

# Notes

## Kinetic Salt Effects and Substituent Effects on Rates of Dimethyl Acetal Formation for Benzaldehydes<sup>1</sup>

T. S. Davis,<sup>2</sup> G. A. Gettys,<sup>2</sup> and D. G. Kubler\*

Department of Chemistry, Furman University,  
Greenville, South Carolina 29613

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We recently reported<sup>3</sup> the effects of para substituents on rates and equilibria for benzaldehyde–benzaldehyde dimethyl acetal interconversions. In that study, which was made in 95% methanol–5% water, a substantial kinetic salt effect was observed. If one compares reactivities for the hydrolysis of a series of acetals (or for the formation of the acetals from the aldehydes) at some given salt concentration, it is not obvious that the rate variations observed can be attributed uniquely to the substituents. Part of the relative change in rate is due to the substituent change and part is due to kinetic salt effects. The interrelationship between these effects has not been established and must be understood before one can be sure of interpretations for structural studies.

We have studied the kinetics of dimethyl acetal formation for para-substituted benzaldehydes at 25.39 °C in 95% methanol–5% water in the presence of various amounts of sodium perchlorate. The catalyst was perchloric acid used at about 10<sup>-4</sup> M. These results are reported along with a preliminary study of the influence of alkali metal perchlorates on the hydrolysis of benzaldehyde dimethyl acetal in water at 25.39 °C.

### Experimental Section

**Preparation and Purification of Reagents. Methanol** (Union Carbide Chemicals Co.) was purified in 3-l. batches by the method of Lund and Bjerrum.<sup>4</sup> Each batch was distilled on a 1.5 × 45 cm protruded metal packed column until the transmittance was 97% or better against a specially purified sample of water at 256 nm. In all cases the water content (Karl Fischer) was less than 0.01% and was usually 0.005% or less.

**95% Methanol–5% Water** was prepared in kilogram lots by taring a 2-l. flask on a solution balance (±0.2 g) and adding 950 g of spectral

grade methanol and 50.00 ml (pipet) of spectral grade water (distilled and deionized).

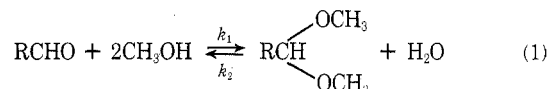
**Salt Solutions.** The LiClO<sub>4</sub>, NaClO<sub>4</sub>, and KClO<sub>4</sub> (G. Frederick Smith Co.) were recrystallized from water three times and dried at 120 °C for 1–2 days. Samples were analyzed for residual water content by the Karl Fischer method and the weights of salt needed for 0.1 M solutions corrected for the water contents. The pH of each batch of purified salt was measured as a function of concentration in water and found not to change from that of water.

**Perchloric acid solution** was prepared by adding 2–3 ml of concentrated perchloric acid (J. T. Baker) to about 500 ml of 95% methanol–5% water. The acid solution was standardized by titration with aqueous KOH solution (phenolphthalein end point.) The acid and base solutions were standardized biweekly. A similar procedure was used for perchloric acid in water.

**Aldehydes.** Benzaldehyde (J. T. Baker), *p*-tolualdehyde, furfural, and *p*-anisaldehyde (Columbia Organic Chemicals Co.) were each washed three times with 5% sodium bicarbonate and once with water, dried over sodium sulfate and distilled under vacuum. The aldehydes were collected in melting point capillary tubes and sealed under vacuum for reasons, and by the procedure, described previously.<sup>3</sup> The weighed, sealed tubes were crushed under the surface of the solvent in a volumetric flask. The flask was filled to the mark with solvent. The aldehyde solution was diluted for the kinetic runs and to check the extinction coefficients. Repeated preparations of the solutions by the sealed tube method throughout this work gave extinction coefficients which varied by less than ±1%. *p*-Bromobenzaldehyde was purified by recrystallization from hexane and then vacuum sublimed.

**Rate Measurements.** The rates at which the aldehydes disappeared were followed by measuring the carbonyl absorptions with a Beckman DU spectrophotometer as a function of time. The details of the system used and the operational method have been described.<sup>3</sup>

The first-order rate constants were calculated for the equilibration



by means of standard expressions modified for our analytical system. For a reversible first-order process for acetal formation corrected for hydronium ion concentrations (using  $[\text{H}_3^+\text{O}] = [\text{HClO}_4]$ )

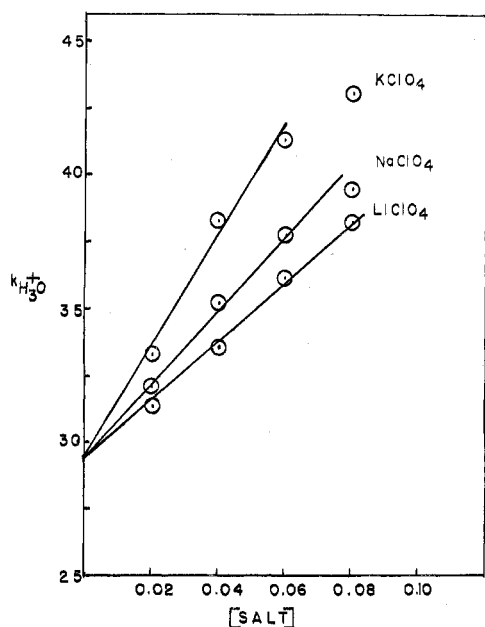
$$k_1 = \frac{-(\text{slope})(A_0 - A_\infty)}{60A_0[\text{H}_3^+\text{O}]} \text{M}^{-1} \text{s}^{-1} \quad (2)$$

with slope = ln(A – A<sub>∞</sub>) vs. time (min); A, A<sub>0</sub>, and A<sub>∞</sub> are the measured absorptions at time *t*, at zero time, and at infinite time, re-

Table I. Kinetic Salt Effects on the Formation of Benzaldehyde Dimethyl Acetals<sup>a</sup>

Aldehyde (registry no.)	[HClO <sub>4</sub> ] <sup>b</sup>	[NaClO <sub>4</sub> ] <sup>b</sup>	k <sub>1</sub> , <sup>c</sup> M <sup>-1</sup> s <sup>-1</sup>	Slope, <sup>d</sup> b	Intercept, <sup>d</sup> k <sub>0</sub>	q <sup>e</sup>
<i>p</i> -Anisaldehyde (123-11-5)	7.286 × 10 <sup>-5</sup>	0.010	6.05 ± 0.25	14.65	5.88	2.49
		0.050	6.58 ± 0.07			
		0.070	6.91 ± 0.33			
		0.100	7.35 ± 0.07			
<i>p</i> -Tolualdehyde (104-87-0)	1.626 × 10 <sup>-4</sup>	0.010	3.71 ± 0.01	9.74	3.58	2.72
		0.050	3.97 ± 0.02			
		0.070	4.31 ± 0.10			
		0.100	4.61 ± 0.09			
Benzaldehyde (100-52-7)	2.689 × 10 <sup>-4</sup>	0.010	1.42 ± 0.02	3.61	1.39	2.60
		0.050	1.53 ± 0.01			
		0.064	1.62 ± 0.01			
		0.100	1.76 ± 0.02			
<i>p</i> -Bromobenzaldehyde (1122-91-4)	3.627 × 10 <sup>-4</sup>	0.010	0.500 ± 0.009	1.30	0.489	2.60
		0.050	0.555 ± 0.003			
		0.070	0.578 ± 0.001			
		0.100	0.621 ± 0.008			

<sup>a</sup> Rates determined in 95% methanol–5% water at 25.39 °C by following spectrophotometrically the disappearance of the carbonyl group at λ<sub>max</sub> in the uv. <sup>b</sup> Concentration in mol l.<sup>-1</sup>. <sup>c</sup> k<sub>1</sub> is the rate constant for acetal formation corrected for  $[\text{H}_3^+\text{O}] = [\text{HClO}_4]$ . <sup>d</sup> The salt effect follows the expression  $k_{\text{H}_3^+\text{O}} = k_0 + b[\text{salt}]$  and the values given here are least-squares terms. <sup>e</sup> q = b/k<sub>0</sub>.



**Figure 1.** Plot of  $k_{H_3O^+}$  vs. concentration of salt for  $LiClO_4$ ,  $NaClO_4$ , and  $KClO_4$  for the hydrolysis of benzaldehyde dimethyl acetal in water at 25.39 °C. The lines were placed by least squares.

spectively.<sup>3</sup> All rate constants were calculated by the method of least squares. One may also calculate the reverse rate constants,  $k_2$ , from this same data if desired,<sup>3</sup> but these values are not reported.

### Results and Discussion

The influence of the concentration of sodium perchlorate (0.0–0.10 M) has been studied on the rates of formation of the dimethyl acetals of *p*-anisaldehyde, *p*-tolualdehyde, benzaldehyde, and *p*-bromobenzaldehyde. The reactions were conducted in 95% methanol–5% water at 25.39 °C with perchloric acid catalyst. The results are summarized in Table I. The kinetic salt effect is summarized by the expression

$$k_{H_3O^+} = k_0 + b[\text{salt}] \quad (3)$$

We have reported<sup>3</sup> that the rates of acetal formation increase as the electron-donating capability of the para substituents increase. Paralleling this rate–structure effect is the kinetic salt effect which the slope term,  $b$ , represents. The values of  $b$  given in Table I are seen to increase as the electron-donating capability of the para substituent increases. It is apparent that the methoxy group has a much greater slope than the bromo group and presumably the slope would be zero for a substituent having a zero rate.

Given the form of the kinetic salt effect for this reaction, are the relative rates for various substituents the same as long as the rates are measured at the same salt concentration? The results show a positive answer to this question. This fact may be seen by taking ratios of the rate expressions (eq 3) for various substituents. The results show an average  $q$  value of 2.60 and represent the slope of a line obtained by plotting the  $b$  terms vs. the intercepts for the para-substituted benzaldehydes. On this basis one may be confident of interpretations of relative rates for substituents providing they are made at the same electrolyte concentration.

Most results of kinetic salt studies of this type have been performed in water and usually the data have been treated by a  $\log k$  vs.  $[\text{salt}]$ .<sup>5,6</sup> It seemed possible that the effects we observed reflected a methanol–water–salt interaction rather than a reactant–salt interaction. Because of this possibility and because we had observed what to us seemed to be a specific salt effect in methanol–water we extended this study to

the hydrolysis of benzaldehyde dimethyl acetal in water. The reaction was conducted at 25.39 °C with perchloric acid catalyst ( $\sim 10^{-5}$  M) used with various amounts of lithium, sodium, or potassium perchlorates.

The preliminary results of the hydrolysis reaction in water are summarized in Figure 1. The plots of  $k_{H_3O^+}$  vs. salt concentration are satisfactorily linear with corrections coefficients of  $r = 0.986$  for  $KClO_4$ ,  $r = 0.995$  for  $NaClO_4$ , and  $r = 0.997$  for  $LiClO_4$ . The kinetic salt effect increases in the order  $Li < Na < K$ . These results show that the salt effect observed for acetal hydrolysis in water is of the same kind as we observed for acetal formation in methanol–water.

The 0.08 M salt values for  $KClO_4$  and  $NaClO_4$  are considerably off the line (although these values were included in the least-squares correlations). This deviation occurs because of a significant change in slope which is observed at about 0.1 M salt for all salts studied to date. The salt effects observed are ion specific and while the results presented demonstrate specific cation effects, specific anion effects have also been observed. Details of this kinetic salt effect for acetal hydrolysis in water are to be reported in more detail. We would note only that the results are of the same form Winstein has observed for the solvolysis of arenesulfonates.<sup>7</sup>

**Registry No.**— $LiClO_4$ , 7791-03-9;  $NaClO_4$ , 7601-89-0;  $KClO_4$ , 7778-74-7; benzaldehyde dimethyl acetal, 1125-88-8.

### References and Notes

- (1) Grateful acknowledgment is given to the National Institutes of Health for a grant (ROI-AM-1124) in support of this work.
- (2) Taken in part from the M.S. Theses of T. S. Davis and G. A. Gettys, Department of Chemistry, Furman University.
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- (7) E. L. Allred and S. Winstein, *J. Am. Chem. Soc.*, **89**, 4012 (1967), and previous papers.

### Acidity Constants of Some 5-Substituted 3-Furoic Acids<sup>1</sup>

Julio P. Ferraz and Luciano do Amaral\*

*Instituto de Química da Universidade de São Paulo, Caixa Postal 20780, São Paulo, SP., Brazil*

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A great number of examples of the application of Hammett's equation to series of reactions of several aromatic heterocyclic systems are found in the literature.<sup>2</sup> In the furanic system, in particular, owing to the difficulty found in the synthesis of  $\beta$ -substituted derivatives, the use of this equation has been restricted almost exclusively to those systems in which the relation between the substituent R and the reacting side chain Y is of the 5-R-2-Y type.

In order to extend the observation made on the transmission of the substituent's effect to the "nonconjugated" 5-R-3-Y relationship in the furanic system, a series of 5-substituted 3-furoic acids were prepared and their  $pK_a$  values were determined and correlated with the corresponding Hammett substituent constants.

### Experimental Section

The <sup>1</sup>H NMR spectra were determined on a Varian T-60 instrument using  $Me_4Si$  as an internal reference. The IR spectra were recorded using a Perkin-Elmer 337 spectrophotometer. All melting and boiling points are uncorrected.