One notes that any solvent effect and any symbiotic effect would tend to compensate each other. For this reason, plus the fact that we doubt that either is very large, we believe one can probably conclude with reasonable certainty that sulfinyl sulfur represents a medium soft electrophilic center analogous to sp^3 carbon.

An interesting aspect of the data for eq 8 in Table IV is that fluoride ion is not a great deal less reactive than chloride ion ($k_F/k_{Cl} = 0.37$). Mislow, *et al.*,[10] have reported that, whereas aryl alkyl sulfoxides racemize readily in aqueous dioxane containing 4 *M* HCl, they are unaffected by aqueous dioxane containing a similar concentration of HF. The present results suggest that the failure of HF to racemize sulfoxides is not due to any lack of reactivity of fluoride ion toward tricoordinate sulfur. Presumably it must therefore be due to the much lower acidity of the hydrofluoric acid solution.

Experimental Section

Preparation and Purification of Materials. The preparation or purification of most of the reagents has already been described.[17] Sodium fluoride, potassium thiocyanate, sodium acetate, and thiourea were all Analytical Reagent grade and were in general further purified by recrystallization before use.

Procedure for Kinetic Runs. The same procedure outlined in an earlier paper[17] was followed in all cases.

Acknowledgment. We appreciate a number of stimulating discussions with Dr. B. Saville regarding HSAB.

General Acid Catalysis of Acetal Hydrolysis. The Hydrolysis of 2-Aryloxytetrahydropyrans

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Abstract: The rates of acid-catalyzed hydrolysis of a series of 2-alkoxy- and 2-aryloxytetrahydropyrans have been measured in 50% dioxane–H_2O. The value of ρ determined for hydrolysis of 2-(*para*-substituted phenoxy)tetrahydropyrans is -0.92. The D_2O solvent isotope effect (k_{D_2O}/k_{H_2O}) progressively decreases as electron withdrawal in the leaving group becomes greater: from 2.82 for 2-ethoxytetrahydropyran to 1.33 for 2-(*p*-nitrophenoxy)-tetrahydropyran. The value of ΔS^* likewise becomes considerably more negative: +7.9 eu in the case of the ethoxy derivative and −7.6 eu in the case of 2-(*p*-nitrophenoxy)tetrahydropyran Thus, it is likely that, as C–O bond breaking becomes easier and at the same time basicity of the acetal decreases, the solvent becomes more involved in the critical transition state with the most probable mechanism for the aryloxy derivatives involving partially rate-determining protonation by hydronium ion. General acid catalysis by formate buffers was also observed for hydrolysis of 2-(*p*-nitrophenoxy)tetrahydropyran and 2-(*p*-chlorophenoxy)tetrahydropyran.

There is little doubt that the acid-catalyzed hydrolysis of acetals generally involves preequilibrium protonation of the acetal followed by a unimolecular rate-determining decomposition to an alcohol and a resonance-stabilized carbonium ion.[1] The recent findings, however, of possible participation by solvent,[2,3] buffer,[2] and neighboring functional groups[4–7] in the rate-determining step of hydrolysis reactions of certain types of acetals are of great importance in regard to the insight provided into the mechanistic possibilities which glycosidic enzymes could be employing. The structural features that will facilitate such mechanisms over the normal A1 mechanism have not as yet been clearly established.

Carboxyl group participation has been postulated to occur in the hydrolysis of *o*-carboxyphenyl β-D-glucoside[4] and 2-methoxymethoxybenzoic acid[5] although the mechanism of the participation is not definitely established. With aliphatic glycosides, 2-carboxyethyl and carboxymethyl β-D-glucopyranoside, however, carboxyl group participation was not observed,[8] nor was intramolecular carboxyl group participation detected in the hydrolysis of ketals of aliphatic alcohols.[9] Piszkiewicz and Bruice[7] did, however, find evidence for neighboring acetamido group participation with *o*- and *p*-nitrophenyl 2-acetamido-2-deoxyglucopyranosides. Thus, glycoside hydrolysis reactions in which neighboring functional groups have been found to participate involve substituted phenoxy derivatives in which the leaving group is quite good in comparison to glycosides of aliphatic alcohols, but with which protonation will be more difficult. However, a systematic study of the effect of the leaving group on the mechanism of acetal or glycoside hydrolysis has not been made. Therefore, the hydrolysis reactions of a series of 2-alkoxy- and 2-aryloxytetrahydropyrans have been studied. These tetrahydropyran derivatives offer several advantages for study over the corresponding glycosides including

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(2) T. H. Fife, *J. Am. Chem. Soc.*, **89**, 3228 (1967).
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(7) D. Piszkiewicz and T. C. Bruice, *ibid.*, **89**, 6237 (1967).
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ease of synthesis and much faster rates of hydrolysis, thereby allowing an extensive study to be made.

Experimental Section

Materials. 2-Ethoxytetrahydropyran and the 2-(*para*-substituted phenoxy)tetrahydropyrans were prepared by the general procedure of Woods and Kramer.[10]

2-Ethoxytetrahydropyran had bp 58–60° (36 mm), n^{23}D 1.4220 (lit.[10] bp 146°, nD 1.4248).

2-(*p*-Methoxyphenoxy)tetrahydropyran had bp 120° (1.5 mm), n^{24}D 1.5244. *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.16; H, 7.76.

2-(*p*-Methylphenoxy)tetrahydropyran had bp 98–99° (3 mm), n^{21}D 1.5176. *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.18; H, 8.52.

2-Phenoxytetrahydropyran had bp 90–92° (3.5 mm), n^{22}D 1.5219 (lit.[11] bp 103° (4 mm), n^{20}D 1.5228).

2-(*p*-Chlorophenoxy)tetrahydropyran had mp 48–49° (lit.[12] mp 48.5–49°).

2-(*p*-Nitrophenoxy)tetrahydropyran was prepared by a modification of the procedure of Woods and Kramer.[10] 2,3-Dihydropyran (8.6 g, 0.1 mol) and *p*-nitrophenol (13.9 g, 0.1 mol) were dissolved in anhydrous benzene. A trace of *p*-toluenesulfonic acid was added as a catalyst, and the mixture was stirred for 3 hr under a nitrogen atmosphere. The mixture was allowed to stand overnight and was then washed with 2% NaOH solution. The aqueous layer was further extracted with ether. The combined organic extracts were dried over anhydrous sodium sulfate. Evaporation of solvent left a residue which was crystallized from an ether–ligroin mixture. After several recrystallizations the material melted at 59–60°. *Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.30; H, 6.00; N, 6.58.

Dioxane was purified by the method of Fieser[13] and was stored frozen in brown bottles.

Kinetic Measurements. The rates of hydrolysis were measured in 50% dioxane–H_2O (v/v) and 50% dioxane–D_2O (v/v). The rates were measured spectrophotometrically with a Zeiss PMQ II spectrophotometer in the case of the 2-phenoxytetrahydropyrans by following the appearance of the phenol product at 330 mμ for the nitro derivative and at 280–295 mμ for other compounds in the series. At the conclusion of each reaction the ultraviolet spectrum of the solution was that of the appropriate phenol. The rates of hydrolysis of 2-ethoxytetrahydropyran were measured by following the increase in absorbance due to the aldehyde product at 280 mμ, with a Beckman DU spectrophotometer equipped with a Gilford Model 2000 recorder. Since only small changes in absorbance (0.06–0.10 OD) were obtained with 2-ethoxytetrahydropyran at the concentrations employed, a chart scale of 0–0.1 OD full scale was utilized. The acetals, dissolved in dioxane, were added directly to the thermostated solution in the cuvette by means of a calibrated dropping pipet. One drop was added and the solution was then stirred vigorously. The rates were followed to completion and the values of k_{obsd} were calculated either by the method of Guggenheim[14] or from the slopes of plots of log $[(OD_\infty - OD_0)/(OD_\infty - OD_t)]$ *vs.* time. Constant temperature in these runs (±0.1°) was maintained by circulating water from a Precision Scientific Co. Temptrol Model 154 constant-temperature circulating bath through a Zeiss constant-temperature cell holder or around the cell compartment of the Beckman DU. In the latter case the temperature of the cell compartment was measured by means of a probe supplied with the Gilford instrument and was monitored continuously. The difference between the cell temperature and the bath temperature was reduced by placing around the cell compartment highly insulating Polycell 1202 foam obtained from Polytron Co., Richmond, Calif.

In the determination of activation parameters, points were obtained at four temperatures (20, 30, 40, and 50°) ± 0.1°. The rates were measured in triplicate at each temperature with an average deviation of less than 2% in the rate constants in all cases.

In work utilizing 99.8% D_2O as solvent, the glass electrode correction formula of Fife and Bruice[15] was employed in the determination of a_D.[16–18]

The pH of each solution was measured on a Model 22 Radiometer pH meter standardized with aqueous buffers. The glass electrode gives the correct pH reading in concentrated dioxane–water mixtures.[19]

Results

Rate constants for hydrolysis of 2-ethoxytetrahydropyran and 2-(*para*-substituted phenoxy)tetrahydropyrans, in 50% dioxane–H_2O (v/v) and 50% dioxane–D_2O (v/v) at 30°, are presented in Table I. The value of

Table I. Rate Constants for Hydrolysis of 2-Ethoxytetrahydropyran and 2-(*para*-Substituted Phenoxy)tetrahydropyrans in 50% Dioxane–H_2O at 30° and pH 1.30

Compd	k_{obsd}, min^{-1}	k_H,[a] l. mol^{-1} min^{-1}	k_D,[b] l. mol^{-1} min^{-1}	k_D/k_H
2-Ethoxytetrahydropyran	0.104	2.08	5.86	2.82
2-(*p*-Methoxyphenoxy)-tetrahydropyran	0.634	12.7	31.5	2.48
2-(*p*-Methylphenoxy)-tetrahydropyran	0.597	11.9	28.5	2.39
2-Phenoxytetrahydro-pyran	0.482	9.64	22.1	2.29
2-(*p*-Chlorophenoxy)-tetrahydropyran	0.259	5.18	10.4	2.01
2-(*p*-Nitrophenoxy) tetrahydropyran	0.0757	1.51	2.01	1.33

[a] $k_H = k_{obsd}^{H_2O}/a_H$. [b] $k_D = k_{obsd}^{D_2O}/a_D$.

k_D/k_H is 2.82 for 2-ethoxytetrahydropyran but is considerably less for the aryloxy derivatives. The solvent isotope effect decreases with increasing electron withdrawal in the *para* position from a value of 2.48 in the case of *p*-methoxy to 1.33 with *p*-nitro.

In Figure 1 is shown a plot of log k_{obsd} for hydrolysis of the 2-(*para*-substituted phenoxy)tetrahydropyrans at pH 1.30 *vs.* σ, the Hammett substituent constant.[20] A linear relationship is observed with a ρ of −0.92.

The rate constants for hydrolysis of 2-ethoxytetrahydropyran, 2-phenoxytetrahydropyran, and 2-(*p*-nitrophenoxy)tetrahydropyran were determined as a function of temperature and are given in Table II. In Figure 2 is shown a plot of the logarithms of these rate constants *vs.* $1/T$°K. The values of ΔH^* and ΔS^* are reported in Table III. The entropy of activation becomes progressively more negative as electron withdrawal in the leaving group increases: from +7.9 eu with 2-ethoxytetrahydropyran to −7.6 eu for 2-(*p*-nitrophenoxy)-tetrahydropyran.

The rate of hydrolysis of 2-(*p*-nitrophenoxy)tetrahydropyran was found to be markedly catalyzed by increasing concentrations of formate buffer at 50°. The observed rate constants obtained at two pH values are

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(17) T. H. Fife and L. K. Jao, *J. Org. Chem.*, **30**, 1492 (1965).
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(20) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

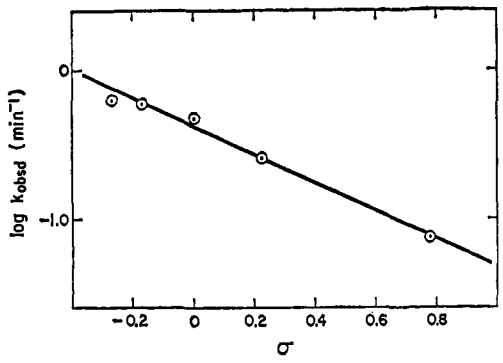


Figure 1. Plot of log k_{obsd} for hydrolysis of 2-(*para*-substituted phenoxy)tetrahydropyrans in 50% dioxane–H_2O at pH 1.30 and 30° *vs.* σ.

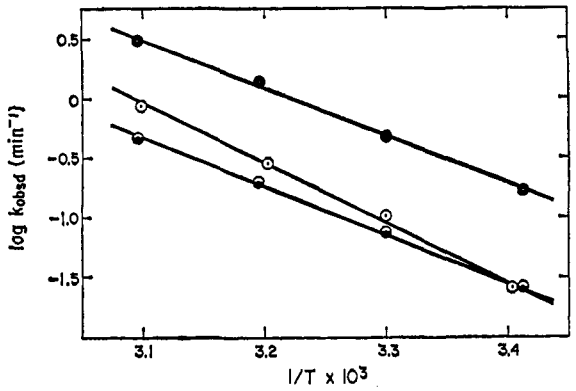


Figure 2. Plot of log k_{obsd} for hydrolysis of 2-ethoxytetrahydropyran (⊙), 2-phenoxytetrahydropyran (●), and 2-(*p*-nitrophenoxy)-tetrahydropyran (◒) in 50% dioxane–H_2O at pH 1.30 *vs.* $1/T$°K.

Table II. Rate Constants (k_{obsd}, min^{-1}) for Hydrolysis of 2-Ethoxytetrahydropyran and 2-(*para*-Substituted Phenoxy)tetrahydropyrans at Various Temperatures in 50% Dioxane–H_2O at pH 1.30

Compd	Temperature, °C 20	30	40	50
2-Ethoxytetrahydropyran	0.0261[a]	0.104	0.313[b]	0.859[c]
2-Phenoxytetrahydropyran	0.168	0.482	1.40	3.10
2-(*p*-Nitrophenoxy)-tetrahydropyran	0.0264	0.0757	0.203	0.470

[a] 20.8°. [b] 39.3°. [c] 49.8°.

Table III. Activation Parameters for Hydrolysis of 2-Ethoxytetrahydropyran and 2-(*para*-Substituted Phenoxy)tetrahydropyrans in 50% Dioxane–H_2O

Compd	ΔH^*, kcal/mol	ΔS^*, eu[a]
2-Ethoxytetrahydropyran	22.2 ± 0.6[b]	+7.9 ± 2.0
2-Phenoxytetrahydropyran	17.9 ± 0.4	−3.0 ± 1.2
2-(*p*-Nitrophenoxy)-tetrahydropyran	17.7 ± 0.2	−7.6 ± 0.6

[a] Calculated at 30° with the rate constants having the units l. mol^{-1} sec^{-1}. [b] The reported uncertainties were calculated from the standard error of a plot of ln k_{obsd} *vs.* $1/T$°K.

plotted in Figure 3 *vs.* total formate concentration (HCOOH + HCOO$^-$). The slopes of the lines increase as pH is decreased showing a kinetic dependence upon the concentration of the acid species. The rate

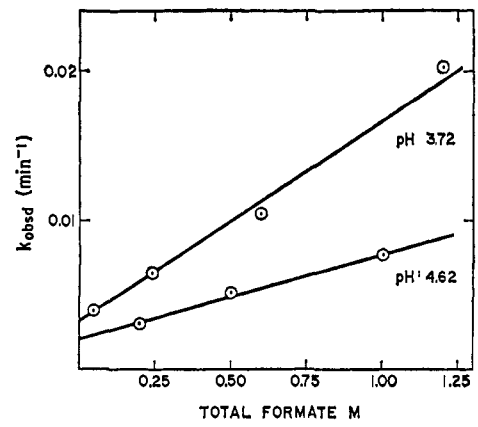


Figure 3. Plot of log k_{obsd} for hydrolysis of 2-(*p*-nitrophenoxy)tetrahydropyran in 50% dioxane–H_2O at 50° *vs.* the total concentration of formate buffer (HCOOH + HCOO$^-$); μ = 0.5 with KCl.

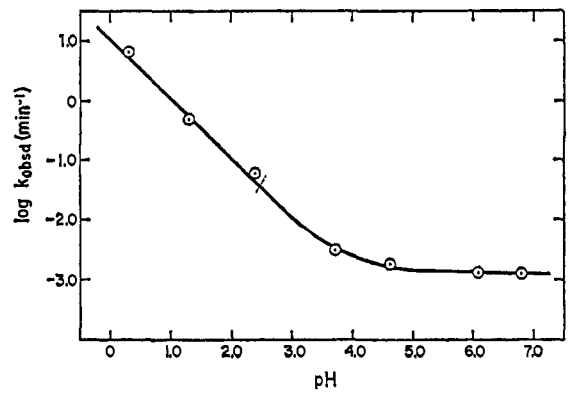


Figure 4. Plot of log k_{obsd} for hydrolysis of 2-(*p*-nitrophenoxy)-tetrahydropyran in 50% dioxane–H_2O at 50° *vs.* pH.

constant for the general acid catalyzed reaction is 0.013 l. mol^{-1} min^{-1}. A smaller formic acid catalysis was observed in hydrolysis of the *p*-chloro derivative at 50° (k_{HA} = 0.0041 l. mol^{-1} min^{-1}). Formic acid catalysis of the hydrolysis of 2-(*p*-methoxyphenoxy)tetrahydropyran was not detected.

Rate constants for the hydrolysis of 2-(*p*-nitrophenoxy)tetrahydropyran at various pH values are reported in Table IV. In those cases where the rates were measured in buffer solutions, the constants were obtained by extrapolation to zero buffer concentration. In Figure 4 is shown a plot of log k_{obsd} *vs.* pH. At low pH the slope is −1.0, but at higher pH a plateau is ob-

Table IV. Rate Constants for Hydrolysis of 2-(*p*-Nitrophenoxy)tetrahydropyran at Various pH Values in 50% Dioxane–H_2O at 50°

pH	k_{obsd}, min^{-1}
0.3[a]	6.49
1.30	0.470
2.40[b]	0.0610
3.72[c,d]	0.0032
4.62[c,d]	0.0019
6.09[c,e]	0.0014
6.80[c,e]	0.0013

[a] 50% dioxane–1 *M* HCl. [b] μ = 0.25. [c] Rate constants found by extrapolation to zero buffer concentration. [d] Formate buffer, μ = 0.5. [e] Acetate buffer, μ = 0.5.

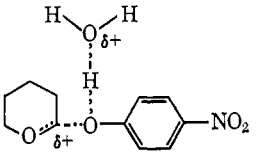
served indicative of a water-catalyzed or uncatalyzed reaction. The line in Figure 4 was calculated employing the equation $k_{obsd} = k_0 + k_H a_H$ and the constants at 50°: $k_0 = 0.0014$ min^{-1} and $k_H = 10.7$ l. mol^{-1} min^{-1}. In alkaline solution (0.05 *M* NaOH) the observed rate constant (0.0013 min^{-1}) is nearly identical with that for the spontaneous reaction.

Discussion

Plots of the logarithms of the rate constants for the acid-catalyzed hydrolysis of substituted phenyl β-D-glucopyranosides *vs.* σ, the Hammett substituent constant, have been found to be linear with slopes of −0.66 and −0.48.[21,22] These values are comparable to that obtained in the present study with 2-(*para*-substituted phenoxy)tetrahydropyrans (−0.92). One possible interpretation of these values is that electron withdrawal in the phenoxy group decreases the equilibrium concentration of protonated intermediate but at the same time increases the ease of carbon–oxygen bond cleavage. Partial cancellation of the opposing effects should give rise to a ρ of small magnitude. In addition to the A1 mechanism, other mechanisms that would also produce compensating effects due to electron withdrawal in the leaving group are the A2, involving attack of solvent on the protonated intermediate, and protonation by hydronium ion concerted with C–O bond breaking.

It has been generally considered that the acid-catalyzed hydrolysis of phenyl glycosides proceeds by an A1 mechanism.[1] Bunnett[23] suggested, however, on the basis of the observed *w* values, that solvent might be participating. Subsequently, Schaleger and Long[24] pointed out that such solvent participation was not likely in view of the highly positive entropies of activation, but this argument is not absolutely conclusive.

From the data in Table I it can be seen that the D_2O solvent isotope effect (k_D/k_H) decreases with increasing electron withdrawal in the leaving group. The value $k_D/k_H = 2.82$ found for 2-ethoxytetrahydropyran is that expected for an A1 mechanism[25] and is comparable to values obtained for other simple acetals.[17,18] The solvent isotope effects for the phenoxy derivatives are considerably less and decrease progressively as electron withdrawal is increased. The solvent isotope effect, $k_D/k_H = 1.33$, found for the nitro-substituted compound is not characteristic of an A1 mechanism and would indicate that a degree of solvent participation is taking place in the hydrolysis of that compound. The most likely mechanism would involve partially rate-determining protonation of oxygen. Thus, the de-



(1)

creasing isotope effects are explainable in terms of the extent of proton transfer, complete in the case of the ethoxy derivative, nearly complete with 2-(*p*-methoxyphenoxy)tetrahydropyran, and then steadily decreasing as increased electron withdrawal makes protonation more difficult and C–O bond breaking easier until with the nitro derivative proton transfer and C–O bond breaking are concerted. The linear σρ plot indicates that no abrupt change in mechanism has occurred in the series. A reaction in which a proton transfer occurs in the transition state might be expected to proceed more slowly in D_2O than in H_2O, but the magnitude of the isotope effect will be dependent upon the extent of proton transfer. The hydrolysis of ortho esters, a reaction currently thought to involve partially rate-determining protonation of oxygen by hydronium ion,[1,26] is generally considerably faster in D_2O than in H_2O.[1,26]

The values of ΔS^* are more negative with greater electron withdrawal in the leaving group, the ΔS^* for 2-(*p*-nitrophenoxy)tetrahydropyran being 15.5 eu more negative than that for 2-ethoxytetrahydropyran. The ΔS^* values for hydrolysis of ortho esters are generally slightly positive or close to zero,[1,26] while vinyl ether hydrolysis, in which rate-determining protonation occurs, often gives a ΔS^* close to zero or moderately negative.[27] Thus, the values of ΔS^* are consistent with a mechanism involving partially rate-determining protonation, as in eq 1, but these values would also be in accord with other mechanisms.[24] Both ΔS^* and the solvent isotope effects are also consistent with an A2 mechanism in which water attacks the protonated acetal, but such a mechanism is less likely than that in eq 1 because solvent attack is normally an unfavorable process in acetal hydrolysis and with the nitro substituted compound nucleophilic catalysis is needed least since bond breaking should be easier than with the other compounds in the series. The change in mechanism for hydrolysis of ortho esters from that normally seen with acetals and ketals is thought to be brought about by the much lower basicity of ortho esters.[1,26] Thus, the same considerations can be applied to the acetals in the present study. Increased electron withdrawal decreases basicity so that, as a consequence, proton transfer is less complete in the transition state.

For a reaction in which the hydronium ion catalyzed reaction involves partially rate-determining protonation, it would be expected that general acid catalysis by the acid component of the buffer would be observed. As seen in Figure 3 a large catalysis by formic acid is observed in the hydrolysis of 2-(*p*-nitrophenoxy)tetrahydropyran. A smaller catalysis was seen with the *para*-chloro derivative, but formic acid catalysis was not detected with 2-(*p*-methoxyphenoxy)tetrahydropyran. Thus, general acid catalysis is dependent upon an electron-withdrawing substituent in the leaving group. It is likely that the different sensitivity to electron withdrawal in the leaving group shown by the general acid and hydronium ion catalyzed reactions is due to C–O bond breaking becoming more important when a weak acid is the catalyst. With hydronium ion protonation can occur without extensive C–O bond breaking, but with a weak acid such bond breaking may be necessary for the new O–H bond to form.[26]

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It should be noted that general acid catalysis was not detected in the hydrolysis of *p*-nitrophenyl β-D-glucopyranoside.[7] With glycosides, the hydroxyl groups will, of course, exert an electron-withdrawing inductive effect on basicity in opposition to that of electron-withdrawing substituents in the *para* position of the phenoxy group.

Only one other example of buffer catalysis in acetal hydrolysis reactions has been previously reported;[2] the hydrolysis of 2-(*p*-methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane was found to be weakly catalyzed by formic acid.[2] Several examples of possible intramolecular catalysis of acetal hydrolysis by various functional groups have been found,[3-7] but for purposes of determining the factors that will facilitate general acid catalysis of acetal hydrolysis, the finding of reactions subject to buffer catalysis is an essential step since the presence of buffer catalysis can be determined in an unambiguous manner. It is of interest that Bruice and Piszkiewicz[9] could not find intramolecular catalysis in the hydrolysis of carboxyl-substituted ketals. The reasons for the lack of catalysis with these compounds are now clear; since the leaving groups are poor, partial proton transfer is unlikely, and alkyl substitution at the reaction center would inhibit any possible nucleophilic attack.

It was found in this laboratory that the acid-catalyzed hydrolysis of 2-(*para*-substituted phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanes in water proceeds in a manner markedly different from that of simple acetals.[2] The application of various mechanistic criteria gave evidence which pointed consistently to a mechanism involving solvent participation in the hydrolysis of these acetals not having an electron-withdrawing substituent in the leaving group. This mechanism difference must be produced by steric inhibition of the A1 reaction due to the presence of methyl groups at the 4 and 5 positions of the 1,3-dioxolane ring since similar 2-(substituted phenyl)-1,3-dioxolanes hydrolyze normally with an A1 mechanism.[17,18] Of the possible mechanisms, including partially rate-determining protonation by hydronium ion or nucleophilic assistance by water in an A2 type of reaction, the A2 mechanism was preferred[2] in view of the extreme slowness of the reactions in comparison to analogous diethyl and ethylene glycol acetals of substituted benzaldehydes, the D_2O solvent isotope effect ($k_D/k_H = 2.4$) which indicated that proton transfer was essentially complete, and the magnitude of the slope (+1.9) of a plot of log $k_{obsd} + H_0$ *vs.* log a_{H_2O}. It has also been found that replacement of hydrogen at the acetal carbon by a methyl group in 2-phenyl-2-methyl-4,4,5,5-tetramethyl-1,3-dioxolane reduces the rate 540 times compared to the corresponding benzaldehyde derivative.[28] Thus, examples have now been found of acetal hydrolysis reactions in which either electronic effects or steric effects can give rise to a mechanism change from the normal A1 mechanism, and it is likely that partially rate-determining protonation will be observed when an electron-withdrawing substituent in the leaving group has substantially reduced basicity.

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(28) T. H. Fife, unpublished data.

A Base-Catalyzed and a Base-Invariant Mechanism in the Rearrangement of Cyclohexenyl to Cyclopentenyl Cations

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Abstract: Two independent mechanisms have been found for the rearrangement of cyclohexenyl to cyclopentenyl cations. One is base catalyzed and the other is base invariant. The ratio of the two paths, and the two products, can be varied by varying the acidity.

With the discovery that many simple allyl cations are stable in aqueous mineral acids,[1] opportunity was provided for directly observing interconversions between such ions. Four general types of such rearrangements have emerged so far. They are (1) the conversion of bicycloalkyl cations to cyclohexenyl cations,[2] (2) the cyclization of linear dienyl cations to cyclopentenyl cations,[3,4] (3) alkyl migrations within cyclopentenyl cations,[5,6] and the contraction of cyclohexenyl cations to cyclopentenyl cations.[2] The purpose of the work reported herein was to examine the effect of structural changes on the last of these four rearrangements.

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