Reaction of Chloroallene (ClA) with 1122. Into a thick-walled Pyrex tube containing 200 μL of ClA cooled in dry ice was condensed ~1.0 mL of 1122. The contents of the tube were triply freeze degassed, and the tube was sealed under vacuum and heated in a sand bath at 160 °C for 24 h. The tube was allowed to cool and was opened, and the excess 1122 was allowed to evaporate. The ^1H (see Figure 1D) and ^{19}F NMR spectra were recorded. The reaction mixture was separated into several fractions by preparative GLC on a 18 ft × $^1/_4$ in. Carbowax 20M (column A) and a 12 ft × $^1/_4$ in. SE-30 (column B) on Chromosorb P. The mixture was subjected to GC–MS, indicating the presence of a 1:1 fraction, a single 1:2 adduct, one major and two intermediate and four minor 2:1 adducts, and a 2:2 adduct fraction. The yields of the major adducts has been estimated by a combination of the integrations of the ^1H and ^{19}F NMR and GC–MS spectra.

34 (fraction 1 from column A and fraction 5 from column B, 20.0%): ^1H NMR δ 3.38 (dt, J_{HH} = 2.93 Hz, J_{HF} = 0.86 Hz, 2 H), 6.83 (p, $J_{HH} \simeq J_{HF}$ = 2.93 Hz, 1 H); ^{19}F NMR δ −20.02 (s); MS, exact mass calcd for $C_5H_3{}^{35}Cl_3F_2$, 205.927, found, 205.929; GC–MS (fraction 1, of mixture of **34**, **35**, and **36**), major fragments at m/e 171 (M − Cl), 136 (M − 2Cl), 111 (M − Cl_2CCH_2), 74 (M − Cl_2CCF_2).

35 (fraction 3 from column A and fraction 6 from column B, 15.8%): ^1H NMR δ 3.47 (dt, J_{HH} = 2.56 Hz, J_{HF} = 0.89 Hz, 2 H), 6.35 (tt, J_{HH} = 2.56 Hz, J_{HF} = 1.24 Hz, 1 H); ^{19}F NMR δ −23.83 (s); MS, exact mass calcd for $C_5H_3{}^{35}Cl_3F_2$, 205.927, found, 205.928.

36 (not isolated from Column A, fraction 4 from column B containing some **35**, 17.3%): ^1H NMR δ 5.02 (ddd, J_{HH} = 2.22, 2.02 Hz, J_{HF} = 0.60 Hz, 1 H), 5.81 (ddt, J_{HH} = 2.22, 2.02 Hz, J_{HF} = 2.02 Hz, 1 H), 5.99 (ddt, J_{HH} = 2.22, 2.22 Hz, J_{HF} = 2.69 Hz, 1 H); ^{19}F NMR δ −23.06 (br d, J_{FF} = 200.9 Hz, 1 F), −23.44 (br d, J_{FF} = 200.9 Hz, 1 F).

37 (fraction 5 from column A and fraction 2 from column B as one very major isomer, 5.8%): ^1H NMR δ 2.67 (ddd, J_{HH} = 13.68 Hz, J_{HF} = 13.68, 4.41 Hz, 1 H), 3.32 (ddd, J_{HH} = 13.68 Hz, J_{HF} = 20.05, 8.71 Hz, 1 H), 4.57 [(apparent dt, J_{HH} = 4.45 (trans), 2.29 (long-range allylic) Hz, 1 H], 4.59 (d, J_{HH} = 4.45 Hz, 1 H), 5.59 (m, 1 H), 5.64 (m, 1 H); ^{19}F NMR δ −21.17 (ddd, J_{HF} = 8.71, 4.41 Hz, J_{FF} = 185.1 Hz, 1 F), −26.37 (ddd, J_{HF} = 20.05, 13.68 Hz, J_{FF} = 185.1 Hz, 1 H); GC–MS, M^+ 280; major fragment ions at m/e 245 (M^+ − Cl), 209 (M^+ − Cl − HCl), 148 (M^+ − 1122).

38 (fraction 7 from column A, fraction 3 from column B, 17.2%): ^1H NMR δ 2.73 (ddd, J_{HH} = 16.46, 2.44, 1.91 Hz, 1 H), 3.04 (ddd, J_{HH} = 14.81 Hz, J_{HF} = 13.09, 7.44 Hz, 1 H), 3.36 (ddd, J_{HH} = 16.46, 7.54, 1.91 Hz, 1 H), 3.50 (ddd, J_{HH} = 14.81 Hz, J_{HF} = 15.83, 9.55 Hz, 1 H), 4.76 (dd, J_{HH} = 7.54, 2.44 Hz, 1 H), 6.19 (t, J_{HH} = 1.91 Hz, 1 H); ^{19}F NMR δ −20.34 (ddd, J_{HF} = 7.44, 9.55 Hz, J_{FF} = 183.9 Hz, 1 F), −22.05 (ddd, J_{HF} = 15.83, 13.09 Hz, J_{FF} = 183.9 Hz, 1 F); GC–MS, M^+ m/e 280; major fragment ions at 245 (M −Cl), 209 (M − Cl, HCl), 148 [M − 1122 (ClA dimer)], 113 (ClA dimer − 35), 86, 77, and 64 (H_2CCF_2). (The GC–MS spectra of the other isomers of **38** were essentially identical.)

38b and **38c** (fraction 6 from column A as a mixture of diastereoisomers, present as a minor components in fraction 2 from column B). **38b** (5.5%): ^1H NMR δ 2.71 (ddd, J_{HH} = 13.74, 12.95, 2.45 Hz, 1 H), 3.30 (ddd, J_{HH} = 13.93 Hz, J_{HF} = 9.09, 19.71 Hz, 1 H), ~3.3 (ddd, J_{HH} = 13.74, 6.15, 0.98 Hz, 1 H), 5.55 (dd, J = 12.95, 6.15 Hz, 1 H), 6.08 (dd, J_{HH} = 2.45, 0.98 Hz, 1 H) (One hydrogen resonance appears in a complex multiplet at δ ~2.7 which could not be unambiguously assigned.); ^{19}F NMR δ −21.17 (ddd, J_{HF} = 4.33, 9.26 Hz, J_{FF} = 185.6 Hz, 1 F), −26.37 (ddd, J_{HF} = 19.71, 14.03 Hz, 1 F).

38c (5.2%): ^1H NMR δ 2.77 (ddd, J_{HH} = 15.46, 6.45, 2.99 Hz, 1 H), 3.30 (ddd, J_{HH} = 15.46, 8.69, 2.99 Hz, 1 H), 4.74 (dd, J_{HH} = 8.69, 6.45 Hz, 1 H), 6.32 (t, J_{HH} = 2.99 Hz, 1 H) [Two hydrogens appear in the δ 2.7–2.8 region which could not be unambiguously identified.]; ^{19}F NMR δ −22.27 (ddd, J_{HF} = 5.7, 8.3 Hz, J_{FF} = 185.8 Hz, 1 F), −25.88 (ddd, J_{HF} = 18.95, 13.31 Hz, 1 F).

38d–g (isolated as a complex mixture as fraction 7 from column B, total < 5%). Vinyl region of ^1H NMR: δ 5.82, 5.91, 6.06, 6.17, and 6.72 (multiplets). The remainder of the ^1H NMR spectrum was too complex to interpret. The ^{19}F NMR spectrum contained many ddd patterns consistent with the structures **38d–g**.

39 (not isolated from column A, fraction 8 from column B as a mixture of **39** and isomers of **38**, 3.2%): ^1H NMR δ 2.61 (br s, 4 H), 5.78 (br s, 2 H).[10]

40 (not isolated from either column A or B, fraction 5 from GC–MS, estimated 5% yield): GC–MS M^+, m/e 338, major fragment ions at m/e 303 (M^+ − Cl), 274 (M^+ − H_2CCF_2), 239 (274 − Cl), 206 (M^+ − $ClCHCCl_2$), 130 ($ClCHCCl_2$), 64 (H_2CCF_2).

41 (not isolated from either column A or B, fraction 15 from GC–MS; estimated yield, ~1%): GC–MS, M^+, m/e 412, major fragment ions at m/e 375 (M^+ − Cl), 350 (M^+ − $ClCHCH_2$), 348 (M^+ − H_2CCF_2), 280 (M^+ − 1122), 245 (M^+ − 1122 − Cl), 216 (280 − H_2CCF_2).

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Registry No. **4**, 10373-79-2; **5**, 103732-80-5; **6**, 103732-81-6; **7**, 96095-73-7; **8**, 96095-72-6; **10**, 103732-78-1; **11**, 103732-77-0; **18**, 103732-82-7; **19**, 103732-83-8; **20**, 103732-84-9; **21**, 103732-85-0; **26**, 103732-86-1; **27**, 103732-87-2; **28**, 103732-88-3; **29**, 103732-89-4; **30**, 103732-90-7; **34**, 103732-91-8; **35**, 103732-92-9; **36**, 103732-93-0; **37**, 103732-94-1; **38**, 103732-95-2; **39**, 103732-96-3; **40**, 103732-97-4; **41**, 103732-98-5; 1,1-dichloro-2,2-difluoroethene, 79-35-6; cyanoallene, 1001-56-5; methoxyallene, 13169-00-1; (phenylthio)allene, 1595-38-6; chloroallene, 3223-70-9.

An Excess Acidity Analysis of Acylal and Thioacylal Hydrolysis in Sulfuric Acid. Variation of ρ with Acidity[1]

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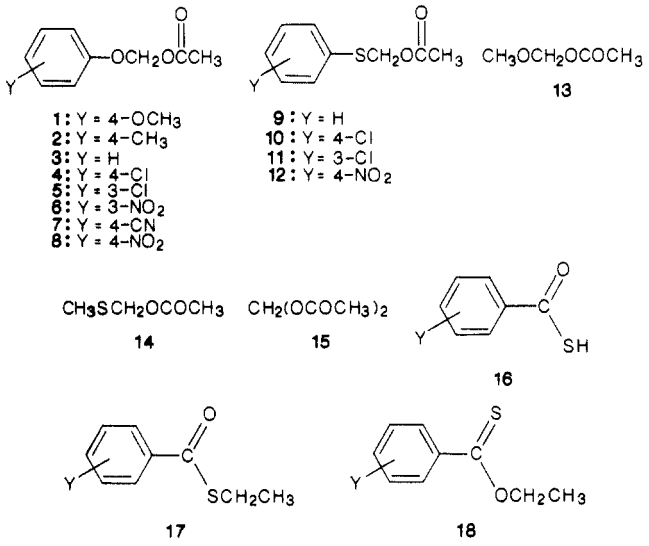
The excess acidity method has been applied to the hydrolysis reactions of some acylals and thioacylals in aqueous sulfuric acid mixtures. At low acidities, aryl thioacylals (RCH_2OCOCH_3, R = ArS) react by an A-2 mechanism involving two water molecules, but for aryl acylals (R = ArO) only one is involved. Both undergo a mechanistic switch to an A-1 pathway at high acidity. Linear free energy relationships for both substrates and both mechanisms were found to give acidity-dependent ρ values. Methoxymethyl (R = CH_3O) and (methylthio)methyl acetate (R = CH_3S) only show the A-1 reaction. Methylene diacetate (R = CH_3COO) has two A-1 hydrolysis pathways, one of them A-2-like, involving attack by an internal nucleophile.

Hammett ρ values are valuable sources of mechanistic information.[2] In acid-catalyzed hydrolysis process, ρ values of −3.64 (in 95% H_2SO_4 at 25 °C)[3] and −3.21 (99.99% H_2SO_4, 45 °C)[4] for methyl benzoates, and +1.99

0022-3263/86/1951-3619$01.50/0

Chart I



(98.7% H_2SO_4, 0 °C)[5] for isopropyl benzoates, are good evidence for an $A_{Ac}1$ mechanism in the former case and $A_{Al}1$ hydrolysis in the latter.[5,6] In more dilute acids, reported ρ values for A-2 hydrolysis processes are +0.10 (40% H_2SO_4, 60.1 °C) for methyl benzoates,[7] and +1.08 (8.54 M $HClO_4$, 95 °C) for benzamides.[8] In the latter case, most of the variation with substituent is ascribed[8] to the effect on the preequilibrium protonation, which has a ρ of +0.92.[9] Similarly, acetanilide hydrolysis has ρ values of +1.87 (20% H_2SO_4, 100.1 °C)[10] and +1.06 (50% H_2SO_4, 100.1 °C),[10] compared to the preequilibrium protonation ρ of +1.40.[11]

It will be apparent from the previous paragraph that, although ρ values are useful, they are not as useful as they might be for reactions in strong acid because they are often reported at different acid concentrations (and temperatures). This makes it difficult to compare different reactions, or different substrates undergoing the same reaction, because little is known about the variation of ρ with acid concentration. For A-S_E2 reactions, e.g., the rate-determining proton transfer process in styrene[12] and phenylacetylene[13] hydrations, ρ^+ does not vary with acid concentration.[12-14] However, it is not known whether or not this is true for A-1 and A-2 hydrolyses. It was in an attempt to remedy this situation that the work described in this paper was undertaken.

A series of substituted phenyl substrates whose hydrolysis rates had been studied as a function of changing acidity was needed. Surprisingly, a suitable series of simple esters is not available, despite all of the work which has been done on ester hydrolysis mechanisms.[15] Accordingly a series of acylals **1**–**8**[16] and thioacylals **9**–**12**,[17] for which good hydrolysis data were available at 25 °C, was selected (Chart I). These interesting compounds exhibit both A-2 and A-1 hydrolyses, at different acidities, and so were most suitable for our purposes. Also studied were **13**, **14**, and **15**.[16-18] Additionally a previous study[19] of some thiobenzoic acid (**16**), *S*-ethyl thiobenzoate (**17**), and *O*-ethyl thiobenzoate (**18**) hydrolyses provided useful information.

The data were analyzed by using the excess acidity method,[20] which has previously been successfully applied to enolizations,[21] several different hydrolyses,[19,22,23] aromatic nitrations,[24] and the acid-catalyzed condensation of acetaldehyde;[25] the method is summarized in the next section.

Kinetic Analysis

For equilibria, the excess acidity method[26] may be summarized as follows. A general thermodynamic equation, eq 2, can be written from the definition of K_{SH^+}, the equilibrium constant of reaction 1, referring to the acid

$$S + H^+ \overset{K_{SH^+}}{\rightleftharpoons} SH^+ \quad (1)$$

$$\log (C_{SH^+}/C_S) - \log C_{H^+} = \log (f_S f_{H^+}/f_{SH^+}) + pK_{SH^+} \quad (2)$$

$$\log (f_S f_{H^+}/f_{SH^+}) = m^* \log (f_{B^*} f_{H^+}/f_{B^*H^+}) = m^*X \quad (3)$$

$$\log I - \log C_{H^+} = m^*X + pK_{SH^+} \quad (4)$$

ionization of protonated substrate SH^+; C is molar concentration and f molar activity coefficient.[27] The activity coefficient ratio term in eq 2 has been shown[27,28] to be linear in the equivalent term for a "standard base" B*, abbreviated X, as shown in eq 3.[27] Values of pK_{SH^+} valid in the aqueous standard state can then be obtained from measured ionization ratios, $I = C_{SH^+}/C_S$, using eq 4; values of X and log C_{H^+} for aqueous H_2SO_4,[27] $HClO_4$,[27] HCl,[29] and

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HBr[29] are available. The slope m^* depends on the type of substrate involved, typically 1.0 for primary aromatic amines,[27,30] 0.6 for amides,[27] 1.8 for carbocations,[29,30] and so on.

For a unimolecular reaction, such as the A-1 hydrolyses of **1–15** in strong acid,[16–18] eq 6 is readily obtained;[20] the

$$SH^+ \xrightarrow[\text{slow}]{k_1} [A^+] \xrightarrow[\text{fast}]{} P \quad (5)$$

$$k_\psi(C_S + C_{SH^+}) = k_1 a_{SH^+}/f_\ddagger \quad (6)$$

observed pseudo-first-order rate constant is k_ψ, and the substrate concentration is written as a sum because the extent of protonation also varies with acidity. Substituting for the protonated substrate activity a_{SH^+}, using eq 7, results in an activity coefficient ratio involving the transition state activity coefficient $f_\ddagger$. This is accounted for by eq 8, essentially an extension of the Kresge α-coefficient assumption for A-S_E2 reactions.[31] Suitable manipulation of eq 6–8 produces eq 9, the rate equation for the A-1

$$a_{SH^+} = a_S a_{H^+}/K_{SH^+} = C_S C_{SH^+} f_S f_{SH^+}/K_{SH^+} \quad (7)$$

$$\log (f_S f_{H^+}/f_\ddagger) = m_1^* \log (f_S f_{H^+}/f_{SH^+}) = m_1^* m^* X \quad (8)$$

$$\log k_\psi - \log (C_S/(C_S + C_{SH^+})) - \log C_{H^+} = m_1^* m^* X + \log (k_1/K_{SH^+}) \quad (9)$$

mechanism, reactions 1 and 5.[20] Here k_1 is the medium-independent rate constant for reaction 5, and m_1^* the corresponding slope; for A-1 reactions $m_1^* > 1$ and is perhaps as high as 2–3,[20] as compared to A-S_E2 reactions, for which $0 < m_0^* (\equiv \alpha) < 1$.[20,31] The protonation correction term $\log (C_S/(C_S + C_{SH^+}))$ can be calculated if necessary using eq 4, if pK_{SH^+} and m^* are known or can be estimated; it is zero if the substrate is unprotonated in the media involved. For essentially fully protonated substrates a modified equation is easily derived.[20]

For bimolecular reactions, for instance, the A-2 hydrolyses of **1–15** in more dilute acid,[16,17] analogous reasoning leads to eq 11, the rate equation for the A-2 mechanism, reactions 1 and 10.[20] Plots against X will now

$$SH^+ + Nu \xrightarrow[\text{slow}]{k_2} [A^+] \xrightarrow[\text{fast}]{} P \quad (10)$$

$$\log k_\psi - \log (C_S/(C_S + C_{SH^+})) - \log C_{H^+} = m_2^* m^* X + \log a_{Nu} + \log (k_2/K_{SH^+}) \quad (11)$$

be curved because of the extra log [nucleophile activity] term. The nucleophile (or base) involved can be uniquely identified, since subtracting log a_{Nu} from both sides of eq 11 will produce a linear plot against X in only one case.[20–23,25] In H_2SO_4 this is usually two water molecules,[19–22] sometimes one or three,[23,25] and may be bisulfate ion in strong acid.[21,23] The slope parameter m_2^* has usually been found to be close to unity,[19–22,25] which can be shown to explain the success of the Bunnett w parameter[32] and later Yates r parameter[15] kinetic treatments for these reactions.

Results

The observed products of the hydrolysis reactions are the corresponding phenols for **1–8**[16] and acetic acid for **13** and **15**;[16] the presence of formaldehyde is inferred from the tendency of the reaction solutions to become cloudy,

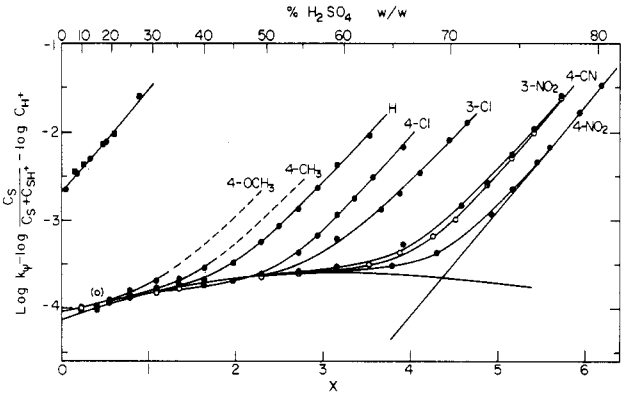

Figure 1. Excess acidity plots, according to eq 9 and 11, for the hydrolyses of acylals **1–6** and **8** (●), **7** (○), and **13** (●, ■) as a function of sulfuric acid concentration at 25 °C. The points are experimental data from ref 16 (circles) and 18 (squares), and the curves are theoretical, based on the data in Table I. The separation into A-2 and A-1 hydrolyses is indicated for the 4-nitro compound **8**.

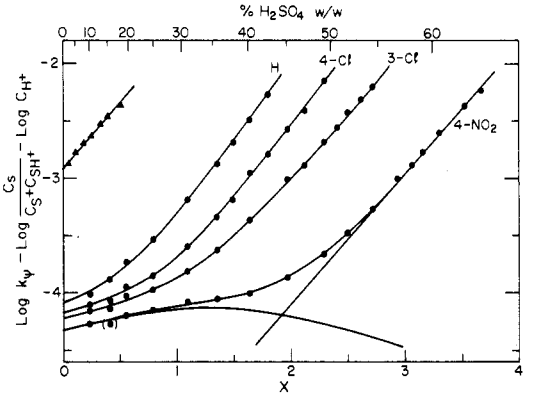

Figure 2. Excess acidity plots for the hydrolyses of thioacylals **9–12** (●) and **14** (▲) in sulfuric acid at 25 °C. Data from ref 17; see Figure 1.

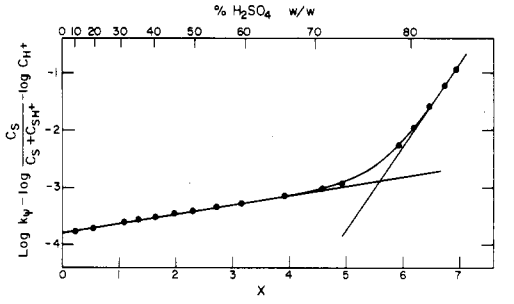

Figure 3. Excess acidity plot for the hydrolysis of methylene diacetate (**15**) in sulfuric acid at 25 °C, showing the two A-1 hydrolyses. Data from ref 16; see Figure 1.

particularly for the activated compounds **1** and **2**, presumably due to phenol–formaldehyde polymerization.[16] For this reason **1** and **2** could not be studied at high acidity.[16] For **9–12** the product is the corresponding thiophenol;[17] **14** gives CH_3SCH_2OH and acetic acid, not methanethiol.[17]

Pseudo-first-order hydrolysis rate constants (k_ψ) at 25 °C as a function of sulfuric acid concentration are given by McClelland for **1–8** and **15**[16] and **9–12** and **14**[17] and results in excellent agreement are reported by Salomaa[18] and McClelland[16] for methoxymethyl acetate, **13**. Also reported are rate constants at several different temperatures for **3**, **9**, **12**, and **14**.[17] The compounds react too quickly to enable individual basicity constants to be determined, so, following McClelland[16,17] and others,[33] pK_{BH^+}

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Table I. Standard State Rate Constants and Slopes for the Reactions of 1–15 in Sulfuric Acid at 25 °C

	A-2 reaction		A-1 reaction			
no.[a]	log (k_2/K_{SH^+})	$m_2^{\ddagger}m^*$	log (k_1/K_{SH^+})	$m_1^{\ddagger}m^*$	$\pm\sigma_y$[b]	N[c]
1	−4.092 ± 0.032	(0.264)[d]	−5.153 ± 0.079	(1.074)[d]	0.031	5
2	−4.050 ± 0.013	(0.281)[d]	−5.548 ± 0.036	(1.083)[d]	0.022	7
3	−4.044 ± 0.020[e]	0.318 ± 0.030	−5.92 ± 0.10	1.109 ± 0.033	0.024	17
4	−4.053 ± 0.015	0.347 ± 0.015	−6.71 ± 0.10	1.166 ± 0.029	0.020	15
5	−4.064 ± 0.026	0.371 ± 0.023	−6.67 ± 0.15	1.025 ± 0.035	0.029	11
6	−4.122 ± 0.022	0.438 ± 0.011	−8.33 ± 0.15	1.167 ± 0.028	0.027	14[f]
7	−4.130 ± 0.023	0.445 ± 0.013	−8.00 ± 0.20	1.114 ± 0.038	0.035	15
8	−4.138 ± 0.012	0.446 ± 0.006	−8.86 ± 0.12	1.194 ± 0.021	0.022	19
9	(−4.195)[d]	(0.338)[d]	−4.759 ± 0.033[g]	1.379 ± 0.026	0.029	14[f]
10	−4.219 ± 0.043	0.36 ± 0.14	−5.159 ± 0.095	1.308 ± 0.047	0.024	12
11	−4.263 ± 0.026	0.413 ± 0.072	−5.321 ± 0.074	1.149 ± 0.030	0.019	14
12	−4.322 ± 0.013[h]	0.479 ± 0.016	−6.381 ± 0.048	1.138 ± 0.015	0.015	19[f]
13			−2.680 ± 0.023	1.171 ± 0.050	0.037	9
14			−2.917 ± 0.012[i]	1.144 ± 0.047	0.023	10
15	−3.798 ± 0.007[j]	0.164 ± 0.003[j]	−11.03 ± 0.13	1.454 ± 0.020	0.013	17

[a] Substrate. [b] Root-mean-square error of the fit. [c] Number of experimental points. [d] Extrapolated from the LFER of the other values in this column. [e] $\Delta H^{\ddagger} - \Delta H^{\circ} = 16.99 \pm 0.37$ kcal mol^{-1}, $\Delta S^{\ddagger} - \Delta S^{\circ} = -28.0 \pm 1.3$ eu. [f] After rejecting one experimental point as being off the curve, to 95% confidence. [g] $\Delta H^{\ddagger} - \Delta H^{\circ} = 23.33 \pm 0.49$ kcal mol^{-1}, $\Delta S^{\ddagger} - \Delta S^{\circ} = -2.1 \pm 1.6$ eu (assuming that $\Delta H^{\ddagger} - \Delta H^{\circ} = 17.42$ kcal mol^{-1} for the A-2 process). [h] $\Delta H^{\ddagger} - \Delta H^{\circ} = 17.42 \pm 0.28$ kcal mol^{-1}, $\Delta S^{\ddagger} - \Delta S^{\circ} = -35.9 \pm 0.9$ eu. [i] $\Delta H^{\ddagger} - \Delta H^{\circ} = 23.14 \pm 0.38$ kcal mol^{-1}, $\Delta S^{\ddagger} - \Delta S^{\circ} = +5.7 \pm 1.3$ eu. [j] A-1 reaction, not A-2 (see text).

values of −4 and m^* slopes of 0.6 were assumed to apply to all of them. This must be a good approximation; **1–15** are all acetate esters protonating at the carbonyl oxygen[33] and should exhibit very little basicity variation. This assumption permitted calculation of the protonation correction terms log ($C_S/(C_S + C_{SH^+})$) required for eq 9 and 11, using eq 4.

Listed values of log C_{H^+} and X[27] were used for excess acidity plots for **1–15** according to eq 9, and these are given in Figures 1–3. As can be seen, **1–12** all show a relatively substrate-independent A-2 reaction (curve) at low acidity, followed by an A-1 process (lines) at higher acidity which is much more substrate-dependent. For instance, the latter process takes over from the A-2 reaction at quite low acidity for **1** and at much higher acidity for **8** (Figure 1). The methoxymethyl and (methylthio)methyl acetates (**13** and **14**) react much more quickly than their (aryloxy)-methyl counterparts, and by an A-1 process exclusively. Methylene diacetate (**15**), however, reacts by two A-1 processes, as can be seen from the two straight lines in Figure 3.

It was found, by subtracting log [water activities][22b] from both sides of eq 11 as described, that the A-2 process involves two water molecules for **9–12**, but only one water molecule for **1–8**. The data were then computer-fitted to a combination of eq 9 and 11, using standard curve-fitting techniques. This gave the slope and intercept results in Table I, from which the theoretical lines in Figures 1–3 were drawn. Standard-state activation parameters were calculated for **3**, **9**, **12**, and **14**, using log C_{H^+} and X corrected to temperature as previously described,[23,30] and these are also given in Table I.

Linear free energy relationships against σ[2c] were plotted for log (k_1/K_{SH^+}) and log (k_2/K_{SH^+}), and these are given in the lower half of Figure 4. (Subscript 1 for A-1, and 2 for A-2, reactions.) It was found that the slope parameters, $m_1^{\ddagger}m^*$ and $m_2^{\ddagger}m^*$, were also linear functions of σ, and these plots are given in the upper part of Figure 4. The LFERs found were as follows: A-2 reaction of acylals **1–8**, log (k_2/K_{SH^+}) = −(0.091 ± 0.019)σ − (4.058 ± 0.010), correlation coefficient r 0.89 (8 points), $m_2^{\ddagger}m^*$ = (0.178 ± 0.015)σ + (0.312 ± 0.010), r 0.99 (6); A-1 reaction of **1–8**, log (k_1/K_{SH^+}) = −(3.21 ± 0.21)σ − (6.052 ± 0.062), r 0.99 (8), $m_1^{\ddagger}m^*$ = (0.093 ± 0.082)σ + (1.099 ± 0.048), r 0.49 (6); A-2 reaction of thioacylals **9–12**, log (k_2/K_{SH^+}) = −(0.163 ± 0.023)σ − (4.195 ± 0.016), r 0.99 (3), $m_2^{\ddagger}m^*$ = (0.182 ± 0.028)σ + (0.338 ± 0.021), r 0.99 (3); A-1 reaction of **9–12**, log (k_1/K_{SH^+}) = −(2.06 ± 0.15)σ − (4.736 ± 0.061), r 0.99 (4), $m_1^{\ddagger}m^*$ = −(0.283 ± 0.088)σ + (1.348 ± 0.055), r 0.92 (4).

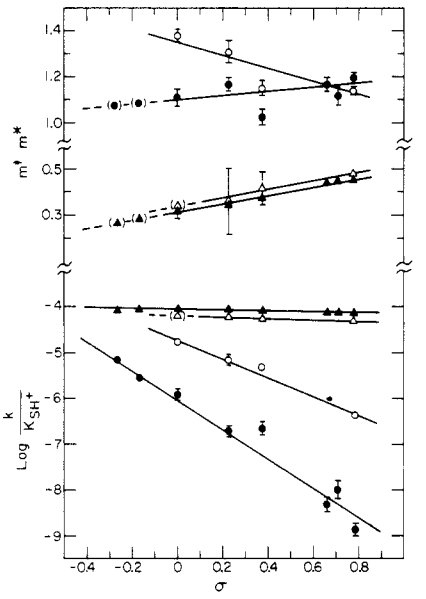


Figure 4. Linear free energy relationships obtained from the results in Table I. Closed symbols, acylals; open ones, thioacylals. Circles, A-1 process, log (k_1/K_{SH^+}) (lower) and $m_1^{\ddagger}m^*$ (upper). Triangles, A-2 process, log (k_2/K_{SH^+}) (lower) and $m_2^{\ddagger}m^*$ (upper).

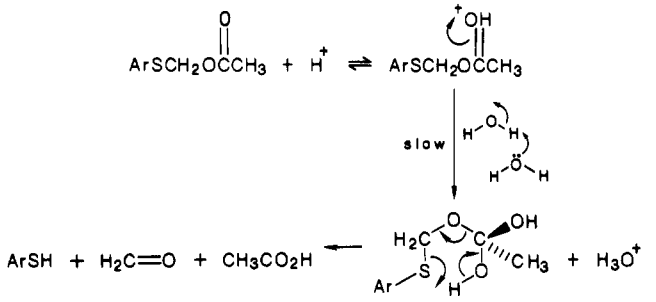
Discussion

Reaction Mechanisms. The excess acidity method is capable of providing mechanistic information which the other methods of analyzing reaction rate data in strong acids[34] cannot. Those mechanistic details which were not revealed in the previous studies of these systems[16–18] will be emphasized here.

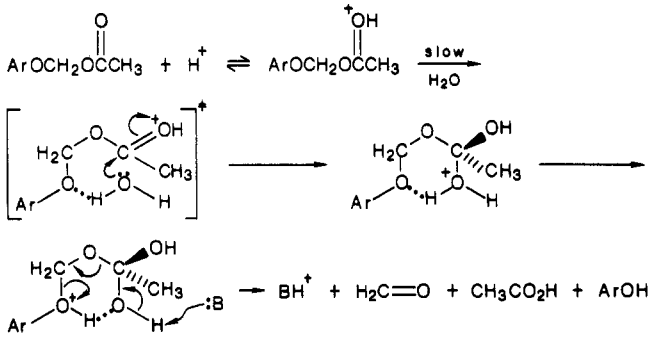
(33) (a) Yates, K.; McClelland, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 2686–2692. (b) Lee, D. G.; Sadar, M. H. *Ibid.* **1974**, *96*, 2862–2867.

(34) (a) Lucchini, V.; Modena, G.; Scorrano, G.; Tonellato, U. *J. Am. Chem. Soc.* **1977**, *99*, 3387–3392. (b) Yates, K.; Modro, T. A. *Acc. Chem. Res.* **1978**, *11*, 190–196. (c) Reference 6, Chapter 5. (d) References 15, 31, and 32.

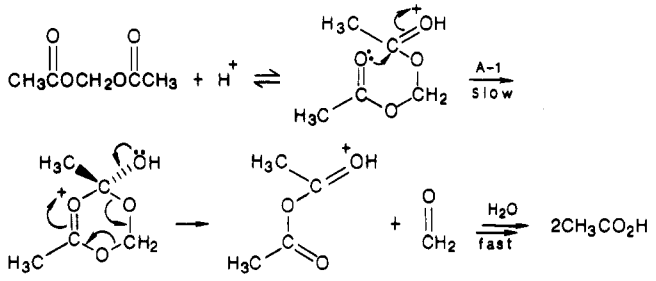
The thioacylals **9–12** undergo hydrolysis involving two water molecules at low acidity, undoubtedly with one acting as a base toward the other, producing a neutral tetrahedral intermediate directly. This is the normal mechanism for ester hydrolysis in sulfuric acid,[22b] shown below. The cyclic breakup of the tetrahedral intermediate shown is reasonable but speculative, since it occurs after the rate-determining step.



The acylals **1–8**, on the other hand, only have one water molecule involved in their low-acidity hydrolysis transition state. This can be reasonably accounted for if the ether oxygen acts as a base, replacing the water molecule base, as shown. This will not happen for the thioacylals, since sulfur cannot act as readily in this way. A simple hydrogen-bond switch, followed by breakup as shown, leads to the products.



Methylene diacetate (**15**) has a low-acidity A-1 hydrolysis mechanism. The difference between **1-12** and **15** is that the latter has a second carbonyl group, and an A-2-like mechanism in which carbonyl oxygen acts as an internal nucleophile toward the carbon of the other carbonyl group, after protonation, accounts very well for this observation. Subsequent extrusion of formaldehyde, as shown, gives protonated acetic anhydride which will hydrolyze much faster than **15** under the reaction conditions.

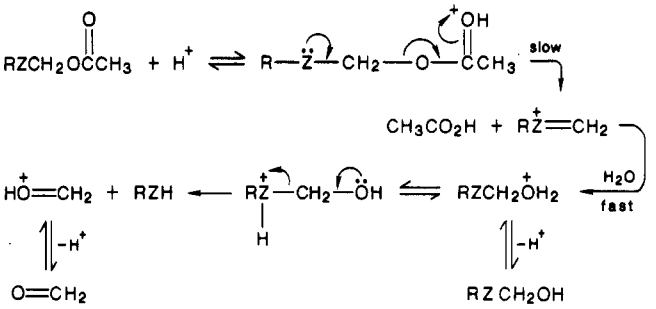


From Table I it can be seen that this reaction of **15** is faster than the A-2 hydrolyses of **1–8** and **9–12**, which is quite reasonable, since the internal nucleophile is a built-in entropic advantage. Otherwise the reactions are very similar. From Figure 4 it is apparent that the acylals react A-2 slightly faster than the thioacylals do (the difference is small but significant). This is also mainly an entropy effect, $\Delta S^{\ddagger}$ for **3** being −28 eu and that for **12** being −36 eu (Table I), which is reasonable considering the differing number of water molecules in the transition states discussed above. Substituents in the benzene rings make very little difference to the rates (Figure 4), which would be expected as the aryl group is too far away to greatly influence the proposed hydrolysis transition states.

Table II. Values of ρ at Different Acid Concentrations

% H_2SO_4 w/w	X	O, A-2	O, A-1	S, A-2	S, A-1
0	0	−0.09	−3.21	−0.16	−2.06
40	1.628	0.20	−3.06	0.13	−2.52
60	3.238	0.48	−2.91	0.43	−2.98
70	4.459	0.70	−2.80	0.65	−3.32
80	6.150	1.00	−2.64	0.96	−3.80
90	7.985	1.33	−2.47	1.29	−4.32

An A-1 mechanism is found exclusively for **13** and **14**, and at high acidities for **1–12** and **15**, as confirmed by the linearities in Figures 1–3 and the $\Delta S^{\ddagger}$ values found for **9** and **14**, −2 and +6 eu, respectively. This can best be explained by invoking alkoxy cations formed in an alkyl–oxygen ester cleavage,[16,17] as shown below (Z = O or S).

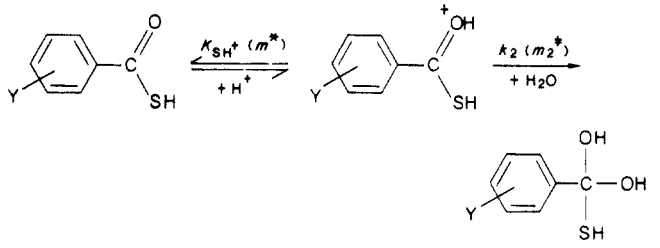


From Figures 1 and 2 and Table I it can be seen that methyl-substituted **13** and **14** (R = CH_3) react by this pathway much faster than aryl-substituted **1–12** (R = Ar) do, which is reasonable, because the lone pairs on Z are delocalized into the benzene ring and thus are less available to assist reaction in the latter case. This initial-state stabilization will be less important for sulfur than it will be for oxygen, which explains the faster rate found for the thioacylals (Figure 4). Also substituents in the phenyl ring will have a larger influence on the reaction in this case, as observed. Methylene diacetate (**15**, R = CH_3CO) reacts much more slowly in the standard state, presumably because the oxygen lone pairs are even less available, due to resonance delocalization onto the carbonyl oxygens.

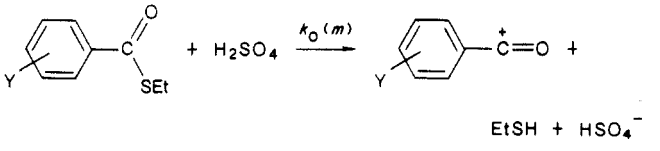
Variation of ρ with Acidity. It was found, as was to be expected, that the excess acidity intercepts were linear in σ, $\log (k/K_{SH^+}) = \rho_1\sigma + c_1$. However, it was also found, unexpectedly, that the excess acidity *slopes* were linear in σ too: $m^{\ddagger}m^{*} = \rho_2\sigma + c_2$. Multiplying the latter by X and combining, we find that the observed rate constants should have a linear free energy relationship which *depends on acidity* (as X): left-hand side of eq 9 or eq 11 $= (\rho_1 + \rho_2 X)\sigma + (c_1 + c_2 X)$. Thus $\rho = \rho_1 + \rho_2 X$, and only if $\rho_2 = 0$ will ρ be independent of the acid concentration. This appears to be the case for rate-determining carbon protonations,[14] but it clearly is not the case here. The equation just derived can be used to work out what the observed ρ would be for different values of X, and this is done for some representative acidities in Table II. It is apparent that the $X = 0$ value is the best one to use for comparisons between different reactions, because this is a standard state value (i.e., valid in a hypothetical ideal 1 M acid solution[26]); it can be seen from Table II that the variation of ρ with acid concentration is quite large, whole units being involved, with even a sign change for the A-2 reactions.

When this was discovered, a survey of our previous work led to other examples of this behavior in the hydrolysis reactions undergone by thiobenzoic acids (16) and thiolo- (17) and thiono- (18) benzoate esters,[19] the correlations usually being against σ^+ rather than σ.

Four thiobenzoic acids were studied,[19] and with pK_{SH^+} values only being available for two of them,[19] reasonable discussion is confined to the combined parameters for the A-2 process shown. The LFERs obtained were log $(k_2/K_{SH^+}) = (0.20 \pm 0.16)\sigma^+ - (4.616 \pm 0.052)$, r 0.66 (4), and $m_2^{\ddagger}m^* = (0.143 \pm 0.044)\sigma^+ + (0.633 \pm 0.009)$, r 0.92 (4). This means that the standard state ρ^+ value of +0.2 becomes +0.7 in 60% and +1.1 in 80% H_2SO_4.

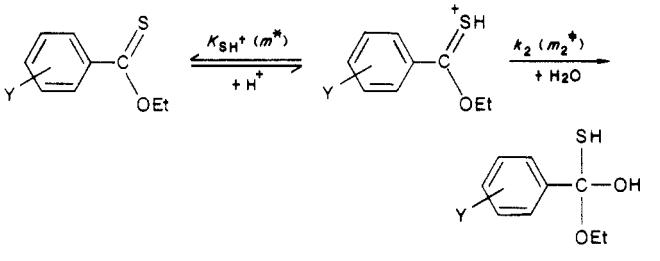


S-Ethyl thiobenzoates undergo rate-determining proton transfer to sulfur from undissociated sulfuric acid molecules, concerted with C–S bond breaking, as shown.[19] A



recalculation of the data[19] shows a good correlation with σ (not σ^+) for both log k_0 and m: log $k_0 = -(8.40 \pm 0.64)\sigma - (4.96 \pm 0.16)$, r 0.98 (8); $m = (0.474 \pm 0.073)\sigma + (0.464 \pm 0.019)$, r 0.94 (8). In this case the standard-state ρ value is an unrealistic one to use, as there are no undissociated H_2SO_4 molecules present in the aqueous standard state. The above equations combine to give ρ values of −5.5, −4.6, and −3.3, in 80%, 90% and 99% H_2SO_4, respectively.

The hydrolysis mechanism for *O*-ethyl thiobenzoates is that shown.[19] In dilute acid the initial protonation is



rate-determining, with log $k_0 = -(0.47 \pm 0.18)\sigma - (6.898 \pm 0.041)$ r 0.76 (7).[19] In more concentrated acids, it is a preequilibrium: $pK_{SH^+} = -(0.908 \pm 0.053)\sigma^+ - (7.966 \pm 0.035)$, r = 0.98 (8); $m^* = -(0.210 \pm 0.024)\sigma^+ + (1.330 \pm 0.017)$, r 0.96 (8). With good pK_{SH^+} values available, log k_2 and $m_2^{\ddagger}$ can be separated out from the combination: log $k_2 = (0.57 \pm 0.17)\sigma^+ + (0.68 \pm 0.10)$, r 0.81 (8); $m_2^{\ddagger} = (0.206 \pm 0.044)\sigma^+ + (1.142 \pm 0.026)$, r 0.89 (8). Thus in 0%, 60%, and 80% H_2SO_4, ρ^+ for pK_{SH^+} is −0.91, −1.59, and −2.20, and ρ^+ for log k_2 is +0.6, +1.2, and +1.8, respectively. The slopes in the m^* and $m_2^{\ddagger}$ correlations cancel out, $(0.21 \pm 0.02) - (0.21 \pm 0.04) = 0$, which means that the combined slopes $m_2^{\ddagger}m^*$ are the same for all substituents; the observed average combined slope was 1.486 ± 0.067.[19]

It is evident that this phenomenon is fairly widespread, at least in processes involving initial protonation at oxygen and sulfur. Carbon protonation apparently does not lead to acidity-dependent $m_0^{\ddagger}$ slopes;[14] no examples involving nitrogen protonation could be found.

Excess acidity slopes, like Bunnett–Olsen ϕ values,[34a,35] are the slopes of LFER plots, and thus have mechanistic value,[20] as explained in the introduction. For instance, the observed $m_1^{\ddagger}$ values are typical for A-1 reactions,[20] being about 1.1/0.6 = 1.8, and the $m_2^{\ddagger}$ values are in the normal range for A-2 reactions,[20] being about 0.4/0.6 = 0.7 (Table I); the latter values appear to differ from 1.0 to the extent that the transition state differs from the protonated substrate. However, it is not immediately obvious what significance the slope of a plot of these quantities against σ, called ρ_2 here, has. These slopes may have empirical mechanistic value, once enough have been collected for comparison purposes. These are probably not enough of them in this paper to draw any real conclusions; most are positive, a few are negative, and there is a tendency to cluster around a value of 0.2. For rate-determining carbon protonations the value is zero.[14]

Nevertheless it can be commented that these ρ_2 values probably reflect the degree of interaction between the protonated transition state and water molecules in the aqueous acid mixture. With increasing acidity the water content decreases, and so solvation decreases, and the influence of substituents on the reaction centre should go up. For instance, substituents in the gas phase have many times the effect of substituents in solution.[36] Thus, it should be expected that absolute values of ρ should increase with acidity, for those cases in which solvation by water molecules is important. This seems to be mostly consistent with what is found; three of the four columns in Table II show this tendency.[37] Carbocations resulting from carbon protonation are not strongly solvated by water molecules, and so do not show this effect; sulfur- and oxygen-protonated substrates are, and do.

In conclusion, it is evident that comparisons between ρ values for reactions in strong acid must be made with some care. Their variation with acidity should, if possible, be measured and extrapolated back to the aqueous standard state, as described herein, for optimum mechanistic meaning.

Acknowledgment. Financial support of this reasearch is by the Natural Sciences and Engineering Research Council of Canada. Valuable discussions with Dr. C. D. Johnson are acknowledged.

Registry No. 1, 57440-09-2; 2, 38084-40-1; 3, 35279-25-5; 4, 57440-10-5; 5, 57440-11-6; 6, 57440-13-8; 7, 57440-12-7; 8, 57440-14-9; 9, 57440-42-3; 10, 57440-43-4; 11, 57440-44-5; 12, 57440-45-6; 13, 4382-76-7; 14, 16437-69-7; 15, 628-51-3.

(35) Bunnett, J. F.; Olsen, F. P. *Can. J. Chem.* **1966**, *44*, 1899–1916.
(36) For instance, see: Mashima, M.; McIver, R. R.; Taft, R. W.; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 2717–2718.
(37) The reason for the exception, the A-1 reaction of the acylals, is not clear at this time.