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The Nature of the Steric Effect in the General-Acid-Catalyzed Hydrolyses of Benzaldehyde Acetals

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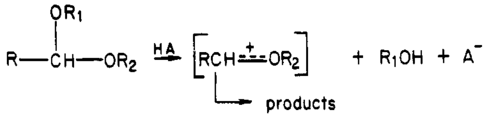
A series of sterically similar dialkyl acetals of benzaldehyde have been synthesized and their rates of hydrolysis measured. A linear plot of log k_{H^+} vs. σ^* yielded $\rho^* = -3.2$ for $PhCH(OR)_2$, where R = CH_2CH_3, CH_3, $CH_2CH_2OCH_3$, CH_2CH_2Cl, or $CH_2C{\equiv}CH$; when R is neopentyl, 2,2,2-trichloroethyl, or 2,2,2-trifluoroethyl, the observed k_{H^+} value is somewhat below the LFER line; when R = *tert*-butyl, the observed k_{H^+} value lies 2 orders of magnitude above the line. It is concluded that relief of steric strain accounts for this 10^2 rate acceleration; in addition, the rate of benzaldehyde di-*tert*-butyl acetal hydrolysis is faster than the rate of acid-catalyzed *tert*-butyl hemiacetal hydrolysis. This gives rise to a change in the rate-limiting step as the pH is changed; acetal hydrolysis is rate limiting above pH 7, hemiacetal hydrolysis is rate limiting below pH 6. The *tert*-butyl hemiacetal breakdown is strongly catalyzed by general acids ($\alpha = 0.6$), just as is the ethyl hemiacetal. Benzaldehyde di-*tert*-butyl acetal shows the same marginal general acid catalysis ($\alpha = 0.9$) as the diethyl acetal. It is concluded that the only significant factor affecting the degree of concertedness of the C–O bond-breaking and the proton transfer processes in the rate-determing step of the hydrolyses of acetals of benzaldehydes is the electronic nature of the leaving group.

Introduction

For more than a decade now, the hydrolyses of acetals have been extensively employed as a physical organic model system to help elucidate, quantitatively, the nature of the catalysis exhibited by lysozyme.[1-3] From the beginning, the objective has been to solve the dilemma posed by the fact that the enzyme employs a general acid catalyst as proton donor (glutamic acid-35), while the acetal hydrolyses studied by physical organic chemists commonly showed no catalysis by the general acids present in buffer solutions. About 10 years ago, the appearance of several review articles[1a,2a,3] clarified the structural features in an acetal which facilitate general acid catalysis. The ultimate objective, of course, has been to provide a sound basis for calculating the rate of hydrolysis, *in solution*, of the lysozyme substrate catalyzed by an acid comparable to glutamic acid-35. This objective has yet to be achieved; however, much work has been expended toward the definition of the three structural features facilitating general acid catalysis. (1) Oxycarbocation stability: R and R_2 groups which help stabilize the intermediate oxycarbocation facilitate general acid catalysis. (2) Leaving group: The better the leaving group, R_1OH (e.g., lower pK_{ROH}), the more general acid catalysis is favored. (3) Steric effect: Ring strain generated by incorporating R and R_2 into part of a three- or four-membered ring or steric strain associated with bulky R_1 and R_2 groups favors general acid catalysis.

Features one and two have been quantitatively defined recently, and it has been demonstrated that the effect of the leaving group is predominant in determining the relative importance of the catalysis of hydrolysis of an acetal by general acids.[4] Therefore, we were interested in the interrelationship (if any) between the steric and electronic effects. That is, is the apparent facilitation of general acid catalysis attributable to steric strain[2] affected by the nature of R_1OH or of R_2? In order to properly examine this question we prepared a series of sterically similar dialkyl acetals of benzaldehyde so as to define a LFER; we then prepared analogous acetals, but possessing bulky alkyl groups (e.g., benzaldehyde di-*tert*-butyl acetal, benzaldehyde dineopentyl acetal, etc.), of different sizes and electronegativities. Surprisingly, only the di-*tert*-butyl acetal of benzaldehyde exhibits a rate acceleration (i.e., a k_{H^+} value larger than predicted by LFER), and even in this instance, there is no facilitation of general acid catalysis; that is, the relative importance of the catalysis by general acids of the hydrolysis of the diethyl and di-*tert*-butyl acetals of benzaldehyde is the same. Thus we conclude that while steric strain may generate an overall rate acceleration, it does not favor one catalyst over another. In other words, the rate acceleration observed for the hydrolysis of benzaldehyde di-*tert*-butyl acetal confers no catalytic advantage to general acids.

Scheme I



Experimental Section

Materials. The di-*tert*-butyl, dineopentyl, and bis(2,2,2-trifluoroethyl) acetals of benzaldehyde were synthesized by the method of Cawley and Westheimer,[5] which involves the reaction of the appropriate alkoxide with benzal bromide (Aldrich Chemical Co.). Other acetals were synthesized[6] from the appropriate alcohol, benzaldehyde, and a catalytic amount of toluenesulfonic acid.[7] All acetals were characterized by ^1H NMR; the spectra were in quantitative agreement with the structure of the substance expected from the synthesis and no extraneous peaks were present.

Methylphosphonic monoacid anion buffers were prepared by neutralizing methylphosphonic acid with 1 equiv of potassium hydroxide; the acid was synthesized from dimethyl methylphosphonate (Aldrich Chemical Co.).[8] The "cacodylic acid" obtained from J. T. Baker proved to be a 60% technical grade; the remaining 40% was an inert salt. Since purification was not deemed worth the effort, a 98% pure $(CH_3)_2AsO_2H$ grade was

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[1] (a) Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581–603. (b) Cordes, E. H.; Bull, H. G. In "Transition States of Biochemical Processes"; Gandour, R. D.; Schowen, R. L., Eds.; Plenum Press: New York, 1978; Chapter 11, pp 429–465.

[2] (a) Fife, T. H. *Acc. Chem. Res.* **1972**, *5*, 264–272. (b) Fife, T. H. *Adv. Phys. Org. Chem.* **1975**, *11*, 1–122.

[3] Dunn, B. M.; Bruice, T. C. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1973**, *37*, 1–60.

[4] Jensen, J. L.; Wuhrman, W. B. *J. Org. Chem.*, in press.

[5] Cawley, J. J.; Westheimer, F. H. *Chem. Ind. (London)* **1960**, 656.

[6] Horning, E. L., Ed., "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, pp 644–646.

[7] A greater quantity of sulfuric acid catalyst was used for the reaction with 2,2,2-trichloroethanol; the reactant solution was ~2 M in H_2SO_4.

[8] (a) Kluger, R.; Wasserstein, P.; Nakoda, K. *J. Am. Chem. Soc.* **1975**, *97*, 4298. (b) Kresge, A. J.; Tang, Y. C. *J. Org. Chem.* **1977**, *42*, 757.

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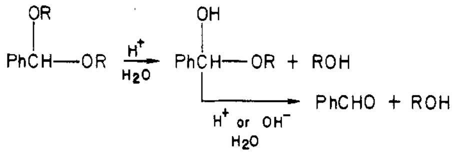
Table I. Values of k_{H^+} for the Hydrolyses of Dialkyl Acetals of Benzaldehyde ($PhCH(OR)_2$) at 25 °C, $\mu = 0.5$ (KCl)[a]

	water		50% dioxane	
R	pH range	k_{H^+}, $M^{-1}\ s^{-1}$ [b]	pH	k_{H^+}, $M^{-1}\ s^{-1}$ [c]
$CH_2C(CH_3)_3$	4.6–5.4	14.1	3.0	2.45
CH_2CH_3	4.6–5.5	155	3.0	7.48
CH_3	4.1–5.0	54.0	3.0	1.92
$CH_2CH_2OCH_3$	3.6–4.6	18.7	3.0	0.63
CH_2CH_2Cl	2.9–4.1	3.90	2.0	0.136
CH_2CF_3	(0.1–0.7)[d]	0.0035	(1.2)[d]	0.0047
CH_2CCl_3	(0.1–1.0)[d]	0.0036	(1.2)[d]	0.0075

[a] Buffer solutions were very dilute so as to minimize buffer catalysis; [buffer] $\leqslant$ 0.02 M. Quenching experiments[15] gave no evidence that hemiacetal buildup was significant. [b] Calculated following procedures recommended in ref 11; calculated from $k_{obsd} = k_{H^+}[H^+]$, where $[H^+]$ is antilog $-pH_{exp}$ and correlation coefficients $\geqslant$ 0.99. Plots of log k_{obsd} vs. −pH gave lines of slopes = 1.01 ± 0.03. [c] Calculated using the single point procedure;[11] $k_{H^+} = k_{obsd}/[H^+]$. [d] Values in parentheses are [HCl]; correlations are generated by using interpolated H_0 values for water[12a] and for 50% dioxane/water.[12b]

Scheme II



obtained from Sigma Chemical Co.

Kinetic Procedures. The kinetic method was that described previously.[9,11] Reactions were monitored by observing the appearance of benzaldehyde at 248 nm (λ_{max}), using either a Pye Unicam SP 8–100 kinetic spectrophotometer, a Beckman Model 25 kinetic system, or a Beckman Model DU specially modified with a constant temperature water bath between the monochrometer and the phototube housing.[10] pH measurements were made by using a Beckman Model 4500 pH meter equipped with a ceramic junction combination electrode.

Results

The pH–Rate Profile. The second-order k_{H^+} values reported in Table I for the series $PhCH(OR)_2$ span a range of reactivity of 10^5. Although each individual kinetic run exhibited excellent first-order behavior and pseudo-first-order data thus obtained gave excellent correlations with the measured pH values (footnote *b*, Table I), we were concerned about the limited solubility of some of the bulkier acetals. The fact that analogous data were obtained in 50% dioxane/water, where artifacts due to solubility problems are not likely, reinforces our conclusion that the aqueous data are totally reliable. In fact, the difference in substituent effect between water and 50% dioxane/water is nearly identical with that which we reported previously for another acetal series.[9,13]

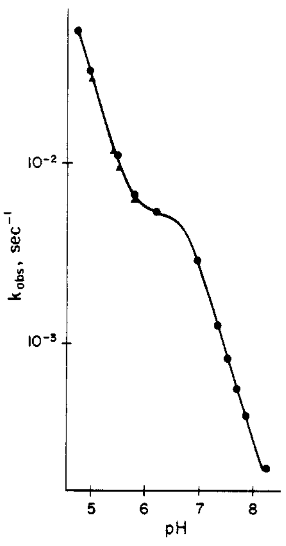


Figure 1. pH–rate profile for the hydrolysis of benzaldehyde di-*tert*-butyl acetal in water at 25 °C, $\mu = 0.5$ (KCl): data from dilute buffers, [buffer] ≤ 0.02 M, ●; data extrapolated to infinite dilution, [buffer] = 0, ▲.

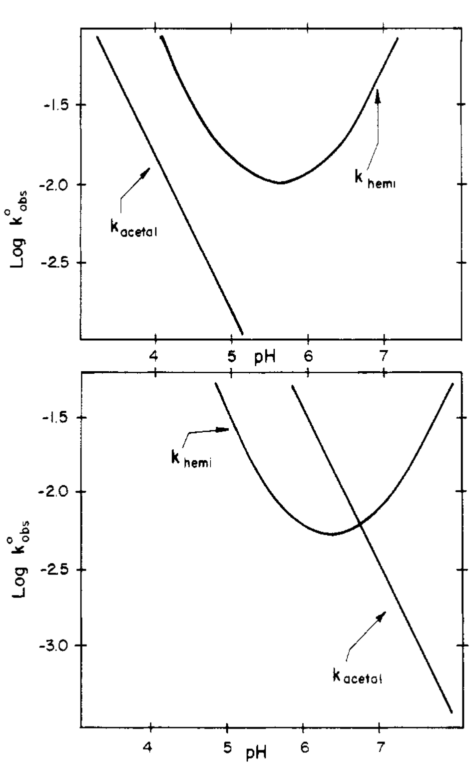


Figure 2. pH–rate profiles for the hydrolyses of benzaldehyde diethyl acetal and ethyl hemiacetal (top) and for the hydrolyses of benzaldehyde di-*tert*-butyl acetal and *tert*-butyl hemiacetal (bottom) in water at 25 °C, $\mu = 0.5$ (KCl). k°_{obsd} denotes the observed rate constant at zero buffer concentration.

The pH–rate profile observed for the hydrolysis of the di-*tert*-butyl acetal of benzaldehyde was not so easily analyzed, because of its sigmoidal shape (Figure 1). The two sets of curves in Figure 2, however, clearly show how the sigmoidal pH–rate profile arises: k_{H^+}(acetal) is subject to a much larger rate acceleration than k_{H^+}(hemiacetal) for R = *t*-Bu relative to R = Et. The overall rate of a multistep process cannot exceed that allowed by the slowest step; therefore, when R = *t*-Bu, the rate-limiting step is *k*(hemi) below pH 6 and *k*(acetal) above pH 7. This entire pH–rate profile confirms the prior report by Capon[14] that

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(9) Jensen, J. L.; Herold, L. R.; Lenz, P. A.; Trusty, S.; Sergi, V. J.; Bell, K.; Rogers, P. *J. Am. Chem. Soc.* **1979**, *101*, 4672–4677.

(10) Jensen, J. L.; Carré, D. J. *J. Org. Chem.* 1971, *36*, 3180–3183.

(11) Jensen, J. L.; Carr, M. D.; Yamaguchi, K. S. *Int. J. Chem. Kinet.* **1983**, *15*, 235–248.

(12) (a) Paul, M. A.; Long. F. A. *Chem. Rev.* **1957**, *57*, 1. (b) Torck, B.; Hellin, M.; Coussemant, F. *Bull. Soc. Chim. Fr.* **1962**, 1657, 1664.

(13) For the LFER set R = CH_2CH_3, CH_3, CH_3, $CH_2CH_2OCH_3$, and CH_2CH_2Cl in Table I, $\rho^* = -3.0$ and -3.2 in water and 50% dioxane-water, respectively; the correlation coefficient is 0.98 in both instances. The prior report for the ArCH(OEt) series was $\rho = -3.2$ and -3.6 in water and 50% dioxane-water, respectively.

(14) Capon, B. *Pure Appl. Chem.* **1977**, *49*, 1001–1007.

Table II. Values of k_{H^+} and k_{HA} for Hydrolyses of Benzaldehyde Di-*tert*-butyl Acetal and Benzaldehyde *tert*-Butyl Hemiacetal at 25 °C, $\mu = 0.5$ (KCl)[a]

substance	k_{H^+}, $M^{-1}\ s^{-1}$	k_{Ac}, $M^{-1}\ s^{-1}$ [b]	k_{Cac}, $M^{-1}\ s^{-1}$ [b]	k_{MP}, $M^{-1}\ s^{-1}$ [b]
acetal	25000		4.0×10^{-3}	2.3×10^{-4}
hemiacetal	2600[c]	0.31	0.12	

[a] Values calculated as described by Figure 3 and the accompanying discussion. [b] Ac = acetic acid, Cac = cacodylic acid, MP = methylphosphonic acid monoanion. pK_{HA} at zero buffer concentration = 4.60, 6.19, and 7.41, respectively. [c] k_{H^+}(hemi) = 2,600 $M^{-1}\ s^{-1}$ calculated from the upper linear portion of the sigmoidal curve depicted in Figure 1. $k_{OH^-} = 3.3 \times 10^4\ M^{-1}\ s^{-1}$ measured by a multimixer stopped-flow procedure,[18] using a Dionex Model D 132 system.

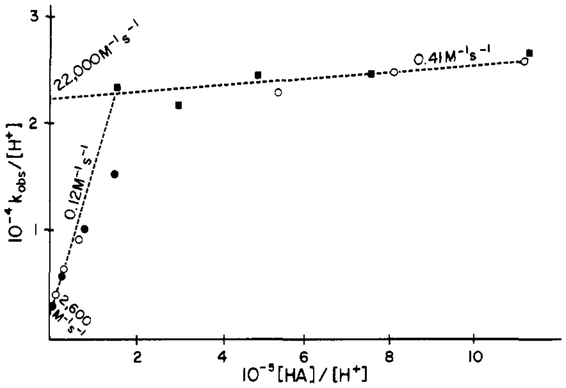

Figure 3. General acid catalysis plot for the apparent hydrolysis of benzaldehyde di-*tert*-butyl acetal in aqueous cacodylic acid—potassium cacodylate buffer at 25 °C, $\mu = 0.5$ (KCl): 5:1 buffer, pH 5.4, ●; 2:1 buffer, pH 5.8, ○; 1:5 buffer, pH 6.9, ■.

the rate-determining step changed around pH 7. We observed non-first-order kinetics near pH 6.5; the kinetics could be treated by our differential method[15] to give two constants: The larger k falls on the k_{acetal} line of Figure 2 and the smaller k falls on the plateau region of the sigmoidal curve. The linear portions of Figure 1 allow accurate calculation of k_{H^+}(acetal) and k_{H^+}(hemi). The line and inverted bell curve depicted in the botton graph of Figure 2 were constructed from k_{H^+}(acetal), k_{H^+}(hemi), and k_{OH^-}(hemi); these values are tabulated in Table II (cf. footnote *c*). The bottom of these inverted bell curves typically[17,21] contain a small k_{H_2O} term (eq 1), which may or may not be distinguishable from zero.[18]

From this analysis it is clear that hemiacetal breakdown is rate limiting below pH 6, acetal hydrolysis is rate limiting above pH 7, and the change in the rate-determining step occurs between pH 6 and 7. These comments, of course, are relative to reactions carried out in buffer solutions at infinite dilution (for practical purposes, $[\text{buffer}]_{total} \le 0.02$ M).

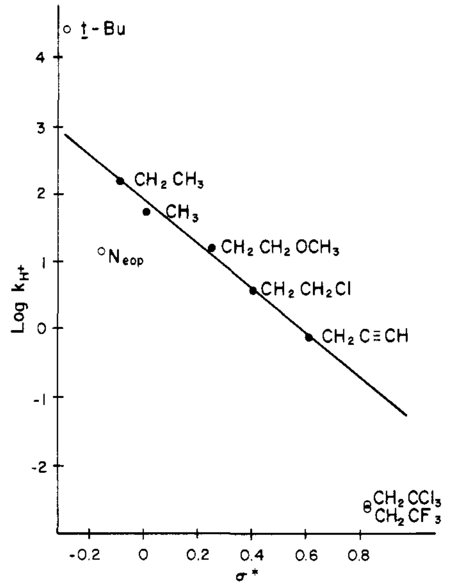

Figure 4. Plot of log k_{H^+} vs. σ^* for the hydrolyses of the $PhCH(OR)_2$ series. $\rho^* = -3.2$ (correlation coefficient = 0.992) for the R = CH_2CH_3, CH_3, $CH_2CH_2OCH_3$, CH_2CH_2Cl, and $CH_2C{\equiv}CH$ set.

Buffer Catalysis. There is a pronounced difference in the effect of the buffer concentration on k (acetal) and k (hemi); indeed, in buffer solutions of pH 6–7, the rate-determining step can be changed by changing the buffer concentration. This is shown most clearly by Figure 3, which includes data from 1:5, 2:1, and 5:1 cacodylic acid–potassium cacodylate buffers at pH values of 6.9, 5.8, and 5.4, respectively. As can be seen by reference to Figure 1, these pH values were chosen so that at pH 6.9 k_{H^+}(acetal) is rate determining, at pH 5.4 k_{H^+}(hemi) is rate limiting, and the changeover pH is near pH 5.8. When the data are plotted as in Figure 4, all of the data for a given buffer should lie on the same curve, *if* the only catalytic species are acidic.[4] We treated these data in the traditional way[16] to demonstrate that k_{A^-} terms are indistinguishable from zero. Thus, although eq 1 holds true for hemiacetal

$$k_{obsd}(\text{hemi}) = k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_{HA}[HA] + k_{A^-}[A^-] + k_{H_2O} \quad (1)$$

hydrolyses, in these acidic buffer systems $k_{HA} > k_{A^-}$ and k_{A^-} for practical purposes is 0. Therefore, in these acidic buffer systems, the equation defining k_{obsd} is strictly analogous to acetal hydrolyses (cf. 2). These observations

$$k_{obsd} = k_{H^+}[H^+] + k_{HA}[HA] \quad (2)$$

are consistent with unpublished results obtained from the breakdown of ethyl hemiacetals of substituted benzaldehydes;[17] that study defines the relationship between substituent (i.e., reactivity) and catalysis and is not yet completed.[18]

Plots such as Figure 3 were constructed from data obtained in acetic acid (pK = 4.6) and methylphosphonate monoacid anion (pK = 6.2) buffers: predictably, the acetic acid catalysis plots showed steep dependence of rate on buffer concentration, and the points for the largest HA concentration fell below the line. In the phosphonate buffer, the rate dependence was mild, with significant downward curvature at low buffer concentrations. Thus, although the total curve arising from a complete change in the rate-limiting step was defined only in cacodylic acid buffers (Figures 3), the general features of the curve were observed in the other buffer systems. The result from this, of course, is that k_{HA} values were measured for hemiacetal

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(15) Jensen, J. L.; Lenz, P. A. *J. Am. Chem. Soc.* **1978**, *100*, 1291–1293.

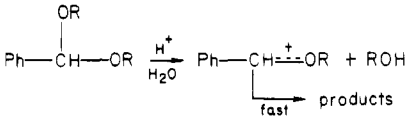
(16) (a) Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969; pp 164–168. (b) Bell, R. P. "The Proton in Chemistry"; 2nd ed.; Cornell University Press: Ithaca, NY, S 1973; p 173.

(17) (a) Hall, R. M., M.S. Thesis, California State University, Long Beach, CA, 1980. (b) Jensen, J. L.; Herold, L. R.; Hall, R. M. "Abstracts of Papers", The Chemical Society Second International Conference on the Mechanisms of Reactions in Solution, University of Kent at Canterbury, July 9–13, 1979, No. C16, pp 147–148. (c) Jensen, J. L.; Hall, R. M. "Abstracts of Papers", Pacific Conference on Chemistry and Spectrscopy, Pasadena, CA, October 10–12, 1979, No. 25, p 31.

(18) Jensen, J. L.; Hall, R. M.; Levan, L. L.; Kanner, R., results to be published in 1984.

(19) Anderson, E.; Fife, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 1701–1704.

Scheme III



breakdown in acetic and cacodylic acid buffers but not in the methylphosphonate buffers; conversely, k_{HA} values were measured for acetal hydrolysis in methylphosphonate and cacodylic acid buffers but not in acetic acid buffers. These values are reported in Table II.

Discussion

The Steric Rate Acceleration. In order to try to differentiate the steric and electronic effects, log k_{H^+} from Tables I and II are plotted against σ^* in Figure 4. The points for R = CH_2CH_3, CH_3, $CH_2CH_2OCH_3$, CH_2CH_2Cl, and $CH_2C{\equiv}CH$ are used to establish the LFER; it is not surprising that the markedly dissimilar R = *tert*-butyl, neopentyl, and trichloroethyl data points fall off the line (e.g., the E_s values are much larger). These data are for the acetal hydrolysis step, and hence there is actually a double variable involved: one group is leaving (as ROH) and the other is remaining behind as part of the oxycarbocation intermediate. We have previously shown, however, that when the group remaining is held constant (as Et) and only the leaving group is varied, $\rho^* = -1.06$ (correlation coefficient = 0.992).[9] Since the LFER in Figure 3 gives a $\rho^* = -3.2$, it is clear that the major rate effect comes from the R group which remains behind as part of the oxycarbocation. Because these effects are not strictly separable, and certainly not equal, we have left the plot as log k_{H^+} vs. σ^* rather than vs. $2\sigma^*$. Clearly the one ρ^* is about −1 and the other about −2; i.e., the substituent effect of the leaving group on the rate of hydrolysis is an order of magnitude smaller.

The important point obvious in Figure 4 is that the k_{H^+} values for the four alkyl groups *tert*-butyl, ethyl, methyl, and neopentyl span a range of more than 10^3. Because the dineopentyl acetal hydrolyzes the slowest and the di-*tert*-butyl acetal the fastest, no combination of electronic and steric parameters can quantitatively fit the data. Qualitatively, we can say that the relief of steric strain that gives rise to the 10^2–10^3 rate acceleration is quite specific; that is, the crowding must be severe and close to the reaction center. The more general bulk effect (R = neopentyl and trichloroethyl) gives rise to a rate deceleration effect that appears independent of the electronegativity of the group.

The relief of steric strain, as measured by the rate acceleration (relative to the LFER line), can be expressed as a differential free energy difference of about 3 kcal mol^{-1}. While this gives rise to a substantial rate acceleration, it is not very large by comparison with the difference in the heats of hydrogenation[20] of *cis*- and *trans*- di-*tert*-butylethylene (9.3 kcal mol^{-1}); however, it is significant that the *cis*- and *trans*-dineopentylethylenes differ by 0.9 kcal mol^{-1}, which is within experimental error of the 1.0 kcal mol^{-1} *cis*- and *trans*-2-butene differential. Thus there is precedent for the specific steric crowding effect observed for the di-*tert*-butyl acetal of benzaldehyde.

Table III. Effect of Steric Strain on Hydrolyses of Acetals and Hemiacetals of Benzaldehyde

substrate	k_{H^+}, M^{-1} s^{-1} [a]	k_{rel}	α
$PhCH(OEt)_2$	160 [b]	1	0.9 [d]
$PhCH(O\text{-}t\text{-}Bu)_2$	25000 [b]	150	0.9 [b]
PhCH(OH)OEt	1000 [c]	6	0.6 [c]
PhCH(OH)O-*t*-Bu	2600 [b]	15	0.6 [b]

[a] 25 °C, μ = 0.5 (KCl). [b] This work. [c] Reference 18. [d] Reference 9.

It bears noting that other explanations for these phenomena have been ruled out. (1) Cawley and Westheimer[5] hydrolyzed benzaldehyde di-*tert*-butyl acetal in ^{18}O-enriched water; the lack of any ^{18}O enrichment in the *tert*-butyl alcohol formed during hydrolysis precludes the intermediacy of a *tert*-butyl carbocation. (2) Quenching experiments[15] were carried out during the hydrolyses of the dineopentyl and ditrichloroethyl acetals to test for the presence of large amounts of hemiacetal; the rate constants reported in Table I are definitely for acetal hydrolysis, since the hemiacetal intermediate does not build up to significant levels during the hydrolysis of these two acetals. Thus we are left with relief of steric strain as the most plausible explanation for the rate acceleration observed. Now the effect that relief of steric strain has on the mode of catalysis will be discussed.

The Absence of a Steric Effect on Concertedness. Since it has long been known that the presence of a better leaving group (e.g., aryl) in the acetal moiety brings about an increased concertedness in the processes required for formation of the oxycarbocation (i.e., proton transfer and C–O bond breaking), it was only reasonable that a steric source rather than an electronegativity source would produce an increased concertedness as well.[2,19] Of course, the premiere criterion for observing this concertedness in these reactions is the determination of the Brønsted α, which provides a measure of the extent of proton transfer in the transition state. The $ArCH(OR)_2$ system can be described semiquantitatively in terms of Hammett ρ and Brønsted α values; the ρ value is an effective measure of the extent of C–O bond breaking achieved in the transition state, and the α is an effective measure of the extent of proton transfer. For the $ArCH(OEt)_2$ system $\rho = -3.2$ and for the $ArCH(OCH_2CH_2Cl)_2$ system $\rho = -3.2$; for $PhCH(OEt)_2$, $\alpha = 0.9$ and for both $PhCH(OCH_2CH_2Cl)_2$ and $PhCH(OEt)OCH_2CH_2Cl$ the Brønsted $\alpha = 0.8$.[9] As previously noted,[4,9] the electronic effect of the leaving group has the predominant effect on the concertedness of the rate-determining step: The better leaving group is associated with the most catalysis (the smaller α) and is nearly independent of other structural differences.

The data for the *tert*-butyl system are summarized in Table III. The significant results are as follows: (1) Though the di-*tert*-butyl acetal exhibits a rate acceleration of 10^2, the Brønsted α is the same as for the electronically similar diethyl acetal. (2) The rate "acceleration" for the *tert*-butyl hemiacetal is quite modest and the Brønsted α values for both the ethyl and the *tert*-butyl hemiacetal are the same, and are markedly smaller (α = 0.6) than the α observed for the corresponding acetal hydrolyses (α = 0.9). These data conclusively show that the rate acceleration associated with relief of steric strain does not affect the degree of concertedness of the proton transfer and the C–O bond-breaking processes. Hence, the only significant factor affecting concertedness in the benzaldehyde acetal series is the electronic nature of the leaving group (R_1 in Scheme I). Recent results on the tetrahydropyran system[4]

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[20] Jensen, J. L. *Prog. Phys. Org. Chem.* **1976**, *12*, 189–228.

[21] Przystas, T. J.; Fife, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 4887 (Figure 5); the upper portion of Figure 2 is our data[17] under exactly the same conditions as the lower portion. Taking into account temperature and ionic strength differences, ref 21 and 17 curves are equivalent.

suggest that this conclusion is rather general.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged (CHE 7907588 and PRM 7919451). J.L.J. spent a 1981–82 sabbatical leave from CSULB in the Chemistry Department, University of California, Irvine, whose kind hospitality and intellectual stimulation were much appreciated.

Registry No. $PhCH[OCH_2C(CH_3)_3]_2$, 56377-78-7; $PhCH(OCH_2CH_3)_2$, 774-48-1; $PhCH(OCH_3)_2$, 1125-88-8; $PhCH(OCH_2CH_2OCH_3)_2$, 71412-83-4; $PhCH(OCH_2CH_2Cl)_2$, 59606-97-2; $PhCH(OCH_2CF_3)_2$, 87088-60-6; $PhCH(OCH_2CCl_3)_2$, 37150-43-9.

Palladium/Polystyrene Catalysts

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The reaction of reactive alkali metal organometallic derivatives of divinylbenzene-cross-linked polystyrene with solutions of dichloro(1,5-cyclooctadiene)palladium(II) to form palladium/polystyrene catalysts is described. Organometallic polymers used in these reactions include polystyryllithium, polystyrylbenzyllithium, polystyrylphenyl(trimethylsilyl)methyllithium and polystyrene-bound sodium anthracene. The palladium/polystyrene catalysts formed in these reactions were characterized by ESCA and electron microscopy, and their activity as hydrogenation catalysts was examined in various solvents and under various conditions of catalyst pretreatment. Comparisons of the catalytic activity of these catalysts to commercial Pd/C in the hydrogenation of various substrates are also made. Novel catalytic activity observed for these palladium/polystyrene catalysts includes some activity as decarbonylation catalysts in reactions with simple alkyl and aryl aldehydes and their use in place of tetrakis(triphenylphosphine)palladium(0) as a catalyst for the formation of tertiary allylamines from allyl esters and secondary amines. The interaction of functional groups such as organolithium and carboxylic acid groups attached to the polystyrene support with the active centers of the hydrogenation catalysts was also demonstrated by their effect on the activity of these hydrogenation catalysts.

Heterogeneous catalysts are often prepared as dispersions of metal crystallites on high surface area inorganic supports by impregnating the support with a solution of a metal salt, removing volatiles, and reducing the oxidized metal to elemental metal.[2] The resulting catalysts are useful in a wide variety of reactions in organic chemistry.[3] In order to avoid the relatively harsh conditions and metal agglomeration often produced by these procedures[4] and to explore the possibility of preparing more modifiable, more reactive, and/or more selective heterogeneous catalysts we have studied the use of reactive organometallic polymers and their reaction with palladium(II) salts as a route to palladium(0) catalysts. Our results described in this paper show that palladium/polystyrene catalysts can be prepared under mild conditions in this manner and that the resulting catalysts compare favorably with other conventional heterogeneous palladium catalysts.

The use of functionalized organic polymers to support catalysts is a topic of current interest especially as it concerns the support of otherwise homogeneous transition-metal complexes.[5] Such studies have included nearly every transition metal and have led to polymer-based catalysts for many different sorts of reactions. It is therefore not surprising that palladium catalysts, which are widely useful in organic chemistry,[6] have also received attention as candidates for attachment on organic polymers. Indeed, palladium species such as phosphine-ligated palladium(0) and phosphine-ligated palladium(II) complexes,[7] bipyridyl-ligated palladium(II),[8] and ionically bound palladium(II)[9] have all been successfully attached to functionalized divinylbenzene- (DVB) cross-linked polystyrene to give useful catalysts. Other novel heterogeneous palladium catalysts have also been prepared from potassium–graphite[10] or as colloidal dispersions in various types of organic polymer matrices.[11] This paper describes the preparation of highly dispersed palladium(0) catalysts by means of initial attachment or reduction of a homogeneous palladium(II) complex using reactive organoalkali metal derivatives of divinylbenzene-cross-linked polystyrene. As is described in detail below, the palladium/polystyrene species resulting from these procedures consist of small palladium(0) crystallites (ca. 20–40 Å in diameter) dispersed throughout DVB-cross-linked polystyrene beads

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[2] Satterfield, C. N. "Heterogeneous Catalysis in Practice"; McGraw-Hill: New York, 1980.

[3] (a) Freifelder, M. "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary"; Wiley-Interscience: New York, 1978. (b) Rylander, P. N. "Organic Syntheses with Noble Metal Catalysts"; Academic Press: New York, 1973.

[4] Ruckenstein, E.; Dadyburjor, D. B. *J. Catal.* **1977**, *48*, 73–86. Jarrell, M. S.; Gates, B. C.; Nicholsen, E. D. *J. Am. Chem. Soc.* **1978**, *100*, 5727–5732.

[5] (a) Minkiewicz, J. V.; Milstein, D.; Lieto, J.; Gates, B. C.; Albright, R. L. *ACS Symp. Ser.* **1982**, *No. 192*, 9–29. (b) Ciardelli, F.; Braca, G.; Carlini, C.: Sbrana, G.; Valentini, G. *J. Mol. Catal.* **1982**, *14*, 1–17. (c) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109–148. (d) Whitehurst, D. D. *CHEMTECH* **1980**, 44–49.

[6] (a) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. II. (b) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer Verlag: Berlin, 1980. (c) Trost, B. M. *Pure Appl. Chem.* **1981**, *53*, 2357–2370.

[7] (a) Bruner, H.; Bailar, Jr., J. C. *Inorg. Chem.* **1973**, *12*, 1465–1469. (b) Pittman, C. U., Jr.; Ng, Q. *J. Organomet. Chem.* **1978**, *153*, 85–97. (c) King, R. B.; Hanes, R. M. *J. Org. Chem.* **1979**, *44*, 1092–1094. (d) Kaneda, K.; Kurosaki, H.; Terasawa, M.; Imanaka, T.; Teranishi, S. *Ibid.* **1981**, *46*, 2356–2362. (e) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc. 1982*, *104*, 6112–6114.

[8] (a) Card, R. J.; Neckers, D. C. *Inorg. Chem.* **1978**, *17*, 2345–2349. (b) Card, R. J.; Liesner, C. E.; Neckers, D. C. *J. Org. Chem.* **1979**, *44*, 1095–1098. (c) Drago, R. S.; Nyberg, E. D.; El A'mma, A. G. *Inorg. Chem.* **1981**, *20*, 2461–2466.

[9] Holy, N. L.; Shelton, S. R. *Tetrahedron* **1981**, *37*, 25–26.

[10] Savoia, D.; Thrombini, C.; Umani-Ronchi, A.; Verardo, G. *J. Chem. Soc., Chem. Commun.* **1981**, 540–541.

[11] (a) Hirai, H. *J. Macromol. Sci., Chem.* **1979**, *A13*, 633–649. (b) Coleman, D. R.; Royer, G. P. *J. Org. Chem.* **1980**, *45*, 2268–2269.