chromatographed over SiO_2 with 20:1 CH_2Cl_2/MeOH to yield 66% of **24** as an oil: ^1H NMR δ 1.13 (d, 3 H), 2.87 (quintet of d, 1 H), 3.64 (dd, 1 H), 3.72 (s, 2 H), 3.73 (dd, 1 H), 3.79 (s, 3 H), 6.87 (dt, 2 H), 7.11 (dt, 2 H; ^{13}C NMR δ 13.32 (q), 47.15 (t), 48.05 (d), 55.27 (q), 64.50 (t), 114.22 (d), 125.80 (s), 130.47 (d), 158.74 (s); MS (*m/z*, relative intensity, EI) 208 ($M^{\bullet+}$, 27), 122 ($ArCH_2^+$, 100).

Acknowledgment. Support of this research by a grant from the U.S.–Israel Binational Science Foundation is gratefully acknowledged. We also thank Prof. A. Padwa for carrying out MM2 calculations on these systems.

Registry No. **5a**, 75-07-0; **5b**, 123-38-6; **5c**, 78-84-2; **5d**, 630-19-3; **5e**, 100-52-7; **5f**, 123-11-5; **5g**, 120-14-9; **5h**, 86-81-7; **5j**, 104-88-1; **7a**, 127865-37-6; **7b**, 128869-24-9; **7c**, 127865-38-7; **7d**, 128869-25-0; **7e**, 127865-39-8; **7f**, 127865-40-1; **7g**, 128869-26-1; **7h**, 128869-27-2; **7i**, 128869-28-3; **7j**, 128869-29-4; **7k**, 128869-30-7; **9a**, 127865-43-4; **9b**, 128869-31-8; **9c**, 127865-44-5; **9d**, 128869-32-9; **9e**, 127865-45-6; **9f**, 127865-46-7; **9g**, 128869-33-0; **9h**, 128869-34-1; **9i**, 128869-35-2; **9j**, 128869-36-3; **9k**, 128869-37-4; **10a**, 127865-48-9; **10b**, 128869-38-5; **10c**, 127865-49-0; **10d**, 128869-39-6; **10e**, 127865-50-3; **10f**, 127865-51-4; **10g**, 128869-40-9; **10h**, 128869-41-0; **10i**, 128869-42-1; **10j**, 128869-43-2; **10k**, 128869-44-3; **11d**, 20429-42-9; **11e**, 102-96-5; **11f**, 3179-10-0; **11g**, 4230-93-7; **11h**, 6316-70-7; **11i**, 1485-00-3; **11k**, 128869-45-4; **12a**, 128869-46-5; **12b**, 128869-47-6; **13a**, 128869-48-7; **13b**, 128869-49-8; **14a**, 127865-32-1; **14b**, 128869-50-1; **15a**, 128869-51-2; **15b**, 128869-52-3; **16a**, 128869-53-4; **16b**, 128869-54-5; **19**, 128869-55-6; *trans*-**20**, 128869-56-7; *cis*-**20**, 128947-26-2; **21b**, 128869-57-8; **21e**, 128869-58-9; **22**, 128869-59-0; **23**, 128900-51-6; **24**, 128869-60-3; CH_3NO_2, 75-52-5; *p*-ClC_6H4CH=CHNO2, 706-07-0; allyl mercaptan, 870-23-5; 3-methyl-1-nitro-1-butene, 33972-66-6; acetone, 67-64-1; cyclohexanone, 108-94-1; furfuryl mercaptan, 98-02-2.

Supplementary Material Available: ^{13}C NMR (δ) spectra for compounds **7a–c,e,g,i–k**, **9 + 10 (a–d)**, **9e**, **10e–g,i,j**, **12a,b**, **13a,b**, **14b**, **15a + 16a**, **15b**, **16b**, **19**, **20**, and **24** (30 pages). Ordering information is given on any current masthead page.

Structure–Reactivity Aspects of Nitroalkyl Acetate Hydrolysis[1a]

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In the first systematic study of hydrolysis of nitroalkyl esters, it was found that hydrolysis of seven dinitro- and trinitroalkyl acetates follow first-order kinetics in the presence of either strong acid ($HClO_4$) or acetate (A^-) buffers. The observed rate constant is given by

$$k_{obs} = k_o + k_H[H^+] + k_{OH}[OH^-] + k_A[A^-]$$

in water at 60 °C at constant (0.2 M) ionic strength. Values of k_H correlate with σ^* and various spectral parameters of the esters taken as measures of the electronic effects of the alkyl group. The value of ρ^* of -0.33 ± 0.03 is consistent with a prior protonation step which is more sensitive to these structural changes than later steps. In contrast, k_{OH} does not correlate with σ^*, $\delta_{^{13}C=O}$ $\delta_{O^{13}CH_2}$, δ_{OCH_2}, or $\nu_{C=O}$. The most likely explanation at the present time for noncorrelation is an enhanced reactivity caused by trinitro substitution.

Although the subject of some of the earliest kinetic studies, the mechanism of ester hydrolysis[2,3] is by no means completely understood. While most authors consider transition states for alkaline hydrolysis similar in structure to tetrahedral intermediates,[4] deuterium[5] and heavy atom[6] isotope effects favor more sp^2-hybridized species mostly due to the desolvation energy of OH^-.[5,7] Also, while OH^- is usually considered a nucleophile, it may function as a

Table I. Nitroalkyl Acetates and σ^* Values[a]

symbol	ester	σ^*
1	CY_3CH_2OAc	1.62[b,c]
2	$CH_3CY_2CH_2OAc$	0.99[b,d]
3	$CY_3CH_2CH_2OAc$	0.579[b,e]
4	$CH_3CY_2CH_2CH_2OAc$	0.352[e]
5	$CY_3CH_2CH_2CH_2OAc$	0.207[b]
6	CFY_2CH_2OAc	1.57[b,f]
7	$CFY_2CH(CH_3)OAc$	1.55[g]

[a] In formulas of esters, Y represents NO_2. σ^* is the value for the entire nitroalkyl group (relative to 0.00 for methyl) determined experimentally, either directly or on a homologue, except for the value for ester **7** which was calculated. [b] A damping factor of 2.8 for inserted CH_2[9d] was used with a σ^* determined for an analogue. [c] Reference 36. [d] Reference 42a. [e] Hine, J.; Bailey, W. C., Jr. *J. Org. Chem.* **1961**, *26*, 2098–2099. [f] Kaplan, L. A.; Pickard, H. B. *J. Org. Chem.* **1970**, *35*, 2044–2045. [g] Calculated from σ^* for **6** according to Perrin, D. D.; Dempsy, B.; Serjeant, E. P. *pK_a Prediction for Organic Acids and Bases*; Chapman and Hall: New York, 1981.

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Table II. Rate Constants for Hydrolysis of Nitro Esters[a]

ester	$10^7 k_o$, s^{-1}	$10^4 k_H$, $M^{-1} s^{-1}$	k_{OH}, $M^{-1} s^{-1}$	$10^4 k_A$, $M^{-1} s^{-1}$
1	33.3 ± 8.6	4.44 ± 0.11	294 ± 19	1.24 ± 0.16
2	3.94 ± 0.06	7.36 ± 0.08	24.5 ± 0.1	0.206 ± 0.009
3	23.7 ± 10.1	9.00 ± 0.25	355 ± 17	1.68 ± 0.16
4	0.12 ± 0.14	10.7 ± 0.3	5.19 ± 0.19	0.009 ± 0.002
5	0.29 ± 0.05	13.9 ± 0.4	14.0 ± 0.1	0.013 ± 0.004
6	20.3 ± 1.6	10.0 ± 0.2	81.4 ± 2.1	2.23 ± 0.42
7	17.5 ± 7.0	3.86 ± 0.08	37.5 ± 7.2	0.221 ± 0.010

[a] In water at 60.0 °C, ionic strength 0.2 M with $NaClO_4$. Uncertainties in rate constants are standard deviations.

general base catalyst as well.[8]

Use of the Taft $\sigma^*\rho^*$ equation[9] has met with a certain degree of success in correlating hydrolysis rates with structural variations in aliphatic systems which do not have the simplifying feature of meta or para substitution on benzene. Various modifications of this equation have been used, for example the addition of an E_s term for residual steric effects.[10-12]

For substitution in the *alkyl* group, corrections for hyperconjugation and an additional steric requirement for atoms in position six relative to the carbonyl oxygen[11,13] give better correlations for alkaline hydrolysis of alkyl acetates.[12] Although one study showed that k_{OH} correlated with pK_a of the leaving alcohol, another concluded that rate differences for longer and more highly branched alkyl groups were due to steric inhibition of solvation.[10] Interpretations of ρ^* for structural modifications involving *only* straight or branched alkyl groups are uncertain however, since σ^* values for these groups do not appear to represent polar inductive effects.[14]

We now report our results on hydrolysis of nitroalkyl acetates. Despite the usefulness of the highly electron withdrawing nitro group as a probe for the electronic requirements of a reaction, no systematic study has been done utilizing this group for aliphatic ester hydrolysis. Acid and base catalysis for nitroalkyl acetates were studied in the same solvent and at the same temperature to avoid the complication of different solvation effects.[10b]

Results and Discussion

The nitro esters studied are shown in Table I in order of decreasing σ^*, with the last two entries involving fluorine substitution. Preliminary experiments showed that both acid-catalyzed (k_H) and base-catalyzed (k_{OH}) hydrolyses could be conveniently studied in water at 60 °C. Runs were carried out at constant ionic strength (0.2 M with $NaClO_4$) in the presence of $HClO_4$ for pH < 2 or in acetic acid/acetate buffers for higher pH. Decrease in ester concentration was followed by HPLC with electrochemical detection.

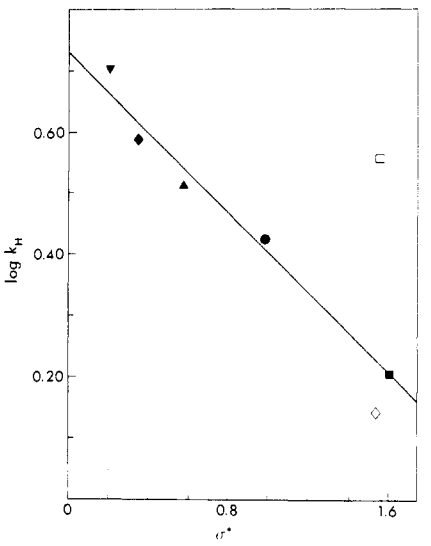

Figure 1. Taft plot for acid catalysis constant k_H ($M^{-1} h^{-1}$) for esters 1 (■), 2 (●), 3 (▲), 4 (◆), 5 (▼), 6 (□), and 7 (◇). Fluorine-containing esters with open symbols.

Rate Constants. Hydrolysis was found to follow rate law 1a with k_{obs} of the form of eq 1b, where k_o represents an uncatalyzed rate, presumably with water as a general base,[8,15] and HA and A^- represent buffer components.

$$v = k_{obs}[\text{ester}] \quad (1a)$$

$$k_{obs} = k_o + k_H[H^+] + k_{OH}[OH^-] + k_{HA}[HA] + k_A[A^-] \quad (1b)$$

Hydrolyses at low pH were carried out with $HClO_4$ in unbuffered media where only the first two terms are important. For each ester, k_{obs} is linearly dependent on $[H^+]$, and the slopes k_H are given in Table II.

Values for k_o and k_{OH} were determined from k_{red} (eq 2) by the extrapolation method of Bell.[16] A series of runs of varying buffer concentrations were made, all at the same buffer component ratio $r = [A^-]/[HA]$ and thus all at the same pH. For these runs, k_{red} is given by eq 3, where C is the total buffer concentration [HA] + $[A^-]$. A graph

$$k_{red} = k_{obs} - k_H[H^+] \quad (2)$$

$$k_{red} = k_o + k_{OH}[OH^-] + C[(rk_A + k_{HA})/(r+1)] \quad (3)$$

$$i = k_o + k_{OH}[OH^-] \quad (4a)$$

$$s = (rk_A + k_{HA})/(r+1) \quad (4b)$$

of k_{red} vs C gives an intercept i which contains k_o and k_{OH} terms (eq 4a). Plotting these intercepts from various series at other pHs gives a straight line with slope and intercept corresponding to k_{OH} and k_o, respectively. Values of k_{OH} and k_o obtained in this way are shown in Table II for each ester.

The slopes of k_{red} vs C plots (eq 4b) contain information on k_A and k_{HA}. Rearrangement of eq 4b shows that plots of $s(r+1)$ vs r have slope k_A and intercept k_{HA}. Values for k_A obtained in this way are also given in Table II for each ester. General acid catalysis is not important, since

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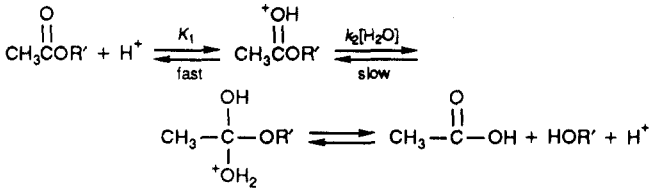
Table III. Spectral Data for Esters 1–5[a]

	$\delta_{^{13}C}$		δ_H			
ester	OCH_2R	$C{=}O$	OCH_2	CH_3CO	$\bar{\nu}_{C=O}$	$\bar{\nu}_{COC}$[as]
1	60.55	167.87	5.364	2.183	1775.0	1202.6
2	63.48	168.78	4.908	2.124	1760.4	1222.0
3	56.78	169.75	4.502	2.043	1750.4	1228.2
4	58.05	169.99	4.265	2.028	1746.4	1228.1
5	61.85	170.45	4.178	2.099	1743.9	1239.1

[a] δ in ppm relative to internal TMS, $\bar{\nu}$ in cm^{-1}, all spectra in $CDCl_3$ solution.

k_{HA} values are zero within experimental error.

Acid Catalysis. A good correlation between k_H and σ^* was found for esters 1–5 (Figure 1), with a slope ρ^* of −0.33 ± 0.03. This result is in general agreement with the low sensitivity of k_H to electronic effects in aryl acetates (ρ^* = −0.20 in 60% acetone–water at 25 °C)[17] and with the $A_{AC}2$ mechanism shown in simplified form below. Since

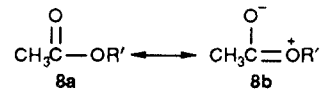


electron-withdrawing groups would retard the prior equilibrium and promote the second step, the observed negative ρ^* requires that nitro substitution influences the first step more than the second, a conclusion reached for monochloro-substituted methyl acetates.[18]

Spectral data,[19] for example ^{13}C chemical shifts[20] or $\bar{\nu}_{CO}$,[21] frequently correlate with polar substituent constants[22] or calculated electron density. It was therefore of interest to determine whether k_H correlated with these measures of electron density. The relevant spectral data for esters 1–5 are summarized in Table III.

Values of k_H for esters 1 to 5 correlate with δ_{OCH_2}, $\delta_{^{13}CO}$ and $\bar{\nu}_{CO}$ as shown in Figure 2. Two of these correlations are in straightforward agreement with the above interpretation that effects on K_1 are more important in determining k_H. More downfield methylene hydrogens (high δ_{OCH_2} in Figure 2A) are more deshielded by electron-withdrawing groups, and the resulting increased $+\delta$ charge would lead to lower K_1 and hence lower k_H values. Similarly, higher $\bar{\nu}_{CO}$ values (Figure 2C) can reflect more electron-withdrawing groups on the carbonyl which would lead to decreased ester basicity, lower K_1 values, and lower rates. Analogous results on chloroacetates were reported by Euranto, et al.[18]

The correlation of k_H with $\delta_{^{13}CO}$ (Figure 2B) is also consistent with this interpretation as can be seen from resonance forms 8 which were used to explain correlations of δ_{CH_3CO} with σ^* for alkyl acetates.[23,24] Electron-withdrawing groups R′ would destabilize **8b**, the form presumably responsible for more downfield shifts by analogy to shifts in α,β-unsaturated esters. Esters with such electron-withdrawing groups would therefore exhibit the more upfield $\delta_{^{13}CO}$ and more resembling **8a** would be less basic. It is not clear why fluorine-containing esters appear abnormal in Figures 1 and 2C.



8a **8b**

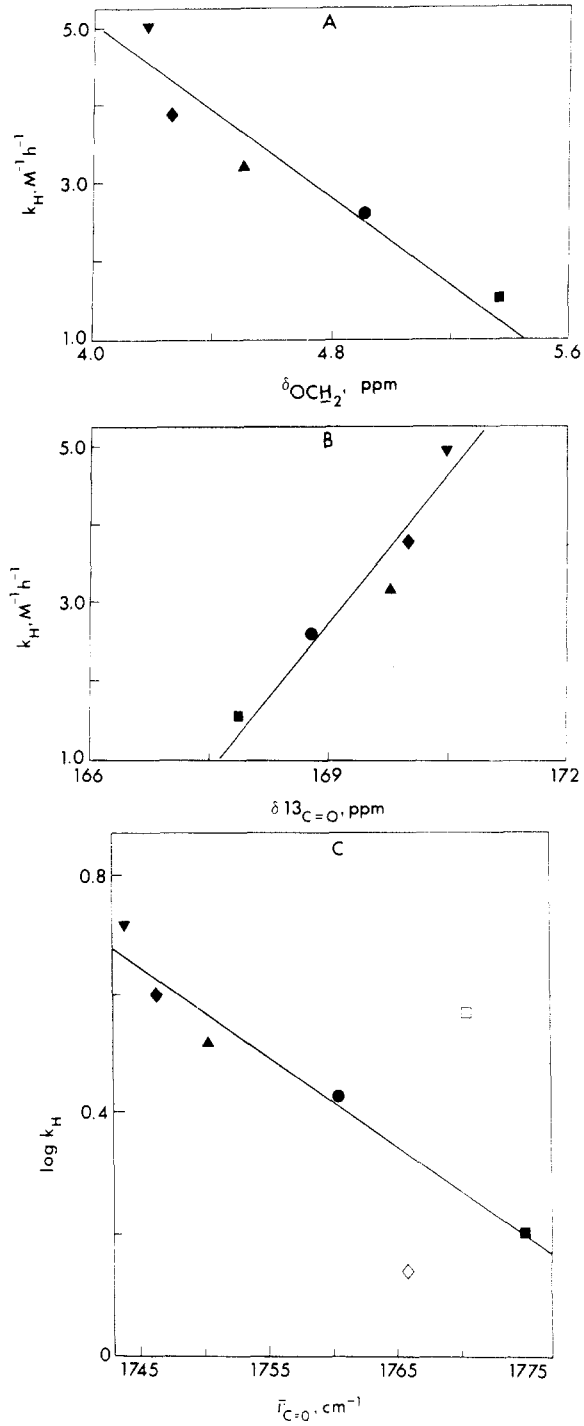


Figure 2. Correlation between k_H and spectral parameters for esters 1 (■), 2 (●), 3 (▲), 4 (◆), 5 (▼), 6 (□), and 7 (◇). (A) with δ_{OCH_2}; (B) with $\delta_{^{13}C=O}$; (C) with $\bar{\nu}_{C=O}$.

Base Catalysis. In contrast to results for k_H, values of k_{OH} do not correlate with σ^* as shown in Figure 3A. (See below for discussion of lines drawn: solid for disub-

(17) Calculated from data in reference 2e, p 138.
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(21) Reference 9b, Chapter 7.
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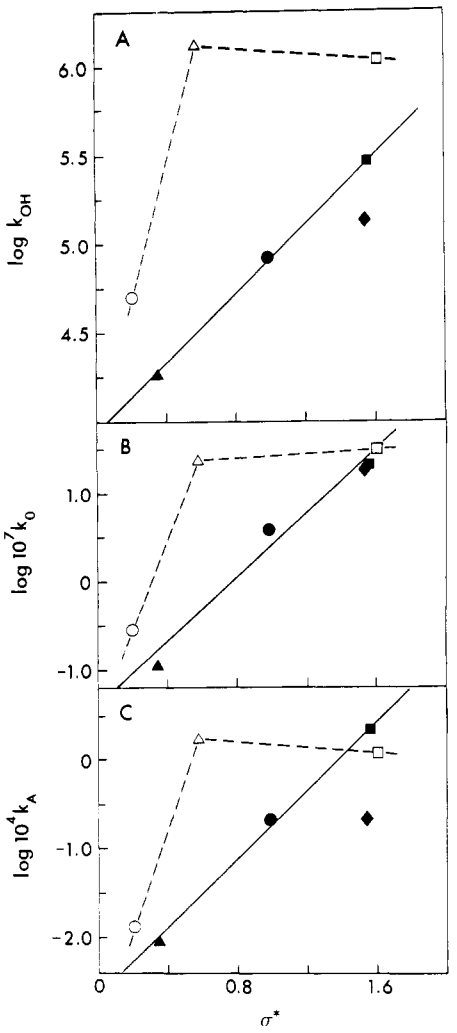
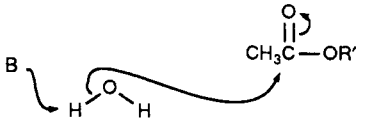


Figure 3. Taft plots of rate constants for esters 1 (□), 2 (●), 3 (△), 4 (▲), 5 (○), 6 (■), and 7 (◆). Solid lines are drawn for dinitro esters (filled symbols). Dashed lines connect trinitro esters to emphasize trends (see text). (A) for k_{OH} (M^{-1} h^{-1}); (B) for k_o (h^{-1}); (C) for k_A (M^{-1} h^{-1}).

stituted, dashed for trisubstituted esters). The same general disposition of points was found for log k_o and log k_A vs σ^* (Figure 3, parts B and C), suggesting similar roles for H_2O, A^-, and OH^-, perhaps that of general base catalysts shown below. In any case, this similarity in plots



make it unlikely that the noncorrelation of k_{OH} with σ^* is due to effects peculiar to OH^-, such as a change in mechanism from direct OH^- attack to general base catalysis for certain R′ groups or unusual OH^- desolvation effects which depend on the nature of R′.[7c]

When the Taft equation is not followed, the usual conclusion is that noncorrelation is due to steric factors.[9b] For alkaline hydrolysis of methyl arylaliphatic carboxylates[25] and aryl benzoates,[26] better correlations are obtained when a steric term E_s is added. For this reason, the Pavelich–Taft equation[27] (eq 5) was applied to the present data, with δ the sensitivity to this term and

$$\log k_{OH}/k°_{OH} = \sigma^*\rho^* + \delta E_s \quad (5)$$

$$E_s = \log k_H/k°_H \quad (6)$$

$$\log k_{OH} = i + \sigma^*\rho^* + \delta \log k_H \quad (7)$$

where the superscript refers to the standard compound ethyl acetate. Although rate constants for this compound and hence E_s were not measured in the present study, k_H for each ester was determined under the same solvent, temperature, and ionic strength conditions as k_{OH} and should give a measure of the steric effect according to the Taft treatment. Substitution of eq 6 into eq 5 gives eq 7 which predicts that log k_{OH} depends linearly on σ^* and log k_H. However, a linear regression of data for esters 1–7 with these variables gives no meaningful correlation (r = 0.66).

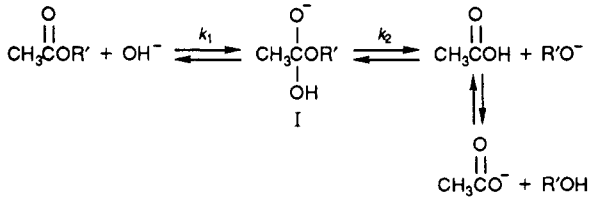
One reason for the noncorrelation of log k_{OH} with σ^* may be the use of inappropriate σ^* values. The σ^* values for R′ in Table I were determined from rates of esterification of $R'CO_2H$ by diphenyldiazomethane, and the generality of σ^* values obtained by this method has been questioned.[9d] In fact, values of σ^* calculated from saponification of methyl carboxylates (eq 8) are irregularly different[25] from σ^* calculated for the same groups from the diphenyldiazomethane esterification rates (eq 9).

$$\sigma^* = [\log (k_{OH}/k°_{OH}) - E_s]/2.48 \quad (8)$$

$$\sigma^* = [\log (k/k°)]/\rho^* \quad (9)$$

Spectroscopic data as more suitable measures of relative electron density were therefore investigated. Since k_{OH} for hydrolysis of RCOOR′ were reported to follow pK_a of R′OH,[28] a correlation between log k_{OH} and $\delta_{O^{13}CH_2}$ might be expected. However, there is no significant correlation with that parameter as well as with δ_{OCH_2}, $\delta_{^{13}CO}$, $\bar{\nu}_{CO}$, or $\bar{\nu}_{COC}$, but rather the same general patterns as found for the σ^* plots.

Sharp breaks in LFERs involving nucleophilic substitution on esters via I[29] were explained[31] by a change in the rate-determining step depending on the relative basicity of incoming nucleophile and leaving alkoxide.



However, this explanation cannot be used in the present case. The pK_a of the present R′OH were estimated from the data of Ballinger and Long[3] (ρ^* = −1.42 in H_2O, 25 °C) and the σ^* values from Table I as 9.4, 13.6, 14.5, and 15.1 for alcohols corresponding to esters 1, 3, 4, and 5. Since these are all more acidic than H_2O (pK_a = 15.7[3]), partitioning of I toward products would be favored with k_1 thereby being the slow step[2a,e,32] for all these esters.

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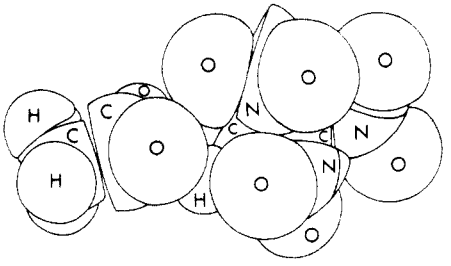
It is also not likely that electronic factors cause a change in the rate-determining step above, as one would then expect two intersecting lines or a curved plot, not the scattered points in Figure 3. Other factors can affect this partitioning,[32b,33] however, such as steric effects[34] which differ for the various R′ groups.

An alternate, useful way to view the present data, as suggested in a previous study in acetonitrile/water,[35] is that trinitro-substituted alkyl esters, in general, react unusually fast. This conclusion would lead one to draw the solid lines in Figure 3 which connect "well-behaved" disubstituted esters. The α-methyl derivative **7** presumably reacts slower (Figure 3, parts A, C) due to steric hindrance analogous to β-substitution in the acyl group.[10] The slope of the log k_{OH} vs σ* line, 0.98, compares favorably with ρ* values of 0.69 for alkaline hydrolysis of alkyl acetates[12] and 1.53 for aryl benzoates.[26]

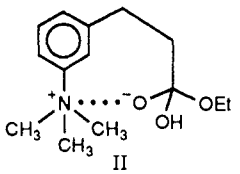
Trinitro Substitution Effects. A possible interpretation of unusually large k_{OH} values is that trinitro-substituted esters undergo a different reaction from disubstituted ones. For example, trinitro-substituted alkanes in the presence of strong bases or oxidizing agents produce dinitro derivatives,[36] and methyl 4,4,4-trinitrobutyrate eliminates nitrous acid in aqueous dioxane at pH 5.[37] Although these reactions seem unlikely under the present conditions (pH < 6 and no acidic α-hydrogen or oxidizing agents), product studies for esters **1** and **2** were carried out. However, only the hydrolysis-type products are observed, namely acetate and the alcohol or its degradation products. Also, for hydrolysis of these esters in acetonitrile/water, no abnormal products are present by NMR.[35]

An interaction of NO_2 with the carboxyl function is suggested by examination of CPK models which show the close proximity of these groups (e.g., see **3**). This prox-

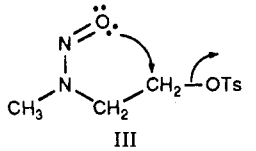


3

imity could lead to an enhanced stabilization of the transition state leading to I by hydrogen bonding,[38] electron-donor (O^- or OH in I) and electron-acceptor (NO_2) attractions,[38d,39] or other electrostatic-type attractions such as proposed[40] to account for the unusually high rate acceleration by a quaternary ammonium group (see II). One could even envision nucleophilic catalysis by nitro groups similar to the anchimeric assistance reported[41] for a nitroso oxygen in solvolysis of tosylates as in III.



II



III

Of these interactions, an electron donor–electron acceptor attraction would clearly be favored by trinitro vs dinitro substitution by analogy to the well-known π-complexes of tetranitromethane.[38d] An interesting observation in this regard is that new long-wavelength maxima appear for trinitro esters **3** and **5** (and possibly **1**) in aqueous buffer compared to their spectra in acetonitrile.[42]

Conclusions. The effect of nitroalkyl structural variations on k_H seems straightforward and appears to be most important early on the reaction coordinate (the prior protonation step). In contrast, the behavior of k_{OH} with σ* appears erratic. One might question the appropriateness of the σ* values, which were based on only one reaction instead of the difference between an acid- and base-catalyzed hydrolysis. Other objections concerning the σ* scale could be raised, but the problem would seem to lie elsewhere since the same type of noncorrelation was found for plots vs spectroscopic parameters.

Explanations could be advanced involving different (irregular) steric effects not correlated by linear free energy relationships. However, since trinitro esters are *more* reactive, one cannot invoke steric inhibition of solvation of I, as this would cause slower rates for the bulky trinitroalkyl groups, contrary to what was observed. Also, although steric effects could alter the partitioning of I, it is not clear why there would be a steric acceleration of bulky nitro groups favoring products. In fact, for alkaline hydrolysis of acetates and lactates,[12] the sign of the δE_s term is negative which corresponds to steric retardation of rates.

At the present time, therefore, the most probable cause of noncorrelation of base catalysis appears to be an unusual reactivity associated with trinitro esters. This effect, however, is not fully understood and deserves further investigation.

Experimental Section

Instrumentation. NMR were taken on a Bruker Am 300-MHz FT spectrometer, UV spectra on a Hewlett-Packard HP 8451 A diode array spectrophotometer, and IR on a Nicolet FT-IR instrument on solutions ca. 1–3% in $CDCl_3$. HPLC analyses were done with a Beckman Model 340 "Organizer" injector (20-μL injection loop), Beckman Model 1200 single piston solvent delivery module, and a Bioanalytical Systems Model LC-4 amperometric detector equipped with a glassy carbon working electrode at −0.7 V and Ag/AgCl reference electrode. The stationary phase was an IBM C_{18} reversed-phase column and the mobile phase 45% acetonitrile by volume, 55% aqueous pH 5 buffer.[44] To reduce

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(42) Since no such absorptions were found for dinitro esters, an unusual interaction of a trinitro group in these systems seems indicated. Blank experiments ruled out the possibility that alcohols from hydrolysis caused the new absorption, although the presence of trace amounts of 1,1-dinitromethide anions from denitration could be responsible for a band in this region of the spectrum.[39,43]
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O_2 interference with the reductive mode of the detector, the mobile phase was purged overnight with N_2 and throughout analyses and was heated to 35 °C to reduce N_2 solubility. Sample transfer lines were sleeved with Tygon tubing filled with positive N_2 pressure to prevent O_2 diffusion into the mobile phase.

Esters. All esters were prepared as previously reported.[35] Esters **2**, **4**, **5**, **6**, and **7** were purified by chromatography on silica gel eluting with methylene chloride/hexane; **2** was further purified by distillation in vacuo and **7** by recrystallization (carbon tetrachloride/hexane). **1** was recrystallized from carbon tetrachloride and **3** from methylene chloride/hexane. The purity of all compounds was checked with TLC and ^1H NMR, which indicated a purity > 95%. Elemental analyses were done on the new esters **4** and **5**. Anal. Calcd for **4**, $C_6H_{10}N_2O_6$: C, 34.95; H, 4.89; N, 13.59. Found: C, 34.92; H, 4.92; N, 13.46. Calcd for **5**, $C_6H_9N_3O_8$: C, 28.69; H, 3.61; N, 16.73. Found: C, 28.94; H, 3.48; N, 16.92.

Solutions. For strong acid runs, the desired amount of 2.0 M $HClO_4$ solution was added to deionized, distilled water and enough 0.2 M $NaClO_4$ to give an ionic strength of 0.2 M. Titration of aliquots with standardized Na_2CO_3 gave the $[H^+]$ used in calculations.

For acetate-buffered runs, pH at 60 °C was calculated from pH at 23 °C by the equation $pH = pH_{23} + 0.056$, which can be derived from the equations $[H^+]_{23} = 1.753 \times 10^{-5}/r$ and $[H^+]_{60} = 1.542 \times 10^{-5}/r$ where the K_a were determined at 0.2 M ionic strength[45a] and r is the same at the two temperatures. Values of $[OH^-]$ were calculated from $[H^+]_{60}$ and $K_w^{60} = 9.614 \times 10^{-14}$.[45b] The salt effect on pH was first determined empirically at 23 °C by adding the desired amount of $NaClO_4$ to the buffer solution and the targeted pH achieved by mixing a $NaClO_4$ solution with standardized NaOAc and $HClO_4$ solutions taking this into account. The $[H^+]$ in the final solutions were determined by titrations in triplicate to an acetate end point with standardized NaOH.

Kinetic Procedure. Samples from stock solutions of the esters[35] (5.0 mM in acetonitrile) to give 30–50 μM concentrations were injected into the above solutions maintained at 60.0 ± 0.1 °C. Aliquots (2.0 mL, taken in triplicate) were removed two to three times per half-life, transferred to 2.0 mL polyethylene snap-cap centrifuge tubes, quenched in an acetone–dry ice bath and stored at −5 °C in the solid state until analysis. Reactions were followed to at least 88% conversion except for **4** which in buffered media was followed from 0.4 to 2 half-lives.

For HPLC analysis, liquified samples at 0 °C were purged with N_2 for 3 min and then to minimize O_2 contamination loaded into the injection loop by drawing the mixture through the waste line and out the syringe port. Plots of peak height vs concentration of authentic samples were linear with zero intercept, and so k_{obs} were calculated from ln (height) vs time curves.

Product Study. NMR spectra were taken of acetic acid, esters **1** and **2** and their corresponding alcohols, first in D_2O and then D_2O/OH^-. The spectra of esters in base gave information about the hydrolysis products, and those of alcohols about possible secondary products from alcohol breakdown in base.

For **2**, ester signals at 2.03, 2.18, an 4.94 ppm decreased in area when NaOH was added, and a new signal at 1.18 ppm due to OAc^- appeared. Other new signals at 2.44 and 4.72 ppm are due to a degradation product(s) of the initially formed alcohol, since signals at these same positions appeared when the alcohol was treated with NaOH. Similar results were found for **1**.

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Supplementary Material Available: Figures of k_{obs} vs $[H^+]$, k_{red} vs C, intercepts i vs $[OH^-]$, and log k_{OH} vs spectroscopic parameters and ^1H NMR spectra of all esters (12 pages). Ordering information is given on any current masthead page.

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Regio- and Stereochemistry in Electrophilic Reactions of 2-Propenyl-1,3-dithiane 1-Oxide

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The unsymmetrical allyllithium generated from 2-propenyl-1,3-dithiane 1-oxide (**2**) reacted at the α-site with halides and most of the carbonyl compounds tried. The α-addition reactions occurred predominantly on the face syn to the sulfinyl group. The α-syn addition reaction of **2** and an aldehyde usually yielded mixtures of the erythro and threo isomers, whose structures were determined by spectral methods. An X-ray diffraction analysis of the threo product **11t** obtained from the reaction with cinnamaldehyde indicated that in the crystal structure the 1,3-dithiane ring exists as a puckered chair conformation with an equatorial sulfinyl oxygen. However, the oxygen is axial in $CDCl_3$ solution as shown by its ^{13}C NMR spectrum.

Introduction

As a continuing study of 2-propenyl-1,3-dithiane (**1**), we herein report the reactions of its monosulfoxide (**2**). The electrophilic reactions of **2** are of interest for several reasons: (i) The anion of dithioacetal monosulfoxide or 1,3-dithiane 1-oxide has been explored as an equivalent for the carbonyl anion in alkylations and conjugate additions.[1] Thus, the anion of **2** can be potentially manipulated as an equivalent of the butenone anion. (ii) The regiochemistry in reactions of heteroatom-substituted unsymmetric allylic anion is a long-standing problem.[2] The present study may serve as an example to demonstrate controlling factors in regioselectivity. (iii) Allylic sulfoxides have been shown to be useful intermediates in organic synthesis.[3] The

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