further at this time. Of more import is the fact that hydroxide ion catalyzed reactions are slowed up by the same salts which speed up the hydrogen ion catalyzed reactions as can be seen by referring to Fig. 7 which is based on the work of Åkerlöf.[9]

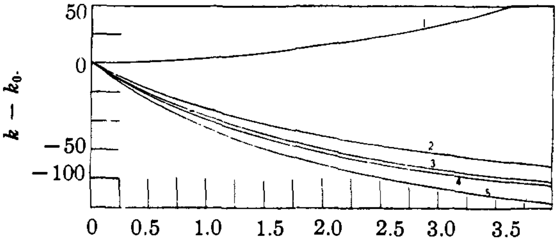

Fig. 7.—$k - k_0$ for diacetone alcohol in 0.10 M NaOH containing 1, KF; 2, KCl; 3, KBr; 4, NaCl; 5, NaBr.

In aqueous solutions acetal probably is solvated, the hydrogen from the water molecules being associated with the acetal oxygens. The first step in the hydrolysis of acetal is a reaction between hydrogen ion and such a solvation complex to form semi acetal, alcohol, and hydrogen ion. The semi acetal then reacts very quickly to form alcohol and aldehyde.

If an "inert" salt is added to such a solution, the salt ions will polarize the water molecules about them, the positive ions orienting the hydrogens outward, and the negative ion the oxygens outward. The degree of ionic character acquired by the water molecules in this process depends on the size and charge of the ions—the smaller the ions the greater the effect.

The association of such a positive ion complex with an acetal molecule will impart to it some degree of semi acetal character which will enable hydrogen ions to react more readily at the other oxygen.

We think of the rate, therefore, as made up of two rates both involving hydrogen ions. The first is the reaction between hydrogen ions and the normally solvated acetal having the specific rate k_1. The second is the reaction between hy-

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(9) G. Åkerlöf, THIS JOURNAL, 48, 3046 (1926).

drogen ions and the acetal-polarized water complex whose specific rate is k_2f (salt).

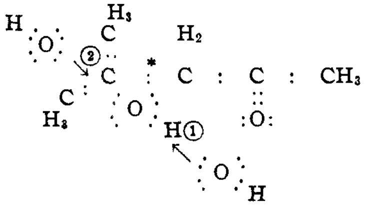
The above reactions involve the addition to a carbon atom of hydroxide ion from water. We might, therefore, expect that negative ions which polarize water so as to render it more hydroxide like in character, to accelerate the reaction. The opposite occurs. The predominant effect of negative ions is one of interference with the above processes, and so we find that for a given positive ion, the larger the negative ion the faster the reaction. The specific rate of hydrolysis of dipropyl formal at 25° in molar potassium chloride is 4.5×10^{-3} while in molar potassium bromide it is 7.0×10^{-3}.

Assumptions similar to the above were used by Olson and Miller[10] to explain the salt effects which they observed in the hydrolysis of optically active β-butyro-lactone. They stated that the increased rate of hydrolysis on the addition of carbonate ions cannot be due mainly to an increased activity of the lactone for, if so, the optical activity of the product would not be changed. They found that it was necessary to assume the speeding up of at least two reactions which changed not only absolutely but also relatively.

The hydrolysis of diacetone alcohol, which is catalyzed by hydroxide ion, also shows large salt effects, but these are opposite in direction to those of the acetal hydrolysis.

We, therefore, assume that the mechanism of the reaction involves the synergistic action of water molecules polarized by negative ions and the antagonistic action of water molecules polarized by positive ions.

The primary action of hydroxide ion may consist either in the removal of the carbinol hydrogen (1), or in the addition onto the carbinol carbon (2)



displacing to the right the pair of electrons marked by an asterisk. The negative ion-water complex then could give assistance by attacking at the point not engaged by the hydroxide ion. A positive ion water complex might produce interference by tending to add to the carbinol oxygen thus reducing the electron displacement.

The nitramide decomposition presents an interesting case of a spontaneous water reaction which shows a large neutral salt effect, and a base (benzoate ion) catalyzed rate which is rather insensitive to the addition of salts. The specific rate of the catalyzed reaction does increase slightly as the concentration of the benzoate ion is increased from 0.0013 (saturated benzoic acid) to 0.04. This may be due to the fact that nitramide is a weak acid and so the concentration of nitramide ion increases in the same ratio even though it remains small. If the reactivity of nitramide ion were greater than that of nitramide, the charge in the specific rate of the catalyzed reaction would be accounted for. The big decrease in the spontaneous reaction may be due merely to the large amount of water about the positive ion which is oriented with the hydrogen outward and, therefore, should not lead to a reaction.

Conclusion

1. The rates of hydrolysis of acetal, dimethyl acetal and dipropyl formal, and the rate of decomposition of nitramide have been measured in a variety of solutions.
2. The activities of these substances in many of the same solutions have been measured.
3. It has been shown that the salt effects are not in conformity with the Brønsted equation.
4. By taking the product of the rates of the acid catalyzed hydrolysis of dimethyl acetal and the base catalyzed decomposition of nitramide in saturated benzoic acid solution it has been shown that the activity theory of reaction rates is not in agreement with the results.
5. By considering the three acid catalyzed rates, we have concluded that the rate is not inversely proportional to the activity coefficient of the substrate.
6. A theory of salt effects based upon the orientation and polarization of water molecules by salt ions has been formulated.
7. The theory has been applied to the above reactions and to the base catalyzed hydrolysis of diacetone alcohol to postulate mechanisms for the reactions.

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RECEIVED MAY 10, 1944

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[10] A. R. Olson and R. J. Miller, THIS JOURNAL, **60**, 2687 (1938).