In the structures of I and II, the $Fe_4S_4^*$ cores show no evidence of the compressed D_{2d} type of distortion apparent in virtually all of the $[Fe_4S_4]^{2+}$ cores in the structurally characterized $[Fe_4S_4^*L_4]^{2-}$ clusters. At least in an asymmetric terminal ligand environment the $[Fe_4S_4^*]^{2+}$ core is not subject to a D_{2d} compression.

The Fe–S* bond lengths in all $[Fe_4S_4^*L_4]^{2-}$ clusters (including the mixed terminal ligand clusters) span a very narrow range. As a result of this apparent constancy of the Fe–S* bond lengths, the volumes of the $Fe_4S_4^*$ polyhedra are very similar for the $[Fe_4S_4^*]^{2+}$ cores[34] in virtually all of the $[Fe_4S_4(SR)_4]^{2-}$ clusters ($\bar{V}_{[Fe_4S_4^*]^{2+}}$ = 9.63 (8) Å^3). Upon reduction, the $[Fe_4S_4^*]^{+}$ cores undergo a small expansion that is associated primarily with the slightly elongated $\overline{\text{Fe–S*}}$ bond length ($\bar{V}_{[Fe_4S_4^*]^{+}}$ = 9.78 (7) Å^3).[53,54]

The redox potentials associated with electron transfer to or from the $Fe_4S_4^*$ cores within the various ferredoxins may well be adjusted by the environmental characteristics of the protein matrix. To a first approximation, one may expect lower reduction potentials for proteins in which the $[Fe_4S_4^*]$ cores reside in structurally flexible cavities that can accommodate the core expansion that accompanies reduction. Higher reduction potentials would be expected for proteins that provide more rigid accommodations for the $[Fe_4S_4^*]^{2+}$ cores. The degree of anisotropy that characterizes the redox-related changes in the $Fe_4S_4^*$ volumes and in the protein ternary structure at present is difficult to ascertain.

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Registry No. I, 80939-30-6; II, 88363-89-7; III, 90867-29-1; IV, 88363-91-1; $(Ph_4P)_2[Fe_4S_4(SPh)_2Br_2]$, 90867-31-5; $(Ph_4P)_2[Fe_2S_2(SPh)_4]$, 84032-42-8; $FeCl_2$, 7758-94-3; KOPh, 100-67-4; NaOPh, 139-02-6; Na-*p*-MePhO, 1121-70-6.

Supplementary Material Available: Listings of observed and calculated structure factors and tables of positional and thermal parameters for all atoms in I–III (49 pages). Ordering information is given on any current masthead page.

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Observation of a Stable Hemiortho Ester Anion. Acidity Constant for a Tetrahedral Intermediate

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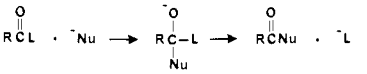
Abstract: Pinacol mono-*p*-nitrobenzoate (POH) undergoes a rapid, reversible cyclization in base producing an anionic tetrahedral intermediate (TO^-), the conjugate base of 2-(*p*-nitrophenyl)-2-hydroxy-4,4,5,5-tetramethyl-1,3-dioxolane (TOH). Presence of the anion is established by changes in UV spectra and by the rate behavior exhibited in the hydrolysis of the ester to pinacol and *p*-nitrobenzoate. Rate constants in base do not rise as rapidly as expected as the ester form is converted to the unreactive TO^-. Interconversion of POH and TO^- occurs in a typical acid:base manner, and UV spectral analysis in base provides $K_b = [POH][OH^-]/[TO^-] = 0.7$. The equilibrium constant $K_0 = [TOH]/[POH]$ for cyclization of the pinacol ester to the neutral hemiortho ester TOH is 8×10^{-4}; this has been measured as the ratio of forward and reverse rate constants. Combination of K_b and K_0 provides a value $K_a = [TO^-][H^+]/[TOH]$ for the acidity constant of the tetrahedral intermediate of $10^{-10.4}$. This number is compared with estimates of tetrahedral intermediate acidity based on substituent effects and free energy correlations, and excellent agreement is noted.

Nucleophilic acyl substitution reactions involving an anionic nucleophilic and an anionic leaving group generally proceed in a simple two-step reaction sequence by way of an anionic tetrahedral addition intermediate. The presence of this intermediate



$$RC(=O)L \cdot {}^-Nu \longrightarrow RC(O^-)(Nu)\text{–}L \longrightarrow RC(=O)Nu \cdot {}^-L \qquad (1)$$

has been established through kinetic arguments,[1-3] notably the observation of carbonyl oxygen exchange during the hydrolysis of acid derivatives.[1] Recently, hemiortho esters $RC(OR)_2OH$, the neutral tetrahedral intermediates of alcohol interchange reactions RCOOR + ROH, have been observed as transient species.[4,5] These hemiortho esters are in general thermodynamically unstable relative to their breakdown products; in the experiments where they are observed some high-energy species such as $RC(OR)_2X$ with X, a good leaving group, is employed as a precursor.

In a recent study[6] involving a nitrogen heterocycle, we encountered a situation where a tetrahedral intermediate anion (QO^-) is generated as a thermodynamically stable form from an acyl precursor (F).

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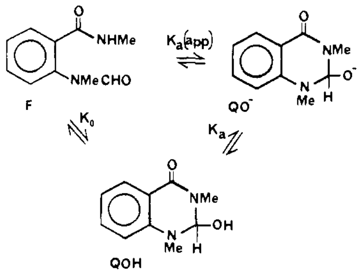
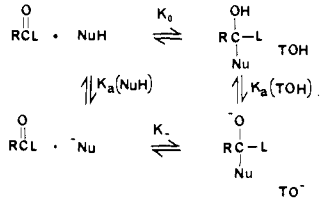


(2)

This type of situation can be analyzed in terms of the general scheme of eq 3. Recognizing that $K_- = K_0K_a(\mathrm{TOH})/K_a(\mathrm{NuH})$



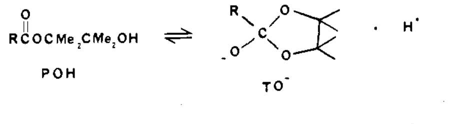
(3)

the situation can be visualized where the intermediate TOH is much more acidic than the nucleophile NuH ($K_a(\mathrm{TOH}) \gg K_a(\mathrm{NuH})$), and the unfavorable addition of the neutral nucleophile ($K_0 < 1$) becomes thermodynamically favorable for the anion ($K_- > 1$). In this case the species which is produced in basic solutions is the tetrahedral intermediate ion, and this forms with an apparent acidity constant $K_a(\mathrm{app}) = [\mathrm{TO^-}][\mathrm{H^+}]/[\mathrm{RCOL}][\mathrm{NuH}] = K_0K_a(\mathrm{TOH})$. In the system of eq 2 we found $K_0 = 1/300$, $\mathrm{p}K_a(\mathrm{TOH}) = 11.1$, and $\mathrm{p}K_a(\mathrm{app}) = 13.6$. The latter value indicates that in solutions more basic than pH 13.6 the anion QO⁻ is the predominant form.

There are several other examples of this type in the literature, although a detailed quantitative analysis have generally not been carried out. Sodium alkoxides in the alcohol solvent add reversibly to activated esters, such as alkyl trifluoroacetates and dialkyl oxalates,[7] these being the only intermolecular examples to date. The sodium salts of 2-sulfhydryl-1,3-dioxolanes and 1,3-dioxanes are formed by treatment of an appropriate hydroxy thionester with sodium hydride.[8] A similar example involving addition of an intramolecular hydroxy group to a complex carbonate has also been noted.[9] Tetrodotoxin[10] is a naturally occurring anionic tetrahedral intermediate (actually zwitterionic). A phosphorus analog—the anionic pentavalent intermediate of a phosphoryl transfer—has also been reported.[11]

As part of our investigations of tetrahedral intermediates we have initiated a study of these and other systems. There are several requirements that must be met if the tetrahedral intermediate anion is to be observed in base solutions. As mentioned previously, $K_a(\mathrm{TOH})$ must be significantly greater than $K_a(\mathrm{NuH})$. Equally important, the neutral equilibrium cannot be so unfavorable that it cannot be turned around by the greater acidity of TOH. Finally, if the anion is to be observed in an aqueous solution the hydroxide ion hydrolysis of RCOL which will obviously occur in strongly basic solutions cannot be too rapid.

A system which appeared to us to meet these requirements involved the cyclization of a pinacol monoester to an anionic dioxolane.



(4)

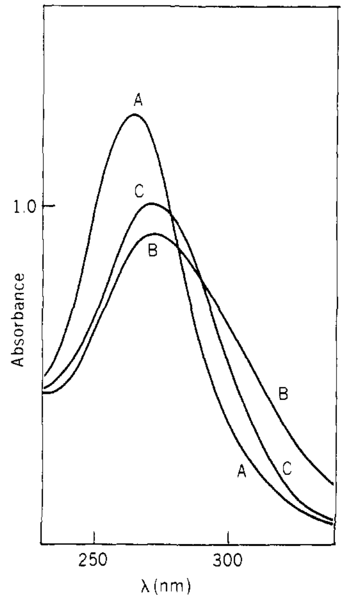


Figure 1. UV spectra of 1.1×10^{-4} M solutions of pinacol mono-*p*-nitrobenzoate. (A) Spectrum in H_2O and initial spectrum in 0.001 M NaOH. (B) Initial spectrum in 1.0 M NaOH, recorded 5–15 s after preparation. (C) Spectrum after hydrolysis in NaOH solutions, identical with the spectrum of *p*-nitrobenzoate anion.

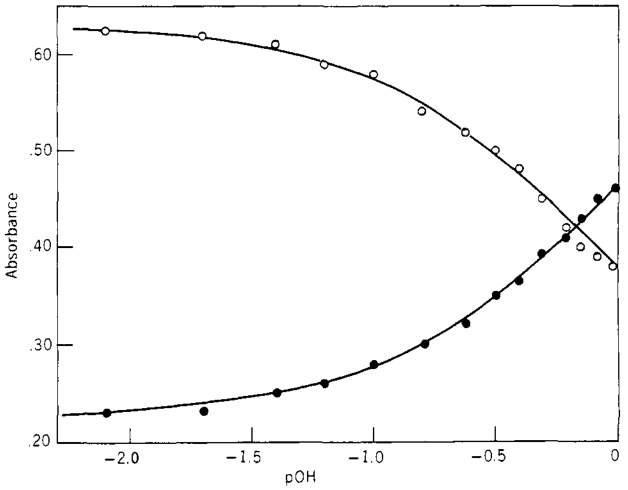


Figure 2. Initial absorbance of solutions of pinacol mono-*p*-nitrobenzoate at 310 nm (●), concentration 1.1×10^{-7} M, and 260 nm (○), concentration 5×10^{-5} M. The quantity pOH = −log [OH⁻].

Equilibrium constants for the neutral cyclization are not too small. We have calculated K_0 for R = phenyl to be 3.7×10^{-5},[12] and with R = CF_3, the neutral intermediate is in fact thermodynamically stable.[13,14] The hydroxy ester, being a tertiary alcohol, should have an acidity constant for OH ionization of 10^{-17}–10^{-19}.[15] As will be discussed later estimates for hemiortho esters make them considerably more acidic. In fact, one goal of this study has been to actually obtain a number for the acidity of such a

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(15) (a) A pK_a value of 19 has been estimated for *tert*-butyl alcohol,[15b] but examination of other values estimated using this approach[15c] suggests that the pK may be somewhat lower. It is, however, generally accepted[15b–f] that in solution *t*-BuOH is a weaker acid than MeOH, whose pK_a is 15.5.[15g] (b) McKewen, W. K. *J. Am. Chem. Soc.* **1936**, *58*, 1124–1129. (c) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; 1st ed.; Harper and Row: New York, 1976; p 153. (d) Hine, J.; Hine, M. *J. Am. Chem. Soc.* **1952**, *74*, 5266–5271. (e) Arnett, E. M.; Small, L. E. *Ibid.* **1977**, *99*, 808–816. (f) Ritchie, C. D. In "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D. Eds.; Dekker: New York, 1976; Vol. 2, p 233. (g) Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1960**, *82*, 795–800.

species. Finally, these are tertiary esters and their saponification should be relatively slow. We do find with R = 4-nitrophenyl that the anion TO^- is formed reversibly in base, and we report here the results of this study.

Results and Discussion

Spectral Identification of Anion. Evidence for the formation of TO^- comes from UV spectra recorded in hydroxide solutions, as shown in Figures 1 and 2. The curve A in Figure 1 is the UV spectrum of pinacol mono-4-nitrobenzoate which is obtained in water and in very dilute NaOH. Saponification does occur in the latter solution and the curve C is the spectrum obtained for the hydrolysis product, the *p*-nitrobenzoate anion. This same curve is obtained on addition of *p*-nitrobenzoic acid to base. Addition of the ester to 1 M NaOH, however, results in a significantly different initial spectrum B. Saponification occurs more rapidly in this solution to produce curve C, and what is perhaps most striking is that at most wavelengths the absorbance change associated with this process is in the opposite direction to that which occurs at low NaOH concentration. The change from A to B is reversible; if the 1 M NaOH solution is neutralized (before significant saponification), the spectrum A is regenerated. This spectral change is also very rapid, being complete within the dead time (2 ms) when a solution of the ester in water is mixed with 2 M NaOH in a stopped-flow spectrophotometer.

Figure 2 shows the initial absorbance of the ester at two wavelengths as a function of hydroxide ion concentration. These curves were obtained in two separate experiments. The 310-nm curve was obtained in a stopped-flow spectrophotometer by mixing an aqueous solution of ester with appropriate base solutions, and the initial absorbance reading was simply read. The 260-nm curve was obtained in a conventional UV instrument; initial absorbance readings were taken 10–15 s after solution preparation and a short extrapolation to zero time carried out. The curves take the form expected of a reversible acid:base reaction of the form of eq 5.

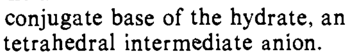
$$TO^- \rightleftharpoons POH + OH^- \tag{5}$$

The behavior can be analyzed by the equation

$$K_b = \frac{[POH][OH^-]}{[TO^-]} = \left(\frac{A_b - A}{A - A_a}\right)[OH^-] \tag{6}$$

where A_b and A_a refer to the absorbance of the base form TO^- and the acid form POH, respectively. We were unable[16] to use a solution sufficiently basic to obtain the former. The data, however, could be fit[17] with K_b and A_b as unknown parameters, yielding at 310 nm $K_b = 0.76 \pm 0.04$ and $A_b = 0.64$ and at 260 nm $K_b = 0.72 \pm 0.05$ and $A_b = 0.18$, these numbers referring to an ionic strength of one.

Two observations provide additional support for our interpretation. First *tert*-butyl *p*-nitrobenzoate, a model for the pinacol ester without the hydroxy group required for cyclization, shows no change in its initial spectrum in concentrated base. Second, *p*-nitrobenzaldehyde does show a change in its spectra (Figure 3) that is very similar to the change exhibited in the initial spectra of the pinacol ester. Benzaldehydes reversibly add hydroxide in base, and with *p*-nitrobenzaldehyde this equilibrium is almost


(7)

$$\mathrm{Ar\overset{O}{\overset{\|}{C}}H} \cdot {}^-\mathrm{OH} \rightleftharpoons \mathrm{Ar\overset{{}^-O}{\overset{|}{\underset{\underset{OH}{|}}{C}}}H} \tag{7}$$

completely to the addition side in 1 M NaOH.[18] The addition product is the conjugate base of the hydrate, and it serves as a model for the tetrahedral intermediate anion.

Hydrolysis Kinetics. As noted, an overall hydrolysis to pinacol and *p*-nitrobenzoate also occurs. The kinetics associated with this are also revealing. As shown in Figure 4, observed rate constants for *tert*-butyl *p*-nitrobenzoate actually show an upward curvature in a plot vs. hydroxide ion concentration. Although this could be associated with a specific salt effect, a more likely interpretation invokes the existence of a second-order dependency on hydroxide ion, in addition to the normal first-order dependency.

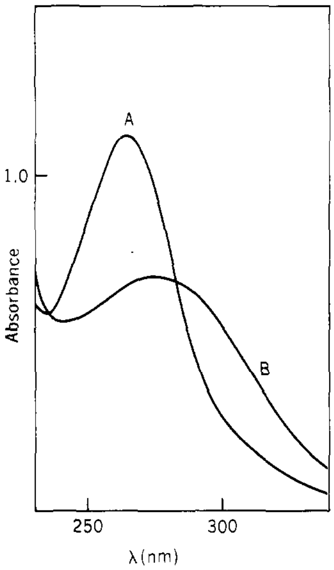


Figure 3. UV spectra of 1.0×10^{-4} M solutions of *p*-nitrobenzaldehyde in H_2O (A) and 1.0 M NaOH (B).

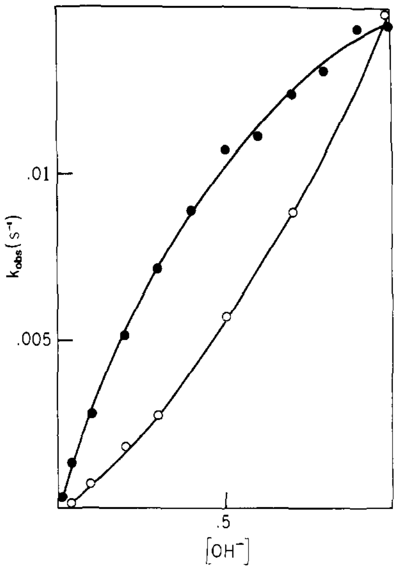


Figure 4. First-order rate constants (25 °C, ionic strength = 1.0) for the hydrolysis of pinacol mono-*p*-nitrobenzoate (●) and *tert*-butyl *p*-nitrobenzoate (○).

$$\text{rate} = k_{obsd}[\text{ester}] = k_2[OH^-][\text{ester}] + k_3[OH^-]^2[\text{ester}] \tag{8}$$

The experimental data can be fit by such a model with $k_2 = 0.0082$ M^{-1} s^{-1} and $k_3 = 0.0067$ M^{-2} s^{-1}. The overall third-order term can be explained by occurrence of a dianionic tetrahedral intermediate in the hydrolysis. The existence of this term is well established in the base hydrolysis of amides and imides.[19] A recent report has shown its presence also in the hydrolysis of two esters, including methyl *o*-methoxybenzoate.[20]

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(16) In addition to technical problems associated with mixing water and very concentrated base, we found that the ester was difficult to dissolve.

(17) With use of the rearranged equation $A = (A_b[OH^-] + K_bA_a)/(K_b + [OH^-])$, and a nonlinear least-squares computer program.

(18) Greenzaid, P. *J. Org. Chem.* **1973**, *38*, 3164–3167. Bover, W. J.; Zuman, P. *J. Chem. Soc., Perkin Trans. 2* **1973**, 786–790. Bover, W. J.; Zuman, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 2531–2536.

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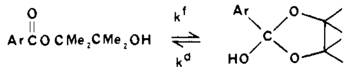
Significant downward curvature is, however, found in the plot with pinacol *p*-nitrobenzoate (Figure 4). This can be explained by the counter-balancing effect of the shifting equilibrium between the ester and the hemiortho ester anion, the latter being unreactive in the saponification. The assumption of both second-order and third-order terms as for the *tert*-butyl ester produces the rate

$$k_{\mathrm{obsd}} = \frac{k_2K_b[\mathrm{OH}^-] + k_3K_b[\mathrm{OH}^-]^2}{K_b + [\mathrm{OH}^-]} \tag{9}$$

The data can be fit to this equation to give $K_b = 0.55 \pm 0.17$, $k_2 = 0.031 \pm 0.003$ M^{-1} s^{-1}, and $k_3 = 0.008 \pm 0.0035$ M^{-2} s^{-1}. The errors in K_b and k_3 are large because of some scatter in the experimental rate data in the more concentrated bases. Taking this into account the agreement between the kinetically and spectroscopically determined K_b values is satisfactory.[21]

Tetrahedral Intermediate Acidity. The K_b value is an apparent value relating the tetrahedral intermediate anion and the ring-opened hydroxy ester. A true K_b value can be determined if the equilibrium constant K_0 relating this hydroxy ester and the neutral tetrahedral intermediate is known.

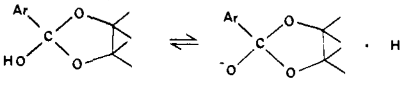


(10)

POH TOH

We have shown with Ar = phenyl[12] that such an equilibrium constant can be experimentally determined, as the ratio of rate constants for formation and decomposition. We have employed the same methodology with the *p*-nitrophenyl substituent and summarize briefly the results here. The hemiortho ester TOH is generated as a transient intermediate by addition of the borofluorate salt of the 2-(*p*-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium cation to aqueous solution. Rate constants represent directly the decomposition of TOH. These follow the expression $k_{\mathrm{obsd}}{}^{\mathrm{d}} = k_{\mathrm{H}}{}^{\mathrm{d}}[\mathrm{H}^+] + k_0{}^{\mathrm{d}} + k_{\mathrm{OH}}{}^{\mathrm{d}}[\mathrm{OH}^-]$ with $k_{\mathrm{H}}{}^{\mathrm{d}} = 1.7$ M^{-1} s^{-1}, $k_0{}^{\mathrm{d}} = 0.15$ s^{-1} and $k_{\mathrm{OH}}{}^{\mathrm{d}} = 2 \times 10^7$ M^{-1} s^{-1}. Rate constants for the formation of the intermediate are obtained from the rate of exchange of a carbonyl ^{18}O-labeled pinacol ester in an acid solution. This occurs via cyclization to the intermediate TOH, which exchanges its exocyclic hydroxy group with solvent via an equilibration with the dioxolan-2-ylium ion. This equilibration in acid solutions is rapid relative to the reverse ring opening. Rate constants for the exchange with the *p*-nitrophenyl ester were measured in three acids and gave $k_{\mathrm{obsd}}{}^{\mathrm{f}} = k_{\mathrm{H}}{}^{\mathrm{f}}[\mathrm{H}^+] + k_0{}^{\mathrm{f}}$ with $k_{\mathrm{H}}{}^{\mathrm{f}} = 1.4 \times 10^{-3}$ M^{-1} s^{-1} and $k_0{}^{\mathrm{f}} = 1.1 \times 10^{-4}$ s^{-1}. The ratios $k_{\mathrm{H}}{}^{\mathrm{f}}/k_{\mathrm{H}}{}^{\mathrm{d}}$ and $k_0{}^{\mathrm{f}}/k_0{}^{\mathrm{d}}$, which should be the same as one another since they are both equal to K_0, are 8.2×10^{-4} and 7.3×10^{-4}, respectively.

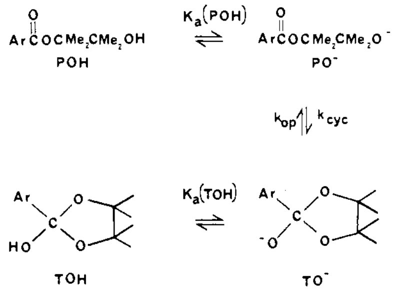
We therefore set $K_0 = 8 \pm 1 \times 10^{-4}$ and $K_b = 0.7 \pm 0.1$ and use pK'_{w} (p([H$^+$][OH$^-$])) at ionic strength = 1.0 as 13.7[22] to calculate pK'_{a} (p([TO$^-$][H$^+$]/[TOH])) of 10.4 ± 0.2 for the equilibrium of eq 11 with Ar ≡ 4-nitrophenyl. This number can be compared with estimates previously made on the basis of linear free energy relationships. Guthrie[23] uses an equation originally proposed by Hine[24] for carbonyl hydrates and has estimated[25,26] for p-$\mathrm{NO_2C_6H_4C(OH)_2OMe}$ a pK_a value of 10.0. Fox and Jencks[27] have proposed a simple alcohol as a starting point, with p$K_a = 15.9 - 8.4\sum\sigma_{\mathrm{I}}$, where σ_{I} is the inductive substituent constant of an attached group. This relation provides[28] pK_a = 10.9 for $\mathrm{C_6H_5C(OMe)_2OH}$, and since ρ = 1.0–1.1 for ionization of $\mathrm{ArCR_2OH}$,[29,30] we estimate 10.2 for the *p*-nitro derivative. The two estimates and the number determined in this work clearly are in good agreement. The cyclic system of this study is of course slightly different, and it is difficult to say what the effect of the ring and the four methyl substituents will be. These variations are quite remote from the reaction center, however, and it is likely that their effect will be small. The general conclusion is that hemiortho esters are considerably more acidic than simple alcohols. As noted by the use of the correlations of Guthrie and of Fox and Jencks, this is associated with the acid-strengthening properties of the two additional electronegative oxygen atoms.



(11)

TOH TO-

Cyclization Kinetics. Although the cyclization in base solutions is too rapid to be followed even by stopped-flow spectroscopy, some idea of the magnitudes of the rate constants can be obtained. The hydroxide ion catalysis of the decomposition of the neutral hemiortho ester TOH undoubtedly proceeds via OH ionization and ring opening via TO$^-$. The catalytic coefficient $k_{\mathrm{OH}}{}^{\mathrm{d}}$ (2×10^7 M^{-1} s^{-1}) is therefore equal to $k_{\mathrm{op}}(\mathrm{K'_a(TOH)}/K'_{\mathrm{w}})$. Since K'_{a}(TOH) is known, k_{op} can be calculated as $10^{3.8}$ s^{-1}. The value of K_b relating POH and TO$^-$ in base solutions (eqs. 5, 6) is equal to $(k_{\mathrm{op}}K'_{\mathrm{w}})/(k_{\mathrm{cyc}}K'_{\mathrm{a}}(\mathrm{POH}))$, so that the product $k_{\mathrm{cyc}}K'_{\mathrm{a}}$(POH) can be calculated as $10^{-9.7}$ M^{-1} s^{-1}. The constant K'_{a}(POH) refers to the ionization of a tertiary alcohol. If this is estimated[15] as 10^{-17}–10^{-19}, then $k_{\mathrm{cyc}} = 10^7$–10^9 s^{-1}. The equilibrium constant $K_- = [\mathrm{TO}^-]/[\mathrm{PO}^-]$ can also be calculated as 10^3–10^5. In other words, the anionic tetrahedral intermediate is strongly favored in this equilibrium.



These calculations reveal that the interconversion of the two anionic forms is extremely rapid. There is, in fact, some resemblance to a proton-transfer reaction, with very little kinetic barrier in the thermodynamically favored direction, the ring closing of PO$^-$. Also, noteworthy is the enormous rate difference—a factor of 10^9–10^{11}—between the intramolecular cyclization in PO$^-$ and the simple addition of OH$^-$ to the same carbonyl.

Experimental Section

Materials. 2-(*p*-Nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane was obtained by condensation in benzene of pinacol and *p*-nitrobenzaldehyde, using *p*-toluenesulfonic acid as catalyst and a Dean-Stark trap to remove water. Workup involved an extraction with aqueous carbonate to remove the acid, drying with $\mathrm{MgSO_4}$, and removal of the benzene. The acetal was purified by recrystallization. 2-(*p*-Nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium tetrafluoroborate was obtained by treatment of the acetal with triphenylcarbenium tetrafluoroborate in dry acetonitrile freshly distilled from $\mathrm{P_2O_5}$, using the procedure reported for the 2-phenyl compound.[31] The salt precipitated from the acetonitrile solution by addition of dry ether freshly distilled from sodium. Pinacol mono-*p*-

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[21] The kinetic data can also be fit without the third-order term ($k_{\mathrm{obsd}} = k_2K_b[\mathrm{OH}^-]/K_b + [\mathrm{OH}^-]$), the fit not being significantly improved when the k_3 term is included. This of course raises a question as to the significance of this term for the pinacol system. However, in the two-parameter fit K_b is found to be 1.2 in not nearly as good agreement with the spectroscopic value. Moreover the third-order term is apparently real for the *tert*-butyl ester unless it is a salt effect, suggesting that it should also be present with the pinacol ester.

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nitrobenzoate was obtained by addition of the salt to a phosphate buffer (pH 7), followed by extraction with ether. Removal of the ether followed by recrystallization (ethanol-water) gave the ester: mp 68–70 °C; NMR δ 8.28 (2 H, d, $J = 9$ Hz), 8.08 (2 H, d, $J = 9$ Hz), 2.5 (1 H, br s), 1.64 (6 H, s), 1.28 (6 H, s). Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.62; H, 6.29; N, 5.08. Pinacol mono-*p*-nitrobenzoate-*carbonyl*-^{18}O was obtained by addition of 82% $H_2{}^{18}O$ to an acetonitrile solution of the salt. The ester analyzed as 74% ^{18}O, the difference probably arising from adventitious moisture present during the preparation. This was then added to a pH 7 buffer and the ester obtained by ether extraction as described above. *tert*-Butyl *p*-nitrobenzoate was obtained from *p*-nitrobenzoyl chloride and *tert*-butyl alcohol.

Kinetics and Spectra. A Cary 2390 spectrophotometer was used for conventional UV studies and a Durrum-Gibson spectrometer for stopped-flow studies. The 310-nm curve in Figure 2 was obtained by mixing on the stopped-flow apparatus a stock aqueous solution of pinacol mono-*p*-nitrobenzoate (2.2×10^{-4} M) with sodium hydroxide solutions of ionic strength 2.0. The absorbance reading at 50–100 ms was recorded as the "initial" absorbance. The 260-nm curve was obtained by the conventional UV with use of a 1-cm cuvette separated into two compartments but open at the top to allow mixing. A stock aqueous solution (1 mL) of pinacol mono-*p*-nitrobenzoate was placed in one side and the NaOH solution (1 mL) in the other. After temperature equilibration these were mixed. Absorbance readings commenced after about 10 s had elapsed and were continued for about 1 min. These were extrapolated to the time of mixing to give the "initial" absorbance. Hydrolysis kinetics for pinacol mono-*p*-nitrobenzoate and for *tert*-butyl *p*-nitrobenzoate were studied by using the increase (or decrease) in absorbance at 310 nm. Plots of ln ($A_t - A_\infty$) vs. time were excellently linear, with their slopes equal to the first-order rate constant. The decomposition of the hemiortho ester 2-(*p*-nitrophenyl)-2-hydroxy-1,3-dioxolane was studied as previously described for the phenyl compound,[12] by addition of a small amount of an acetonitrile solution of the dioxolan-2-ylium to aqueous acids and buffers. The change in absorbance at 290 nm was monitored. Oxygen exchange in pinacol mono-*p*-nitrobenzoate-*carbonyl*-^{18}O was followed as previously described.[12] In brief, the labeled ester (0.39) was added to 2 L of acid solution (0.1, 0.01, 0.001 M) and the solution thermostated at 25.0 °C. After the appropriate time, samples were withdrawn and the ester removed by extraction (no hydrolysis occurs during the time required for exchange). Four to five points were obtained for each kinetic run covering up to 2 half-lives of the exchange. Mass spectral analysis was conducted by using the ratio 269/267 corresponding to the ^{18}O and ^{16}O parent ions of the ester.

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Registry No. POH (Ar = 4-nitrophenyl), 90269-18-4; TO^- (Ar = 4-nitrophenyl), 90269-19-5; TOH (Ar = 4-nitrophenyl), 90269-20-8; 2-(*p*-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane, 16837-06-2; triphenylcarbenium tetrafluoroborate, 341-02-6; 2-(*p*-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium tetrafluoroborate, 90365-40-5; pinacol mono-*p*-nitrobenzoate-*carbonyl*-^{18}O, 90269-21-9.

The Question of Reversible Formation of Bromonium Ions during the Course of Electrophilic Bromination of Olefins. 1. Formal Transfer of Br^+ to Scavenger Olefins from the Solvolytically Generated Bromonium Ions of Cyclohexene and Cyclopentene

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Abstract: *trans*-2-Bromo-1-[((4-bromophenyl)sulfonyl)oxy]cyclohexane and -cyclopentane (**1** and **2**), when solvolyzed at 75 °C in glacial acetic acid containing Br^- and a scavenger olefin (cyclopentene for **1** and cyclohexene for **2**) generate free molecular Br_2 as is evidenced by the formation of crossed products. **1** is more prone to yield crossed product than is **2**. In the absence of added Br^-, the amount of crossed product formed in the solvolysis is small. The results are interpreted in terms of competitive Br^- capture of the intermediate bromonium ions produced during the course of solvolysis at Br^+ and carbon, the latter event leading to trans dibromide products of the starting material, while the former event generates Br_2 and olefin. The results of these experiments, when applied to electrophilic Br_2 addition to alkenes, strongly suggest that the intermediate bromonium ions are formed reversibly. Furthermore, evidence is presented which indicates that the bromonium ion of cyclohexene reverses to a greater extent than does the bromonium ion of cyclopentene. The demonstration of such reversibility of formation of bromonium ions from simple alkenes introduces a rather severe complication into the analysis of kinetic structure–reactivity data. These observations might be invoked to explain at least part of the 6–25-fold increase in reactivity in electrophilic addition of Br_2 exhibited by cyclopentene over cyclohexene.

I. Introduction

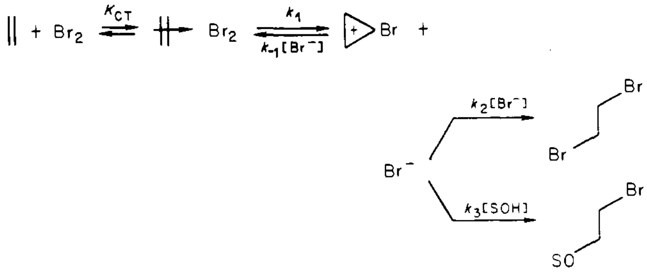
The electrophilic bromination of olefins has been extensively studied and is undoubtedly the most commonly presented example of a reaction typical of unsaturated systems.[1] Indeed every textbook of organic chemistry devotes considerable space to discussion of this ostensibly simple process.

The rates of Br_2 addition to typical olefins are described by a general equation (eq 1)[1] containing a variety of kinetic terms

$$-d[Br_2]/dt = [olefin](k_1[Br_2] + k_2[Br_2]^2 + k_{Br_3^-}[Br_2][Br^-]) \qquad (1)$$

depending upon the presence of Br^- and concentration of Br_2.

Scheme I



Robertson and co-workers[2] first established the importance of the second-order term (k_2) at high [Br_2]. In solvents of reduced

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