problems should affect the percent retention of the acetate.

Experimental Section

Acetic acid used for solvolysis reactions was distilled and stored with 1% distilled acetic anhydride added. LiClO₄ was predissolved in the acetic acid. *cis-* and *trans-*1-phenyl-1-propene and 3-phenyl-3-propene were purchased from Chemical Samples and Aldrich Chemical Co.

GLC was done on a Hewlett-Packard 5700A utilizing a 6 ft × $^1/_4$ in. glass column (OV-17) with a column temperature of 130 °C, an injection temperature of 200 °C, and a detector temperature of 300 °C. A flame-ionization detector was used. All peaks were compared to authentic materials synthesized in an unambiguous way. Optical rotations were determined by using a Perkin-Elmer 141 polarimeter with a water-jacketed cell at 25 °C. Proton magnetic resonance spectra were obtained on a Hitachi Perkin-Elmer R-24 spectrometer.

Preparation of Optically Active Materials. 1-Phenyl-2-propanol (Columbia Organic Chemical Co.) was resolved via the brucine salts of its phthalic acid half-ester.[7] Alcohols having $[\alpha]^{25}_D$ +40.8, +40.2, and +39.7 (CHCl₃) were obtained. Previous literature reported $[\alpha]^{25}_D$ +36.68[8] and +38.7[9] (CHCl₃). Less pure enantiomeric alcohol, $[\alpha]^{25}_D$ −20.2, −22.1 (CHCl₃), was obtained from the filtrates of the brucine salt recrystallizations.

Optically active 1-phenyl-2-propyl acetate and tosylate[10] were prepared by standard procedures. All products were checked by proton NMR and boiling point or melting point.

Solvolysis Reactions. A 10-mL sample of 0.15 M optically active 1-phenyl-2-propyl tosylate dissolved in acetic acid (with or without added salt) was reacted at 75 °C for 5.5 days. The reactions were quenched with ice–water and the organic materials extracted with several portions of ether. The combined ether phases were washed carefully with saturated NaHCO₃ until all of the acid was removed. The organic phase was then washed with saturated NaCl and dried over Na₂SO₄, and the ether was evaporated on a rotary evaporator. In all cases the product was a yellow to amber oil. The product was distilled in a microdistillation apparatus at 1 mm. The distillate was a colorless oil.

A weighed amount of distillate was dissolved in exactly 2 mL of CHCl₃, and its optical rotation was determined. Another portion of the distillate was dissolved in CCl₄ and analyzed by GLC.

The GLC analysis showed only the expected olefins and the acetate product in all cases; the relative amounts of olefin products were determined from the GLC data. The specific rotation ($[\alpha]^{25}_D$ in CHCl₃) was calculated by using a weight of distillate which had been corrected for the amount of olefin present.

Stopped-Flow Trapping of the Hemiacetal Intermediates of the Hydrolysis of Acetals

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Stopped-flow experiments are described where partially hydrolyzed acetals in dilute acid solutions are mixed with various buffers to give final solutions of pH 7–10. A relatively rapid first-order reaction is observed, with rate constants mainly dependent on hydroxide ion concentration. This reaction is attributed to hemiacetal intermediates which have accumulated during the hydrolysis of the acetals in the acetate buffer, corroborating a similar suggestion by Jensen and Lenz (*J. Am. Chem. Soc.* **1978**, *100*, 1291). Second-order rate constants for hydroxide ion catalyzed decomposition of a series of hemiacetals are reported. A substantial dependency of leaving group is seen in the series 4-ClC₆H₄CH(OH)OR with β_{lg} = −1.3. Very little dependency on aromatic substituent is found in the series ArCH(OH)OEt.

The hydrolysis of acetals is now generally accepted[1] to occur via a three-stage reaction mechanism: (1) generation of an oxocarbonium ion, (2) hydration of this cation to form a hemiacetal, and (3) decomposition of the hemiacetal. Until recently, simple acyclic acetals were considered to undergo hydrolysis with the first reaction stage being rate limiting, the two subsequent stages being rapid. This means that the two intermediates, the oxocarbonium ion and the hemiacetal, are present during hydrolysis only in small stationary-state amounts and cannot be detected.

In 1975, Capon and co-workers[2] reported that the acylals α-acetoxy-α-methoxytoluene and α-(chloroacetoxy)-α-methoxytoluene have the third reaction stage rate limiting in the overall hydrolysis. That is, the hemiacetal intermediate, benzaldehyde methyl hemiacetal, is formed from the acylals more rapidly than it decomposes. Addition of the acylals to aqueous solutions results in the (rapid) formation of this hemiacetal, and what is obtained by following spectroscopically the rate of benzaldehyde formation is the rate of hemiacetal decomposition. The acylals of that study are unusual in that there is present a carboxylate group, a relatively good leaving group, and this results in a first reaction stage which is considerably accelerated relative to the third reaction stage. Hemiacetals have also been detected during hydrolysis of other acetals where there is an accelerated first reaction stage, this being due in one system to release of steric conjestion[3] and in other systems to release of ring strain.[4,5]

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(1) Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581.

(2) Capon, B.; Hall, J. H.; Grieve, D. M. A. *J. Chem. Soc., Chem. Commun.* **1976**, 1034.

(3) Capon, B. *Pure Appl. Chem.* **1977**, *94*, 1001.
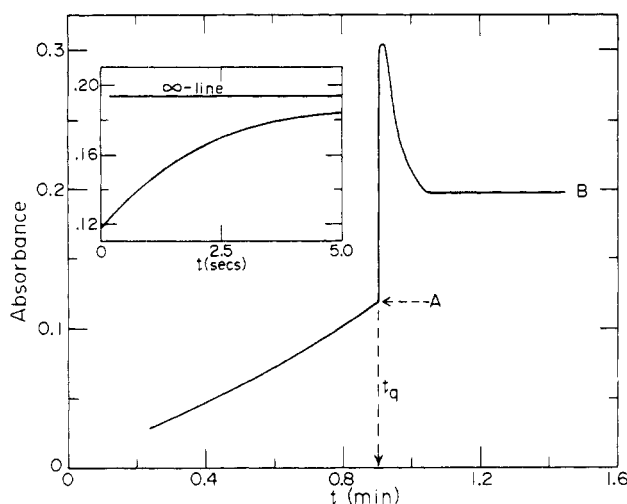
Figure 1. Absorbance change for p-methylbenzaldehyde diethyl acetal. The graph shown in the main figure is that of Jensen and Lenz[6] and represents the absorbance change in dilute acetate buffer up to the point t_q, where excess 1 M KOH was injected into the solution. The insert shows an oscilloscope trace obtained from a stopped-flow spectrometer when the acetal in dilute acetate buffer is mixed after a time corresponding to t_q with phosphate buffer such that the pH after mixing is 7.0.

More recently, experiments were reported by Jensen and Lenz[6] which suggested that hemiacetal buildup may be more general, occurring even during the hydrolysis of diethyl acetals of benzaldehydes. This could have serious implications, since it forces a reexamination of many kinetic studies of acetal hydrolysis reactions where it has been implicitly assumed that what was observed was the rate of the first reaction stage. We felt it desirable, therefore, to verify the observations of Jensen and Lenz and report here the results of our approach based on the use of stopped-flow spectroscopy to carry out the procedure which traps the hemiacetal. This approach confirms the buildup of hemiacetal, and, in addition, provides kinetic information for its decomposition.

Results and Discussion

Jensen and Lenz[6] were led to their conclusions by the observation of an induction period for benzaldehyde formation in the hydrolysis of the benzaldehyde acetals. Such an induction period arises in a kinetic system of the type shown in eq 1, where the first-order rate constants[7] k^1 and

$$I \xrightarrow{k^1} II \xrightarrow{k^3} III \qquad (1)$$
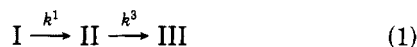
k^3 are of a similar order of magnitude. This must also mean that the intermediate II, the hemiacetal in this case, accumulates in significant amounts during the conversion of I to III. This buildup was verified by a second experiment in which excess sodium hydroxide was rapidly added to a solution of the acetal which was partially hydrolyzed in a weakly acidic solution. This has the result of quenching the first reaction stage which is hydronium ion catalyzed, and therefore no further aldehyde can form from the acetal. However, hemiacetal decomposition is subject

to hydroxide ion catalysis as well as hydronium ion catalysis,[2,8,9] and therefore aldehyde can still form after hydroxide ion addition from any hemiacetal which had accumulated. This was indeed the case, the presence of significant amounts of hemiacetal being indicated by the fact that the absorbance before quenching (A, Figure 1) was significantly less than the absorbance after quenching (B). The difference between the absorbances at A and at B provides a measure of the actual amount of hemiacetal which has accumulated at the time immediately before quenching.

Jensen and Lenz conducted this experiment on a conventional UV spectrometer by injecting concentrated hydroxide solution directly into a UV cell. Our approach uses stopped-flow spectroscopy and is based on the reasoning that if the absorbance change in the basic solution represents hemiacetal decomposition, the kinetics of this process should be observable. Experimentally, we place in one syringe of a stopped-flow apparatus a solution of acetal undergoing hydrolysis in a dilute acetate buffer (total concentration 0.002–0.005 M, pH 4–5). The other syringe of the apparatus contains excess carbonate, tris-(hydroxymethyl)aminomethane (Tris), or phosphate buffer such that the pH of the solution obtained after mixing is in the range 7–9.5. This increase in pH is sufficient to ensure that the first reaction stage is quenched, while the kinetic results of Capon and co-workers[2] suggested that in this pH region the rate of hemiacetal decomposition was within the capability of the stopped-flow technique. Indeed, on mixing the two solutions, there is obtained a first-order reaction (Figure 1, insert) corresponding to the absorbance change observed on quenching with hydroxide.[6] As reported previously,[6] the starting point for this process, as well as its total amplitude, is dependent on the length of time that the acetal has been dissolved in the acetate buffer, and the reaction completely disappears when the acetal in the acetate buffer is completely converted to aldehyde. The reaction follows first-order kinetics, and in a given solution the first-order rate constant is independent of the time of quenching. These experiments are like those conducted by Jensen and Lenz, except that they involve a different quenching technique. In our case the observation that the absorbance change occurs in a first-order process offers further evidence that it is the result of a chemical event, and it is not an artifact associated with the mixing of two different aqueous solutions.[10]

The stopped-flow approach has the added advantage of providing kinetic information for the process which occurs after quenching. Table I lists first-order rate constants for the reaction observed in experiments starting with benzaldehyde diethyl acetal; Figure 2 depicts a rate–pH profile based on the data at ionic strength 0.05 extrapolated to zero buffer concentration. The kinetic data do show the behavior that is expected of hemiacetal decomposition.[2,8,9] The reaction is catalyzed by hydroxide ion and is also general-base catalyzed, as shown by the experiments with phosphate buffer. Buffer catalysis is only slight or absent altogether in the experiments with Tris

(4) Mori, A. L.; Parzio, M. A.; Schlaleger, L. L. *J. Am. Chem. Soc.* **1972**, *94*, 5034. Mori, A. L.; Schlaleger, L. L. *Ibid.* **1974**, *96*, 5039.

(5) Atkinson, R. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 819.

(6) Jensen, J. L.; Lenz, P. A. *J. Am. Chem. Soc.* **1978**, *100*, 1291.

(7) (a) We have chosen the symbols k^1 and k^3 since they refer to the first and third reaction stages of acetal hydrolysis. Stage 2, the hydration of the oxocarbonium ion, is undoubtedly very fast.[7b,c] (b) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238. (c) McClelland, R. A.; Ahmad, M. *Ibid.* **1978**, *100*, 7031.

(8) Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1.

(9) Funderburk, L. H.; Aldwin, L.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 5444.

(10) Some concern has been expressed over the mixing of aqueous solutions of different pH in a stopped-flow spectrophotometer. We find no reaction when the two solutions are mixed in the absence of substrate or when they are mixed after complete conversion of acetal to aldehyde. One must be careful about mixing effects of different solvents in these type of experiments. For example, we find that mixing of acetonitrile and water solution for studying acetal hydrolysis can give rise to absorbance changes which are due to solubility phenomena and not due to chemical processes in solution.

Table I. Observed Rate Constants for the Decomposition of Benzaldehyde Ethyl Hemiacetal Trapped as an Intermediate in the Hydrolysis of Benzaldehyde Diethyl Acetal[a-c]

Carbonate (Ionic Strength 0.05)

[NaHCO$_3$]	[Na$_2$CO$_3$]	pH	k_{obsd}	[NaHCO$_3$]	[Na$_2$CO$_3$]	pH	k_{obsd}
0.02	0.0100	9.82	47.5	0.0286	0.0070	9.51	22.3
0.015	0.0075	9.79	48.5	0.0143	0.0035	9.46	21.5
0.010	0.0050	9.78	46.2				

Tris (Ionic Strength 0.05)

[Tris]	[Tris·HCl]	pH	k_{obsd}	[Tris]	[Tris·HCl]	pH	k_{obsd}
0.1	0.0500	8.62	2.87	0.020	0.0500	7.90	0.601
0.075	0.0375	8.64	2.82	0.015	0.0375	7.90	0.583
0.050	0.0250	8.61	2.84	0.010	0.0250	7.87	0.598
0.025	0.0125	8.59	2.77	0.005	0.0125	7.88	0.612

Phosphate (Ionic Strength 0.05)

[NaH$_2$PO$_3$]	[NaH$_2$PHO$_4$]	pH	k_{obsd}	[NaH$_2$PO$_4$]	[Na$_2$HPO$_4$]	pH	k_{obsd}
0.0071	0.0143	7.61	0.370	0.020	0.0100	6.99	0.121
0.0053	0.0107	7.56	0.324	0.015	0.0075	6.97	0.106
0.0036	0.0071	7.52	0.288	0.010	0.0050	6.93	0.093

Phosphate (Ionic Strength 0.50)

[NaH$_2$PO$_4$]	[Na$_2$HPO$_4$]	k_{obsd}	[NaH$_2$PO$_4$]	[Na$_2$HPO$_4$]	k_{obsd}	[NaH$_2$PO$_4$]	[Na$_2$HPO$_4$]	k_{obsd}
0.0193	0.0770	0.351	0.0454	0.0682	0.241	0.0833	0.0555	0.191
0.0154	0.0616	0.310	0.0363	0.0546	0.210	0.0666	0.0444	0.161
0.0115	0.0462	0.280	0.0272	0.0409	0.156	0.0500	0.0333	0.127
0.0077	0.0308	0.235	0.0181	0.0273	0.140	0.0333	0.0222	0.103
0.0038	0.0154	0.197	0.0091	0.0136	0.102	0.0167	0.0111	0.072

[a] All concentrations are after mixing in the stopped-flow spectrophotometer. Solutions also contain 0.001–0.005 M NaOAc. [b] pH values are measured values. [c] Values of k_{obsd} are in units of s^{-1}, temperature 25 °C.

and carbonate buffers, but this is probably due to a combination of the relatively low concentrations of buffer used in these experiments and the large contribution of hydroxide ion catalysis. Rate–pH profiles for hemiacetal decomposition level off at lower pH,[2,8,9] as water catalysis (and eventually hydronium ion catalysis) assumes importance. The water catalysis would show up as an intercept in a plot such as that of Figure 2. In general, we obtain intercepts in such plots very close to zero and are therefore unable to accurately determine the water rate constants. It should be noted that the approach used here does not work in solutions where the pH is less than 7, since the hydronium ion catalyzed first stage is not completely quenched, and stopped-flow traces such as that depicted in Figure 1 show increasing end points as acetal is slowly converted to aldehyde.

Final arguments are based on comparisons of the numerical values of the rate constants and follow two lines of reasoning. Rate constants for the decomposition of benzaldehyde methyl hemiacetal have previously been reported when this compound was generated from acylal precursors.[2] At 15 °C and ionic strength 0.05, the value found for $k^3_{OH^-}$, the second-order rate constant for hydroxide ion catalysis, is 6.9 × 10^5 M^{-1} s^{-1}. Our experiments starting with benzaldehyde dimethyl acetal furnish a value of $k^3_{OH^-}$ of 30.3 × 10^5 M^{-1} s^{-1} at 25 °C and ionic strength 0.05, in satisfactory agreement, considering the different temperatures involved. A second piece of evidence is obtained from experiments starting with benzaldehyde methyl phenyl acetal, where a value of $k^3_{OH^-}$ of 30.7 × 10^5 M^{-1} s^{-1} is found. The mixed acetal has been suggested to hydrolyze with loss of phenol in stage 1[11] and is therefore expected to generate the same intermediate hemiacetal as that produced from benzaldehyde dimethyl acetal. In other words, the mixed acetal and the symmetric acetal

(11) Capon, B.; Nimmo, K. *J. Chem. Soc., Perkin Trans. 2* 1975, 113.

Table II. Rate Constants for the Hydroxide Ion Catalyzed Decomposition of Hemiacetals[a]

R$_1$	R$_2$	R$_3$	$10^{-5}k^3_{OH^-}$, M^{-1} s^{-1}
4-CF$_3$C$_6$H$_4$	Et	H	11.9
4-CNC$_6$H$_4$	Et	H	9.7
3-ClC$_6$H$_4$	Et	H	7.5
4-ClC$_6$H$_4$	Et	H	5.9
C$_6$H$_5$	Et	H	7.2
4-CH$_3$C$_6$H$_4$	Et	H	10.4
4-CH$_3$OC$_6$H$_4$	Et	H	13.7
C$_6$H$_5$	Me	H	30.3
4-ClC$_6$H$_4$	Me	H	29.9
4-ClC$_6$H$_4$	CH$_2$CH$_2$OMe	H	72
4-ClC$_6$H$_4$	CH$_2$CH$_2$Cl	H	1060
4-ClC$_6$H$_4$	Me	Me	266
Me	Me	Me	20.1
C$_6$H$_5$	Me	H	30.7

[a] At 25 °C and μ = 0.05. The acetals were generally hydrolyzed in dilute acetate buffer solutions and these were quenched with various basic buffers to give an appropriate pH. For p-cyanobenzaldehyde diethyl acetal, the acidic buffer was bromoacetate. For p-chlorobenzaldehyde bis(2-chloroethyl) acetal, the acidic buffer was formate. [b] The precursor of this species in each case was the symmetrical acetal except for the last compound in the table. In this case, the precursor was benzaldehyde methyl phenyl acetal.

should show identical kinetic behavior in the quenching experiments, and this is indeed observed.

Other acetals which have been studied and which have been found to produce a significant reaction on quenching are listed in Table II, along with values of $k^3_{OH^-}$. These values are based on observed rate constants obtained at three to five different values of pH and on extrapolation to zero buffer concentration, where this is appropriate.
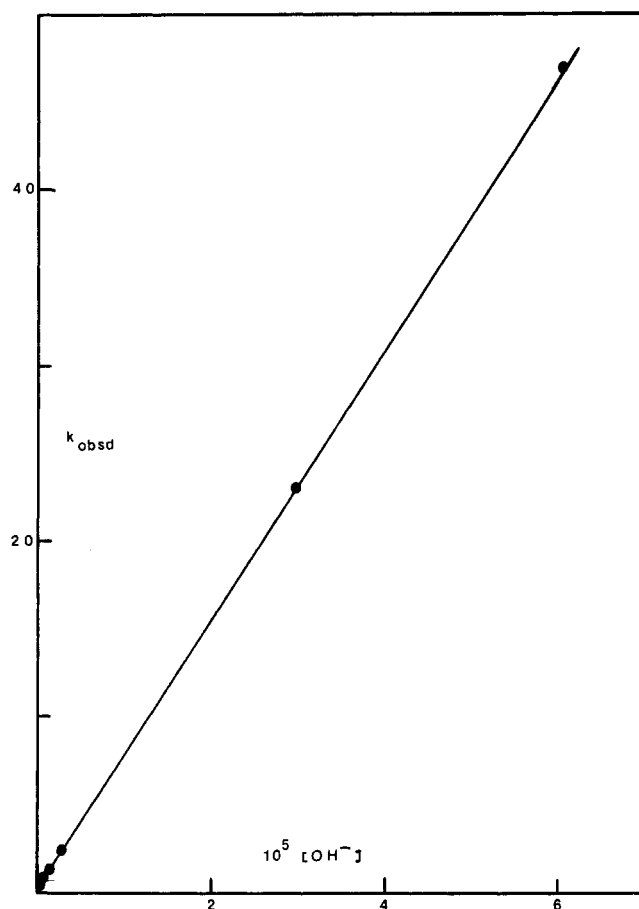
Figure 2. Rate constants for the decomposition of benzaldehyde ethyl hemiacetal as a function of hydroxide ion concentration (25 °C, ionic strength 0.05). Points are based on extrapolation to zero buffer concentration, where this is necessary.

The extent of buildup of hemiacetal in the acid solution varies considerably throughout this series. Entry in Table II implies that sufficient hemiacetal accumulates to produce a reaction on quenching capable of giving accurate first-order constants, that is, an optical density change of at least 0.01 absorbance units.

A number of qualitative features can be noted regarding the extent of hemiacetal buildup.

(i) In the series $ArCH(OEt)_2$ the same observation made by Jensen and Lenz[6] can be noted, namely, a trend to increasing amounts of hemiacetal accumulation during hydrolysis with decreasing σ value of the aromatic substituent.

(ii) A trend is also seen in the series $4\text{-}ClC_6H_4CH(OR)_2$, hemiacetal buildup decreasing significantly with increased electron withdrawal in R. In fact, no hemiacetal can be detected in the hydrolysis of $4\text{-}ClC_6H_4CH(OR)_2$ when R = CH_2CH_2Br and $CH_2C\equiv CH$. This tendency can be explained in terms of the effect of variation in R on the relative rates of stage 1 and stage 3. Both reaction stages
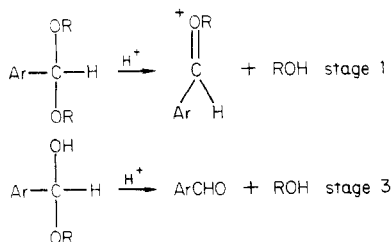
have OR as a leaving group, and it is reasonable to assume that its leaving tendency in each stage will be similar,[12] at

least in acid solutions where the hemiacetal decomposition involves hydronium ion catalysis. Stage 1 has a second R group which remains in the oxocarbonium ion. Increased electron withdrawal in R will destabilize this ion and therefore retard stage 1. The overall result is that stage 1 is slowed by increased electron withdrawal in R relative to stage 3, and this results in less accumulation of hemiacetal.

(iii) The accumulation of a significant quantity of hemiacetal during hydrolysis of benzaldehyde methyl phenyl acetal was not anticipated by Jensen and Lenz.[6] However, the value of $k^1_{H^+}$, the rate constant for the first reaction stage, is in fact somewhat greater for the mixed acetal as compared to the dimethyl acetal. Since a common intermediate is generated, the rate of stage 3 will be the same in each case. Therefore, if the dimethyl acetal shows significant hemiacetal accumulation, as it does, so must the methyl phenyl acetal.

(iv) Hemiacetal buildup is also found with the acetals of two ketones, acetone and 4-chloroacetophenone, an observation which extends the generality of this phenomenon.

(v) No hemiacetal (or hemiortho ester) accumulation is observed on quenching partially hydrolyzed solutions of benzophenone dimethyl acetal, 2-phenyl-1,3-dioxane, and trimethyl orthobenzoate. This finding with the latter compound is not surprising. The hemiortho ester intermediate $PhC(OMe)_2OH$ is detected as an intermediate in the hydrolysis of anilide acetals $PhC(OMe)_2NMeAr$, and its rate of decomposition in acid is 3 orders of magnitude greater than the rate of oxocarbonium formation from $PhC(OMe)_3$.[13]

Perhaps the most important aspect of our approach is its capability of generating numerical rate constants for base-catalyzed hemiacetal decomposition and the bearing that our present results have on the mechanism of the hydroxide ion catalyzed reaction. We can start by noting the large leaving-group effect in the series $4\text{-}ClC_6H_4CH\text{-}(OR)OH$. A plot of log $k^3_{OH^-}$ vs. pK_{ROH} produces a value of β_{lg} of -1.3. A similar trend is also seen in the hydroxide ion catalyzed decomposition of formaldehyde hemiacetals, with $\beta_{lg} = -1.1$.[9] These large values of β are indicative of a late transition state for alkoxide ion expulsion, with considerable development of negative charge on the alkoxide oxygen.

For the series $ArCH(OH)OEt$ values of $k^3_{OH^-}$ show little dependency on the nature of the aromatic substituent, varying by a factor of about 2 over the range of substituents studied (Table II). A Hammett correlation using σ substituent constants is in fact U shaped, with a small negative slope for electron-donating groups and a small positive slope for electron-attracting groups. Although the actual variation in the rate constants is small, this behavior is probably real. A U-shaped Hammett plot has been recently reported for a somewhat similar reaction, the hydroxide ion catalyzed decomposition of the bisulfite adducts of a series of acetophenones (eq 2).[14]

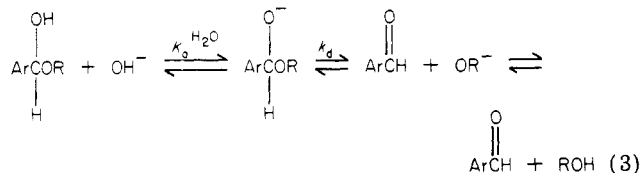The mechanism of the hydroxide reaction has been

(12) (a) Although a direct comparison of leaving-group effects on the two stages has not been made, some evidence is available consistent with the suggestion. The first stage in the hydrolysis of 2-alkoxy-2-phenyl-1,3-dioxolane ortho esters shows a small decrease in rate with increased electron withdrawal in the alkoxy group.[12b] A similar small decrease is observed in the hydronium ion catalyzed decomposition of formaldehyde hemiacetals, $CH_2(OH)OR$.[9] (b) Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *J. Am. Chem. Soc.* **1979**, *101*, 2669.

(13) McClelland, R. A.; Somani, R. *J. Chem. Soc., Chem. Commun.* **1979**, 407.

(14) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288.

$$\text{ArCCH}_3 \xrightarrow{\text{OH}^-} \text{ArCCH}_3 + \text{HSO}_3^- \tag{2}$$
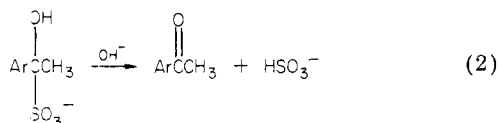
proposed to involve the stepwise route outlined in eq 3,[9]

$$\text{ArCOR} + \text{OH}^- \underset{\xleftarrow{}}{\overset{K_0, H_2O}{\rightleftharpoons}} \text{ArCOR} \overset{k_d}{\rightleftharpoons} \text{ArCH} + \text{OR}^- \rightleftharpoons$$

$$\text{ArCH} + \text{ROH} \tag{3}$$

in which case $k^3_{OH^-}$ is actually a composite rate constant, being equal to $k_d K_a$. Arora, Cox, and Sorensen[15] have recently reported rate and equilibrium constants for the reversible addition of methoxide ion to a series of benz-aldehydes, in methanol as solvent (eq 4), and also list

$$\text{ArCH} + \text{MeO}^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \text{ArCOMe} \tag{4}$$
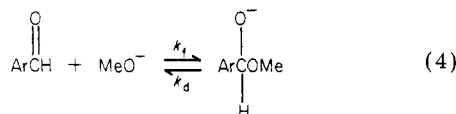
$$K_{MeO^-} = k_f / k_d \tag{5}$$

values of the equilibrium constant for the addition of neutral methanol (eq 6). From the data reported the

$$\text{ArCH} + \text{MeOH} \underset{\rightleftharpoons}{\overset{K_{MeOH}}{\rightleftharpoons}} \text{ArCOMe} \tag{6}$$
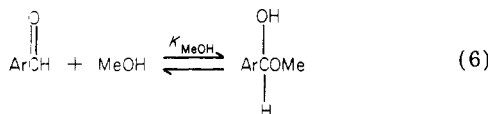
following ρ values can be obtained:[16] $\rho(K_{MeOH}) = 2.1$, $\rho(K_{MeO^-}) = 3.0$, $\rho(k_f) = 2.2$, and $\rho(k_d) = -0.8$. It can be noted that the ratio K_{MeO^-}/K_{MeOH} is equal to K_a^{MeOH}, as defined in eq 7. The reaction in methanol analogous to that which

$$\text{ArCOMe} + \text{MeO}^- \underset{\rightleftharpoons}{\overset{K_a^{MeOH}}{\rightleftharpoons}} \text{ArCOMe} \overset{k_d}{\rightleftharpoons} \text{ArCH} + \text{MeO}^- \tag{7}$$
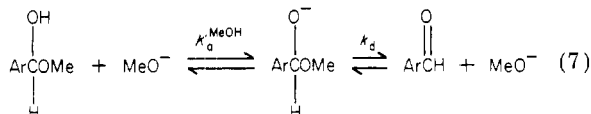
we are observing in water is the methoxide ion catalyzed decomposition of the hemiacetal, $k^3_{MeO^-} = k_d K_a^{MeOH}$, for which $\rho(k^3_{MeO^-})$ can be calculated as $\rho(k_d) + \rho(K_{MeO^-}) - \rho(K_{MeOH})$. This is zero, predicting, therefore, very little substituent effect for $k^3_{MeO^-}$, precisely as we find for the $k^3_{OH^-}$ process in water.

Our results further corroborate earlier conclusions,[9,15,17] originally due to Bell and Sorensen,[17] that the transition state in the hydroxide ion catalyzed decomposition of hemiacetals and aldehyde hydrates is unusual. For example, values of β_{lg} are indicative of a late transition state from the point of view of the expulsion of the alkoxide ion from the hemiacetal monoanion, while the ρ value suggests an early transition state from the point of view of the development of the carbon–oxygen double bond. This type of contradiction has been discussed in detail elsewhere[9,15,17] and is resolved in terms of an imbalance in the transition state in the extent to which various processes have occurred, in particular, an imbalance in the extent of C–O bond breaking and the solvation of the incipient alkoxide ion.

Experimental Section

Acetone dimethyl acetal was freshly distilled (spinning band) commercial product. The dimethyl and diethyl acetals of the substituted benzaldehydes were prepared in the standard manner from the benzaldehyde, a catalytic amount of mineral acid, and either trimethyl orthoformate or triethyl orthoformate.[18] The 4-chloroacetophenone dimethyl acetal was made by the same procedure. The bis(2-methoxyethyl) and bis(2-chloroethyl) acetals of 4-chlorobenzaldehyde were made by azeotropically distilling the water (benzene) from a mixture of the 4-chlorobenzaldehyde, the corresponding alcohol, and p-toluenesulfonic acid. The methyl phenyl acetal of benzaldehyde was made by Capon's procedure.[11] All acetals were purified by fractional distillation until the main fractions were free of carbonyl impurity (IR). Product identities were confirmed by literature properties and by IR and NMR spectroscopy.

The buffer solutions were prepared from the best commercial grade reagents without further purification.

Reactions were observed on a Durrum-Gibson stopped-flow spectrophotometer, Model 110. Kinetic analyses were initially carried out by photographing an oscilloscope trace of an optical density change. In later runs, the photomultiplier output was digitized and fed to a Tektronix 4051 minicomputer equipped with a graphic display. First-order rate constants were calculated as slopes of plots of ln $(A_\infty - A_t)$ vs. time. Plots were excellently linear over several half-lives.

The experimental approach was to place the quenching buffer in one syringe of the stopped-flow apparatus and allow it to thermally equilibrate. The acid buffer (generally an acetate buffer) was thermally equilibrated in an external water bath. Acetal was added to this solution, and it was rapidly loaded into the other syringe of the stopped-flow apparatus. This procedure allows the quenching to be done within 30–40 s after the addition of the acetal to the acid buffer. The nature of the Durrum-Gibson stopped-flow instrument is such that in a given run only a small amount of the solutions in each syringe is mixed, and it is possible to reset the apparatus and repeat the mixing very quickly. In general, we carried out three to five mixings with a given pair of solutions over a time period of 1–2 min. Rate constants from each of these agreed to within 3% and were averaged.

The values of pH used in calculating $k^3_{OH^-}$ are measured values, based on mixing the acetate buffer and the quenching buffer in a 1:1 (v/v) ratio. Control experiments demonstrated that the pH values of solutions actually mixed on the stopped-flow spectrophotometer are identical. Hydroxide ion concentrations were calculated as (antilog $-pH$)/10^{-14}.

(15) Arora, M.; Cox, B. G.; Sorensen, P. E. *J. Chem. Soc., Perkin Trans. 2* **1979**, 103.

(16) We have used the Hammett $\sigma\rho$ relationship rather than correlation with log K_{MeOH} as done by Arora, Cox, and Sorensen,[18] since the set of aldehydes is different in the two studies. The ρ values for the methanol data are in fact based only on points for 4-Cl, 3-Cl, 3-NO$_2$, and 4-NO$_2$.

(17) Bell, R. P.; Sorensen, P. E. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1594.

(18) Davis, T. S.; Fiel, P. D.; Kubler, D. G.; Wells, D. J. *J. Org. Chem.* **1975**, *40*, 1478.