Mechanisms of Ester Hydrolysis in Aqueous Sulfuric Acids[1]

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Abstract: The rates of acid-catalyzed hydrolysis of methyl, *n*-propyl, isopropyl, *sec*-butyl, benzyl, phenyl, *p*-nitrophenyl, and *p*-chlorophenyl acetates have been investigated over a wide range of acidity (10–90% aqueous H_2SO_4) by means of spectrophotometric methods. First-order kinetics were obtained in every case, and the rate constants show one of three types of acid dependence, varying with ester structure: (i) a rate maximum at intermediate acidities followed by very slow hydrolysis in very concentrated acids; (ii) a rate maximum at intermediate acidities followed by a sharp increase in rate in very concentrated acids; and (iii) a continuous increase in hydrolysis rate with increasing acid concentration, becoming very rapid even at moderate acidities. These different rate–acidity dependences have been treated uniformly as a function of H_0 and the water activity to yield reaction parameters which are explicable in terms of a change in mechanism at some intermediate acidity for each ester, either from $A_{Ac}2$ to $A_{Al}1$ or from $A_{Ac}2$ to $A_{Ac}1$, depending strongly on ester structure.

The kinetic response of ester hydrolysis to changes in acidity has been investigated mainly in the dilute acid region where the information to be gained about detailed mechanisms is quite limited. This is chiefly because one important reaction variable, the water concentration (or activity), remains effectively constant. More detailed mechanistic information has come from the classical O^{18}-exchange studies of Bender[3] and others. This work was also confined to the dilute acid region, and while extremely valuable, this approach does not always permit unequivocal decisions about reaction mechanisms. Although a few ester hydrolyses have been studied in more concentrated acids,[4,5] no systematic investigation of the dependence of hydrolysis rate on acid concentration has yet been made for esters. We therefore thought it of interest to investigate the variation of hydrolysis rate for simple esters over as wide a range of acid concentrations as possible, in the hope of obtaining further detailed information about the various possible mechanisms and under what conditions they occur. Of the four mechanisms possible for acid catalysis, namely the $A_{Ac}1$, $A_{Ac}2$, $A_{Al}1$, and $A_{Al}2$ mechanisms,[6] it is generally believed that apart from a few special cases, all ordinary esters hydrolyze by the $A_{Ac}2$ pathway. The few clearly recognized exceptions such as *t*-butyl esters and mesitoates which are believed to hydrolyze by the $A_{Al}1$ and $A_{Ac}1$ mechanisms, respectively,[7] occur because of special structural factors in the ester. It is therefore of interest to investigate to what extent combinations of changes in structure, acidity, and water activity can lead to different mechanisms of hydrolysis even for ordinary esters.

Results and Discussion

The esters chosen for study were all acetates, so that the effect of varying one structural parameter at a time

could be investigated. These were the methyl, *n*-propyl, isopropyl, *sec*-butyl, benzyl, phenyl, *p*-chlorophenyl, and *p*-nitrophenyl esters. Ethyl acetate was not investigated since rate data covering the entire range of sulfuric acid concentrations have been reported[8-10] for this ester. The rate of hydrolysis of each ester was measured at 25° in aqueous sulfuric acid solutions covering as wide a range as possible. The acid range used was limited in some cases by high reaction velocities or by sulfonation reactions in the more concentrated region. Simple first-order kinetics were obtained in every case, acid concentration being effectively constant during each run, and the pseudo-first-order rate constants obtained for all eight acetates are listed in Table I. Each rate constant is the mean of at least two, and sometimes three or four independent determinations. It can be seen from these results that several of the esters exhibit local rate maxima at intermediate acid concentrations (50–60% H_2SO_4), similar to those previously reported[11] for amide hydrolysis, but occurring at much higher acid strengths. That the rate dependence on acid concentration is quite different for the various types of ester can be seen more clearly by plotting rate profiles of k_1 *vs.* % H_2SO_4 as shown in Figure 1. Literature values[9,10] for ethyl acetate have been included in Figure 1 for comparison. The rate–acidity profiles obtained clearly belong to one of three types. Type i is characterized by an initial steady increase in rate with acid concentration, passing through a maximum at about 50–60% acid, followed by a rate decrease almost to zero by 80% acid with a final modest rate increase in the 85–100% region. Very similar behavior of this type is obtained for all three primary alkyl esters, as shown in Figure 1. Type ii behavior, shown by the secondary alkyl and benzyl esters, exhibits a rate maximum similar to type i at about 50–55% acid, but this is followed by a very sharp increase in rate well before the rate has approached zero. The acid region in which this sharp rate increase occurs depends markedly on the structure of the ester. Type iii differs from the previous two in having no ob-

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(3) M. L. Bender, *J. Am. Chem. Soc.*, **75**, 5986 (1953); M. L. Bender, R. D. Ginger, and J. P. Uink, *ibid.*, **80**, 1044 (1958).

(4) J. F. Bunnett, *ibid.*, **83**, 4956 (1961). This article contains a list of all pertinent references to 1961.

(5) C. A. Lane, *ibid.*, **86**, 2521 (1964).

(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 754.

(7) C. A. Bunton, A. E. Comyns, and J. L. Wood, *Research* (London), **6**, 383 (1951); C. A. Bunton, E. D. Hughes, C. K. Ingolid, and D. F. Meigh, *Nature*, **166**, 680 (1950); H. P. Treffers and L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 1708 (1937).

(8) C. A. Lane and M. F. Cheung, *ibid.*, in press; see also ref 3.

(9) R. P. Bell, A. L. Dowding, and J. A. Noble, *J. Chem. Soc.*, 3106 (1955).

(10) D. Jaques, *ibid.*, 3874 (1965).

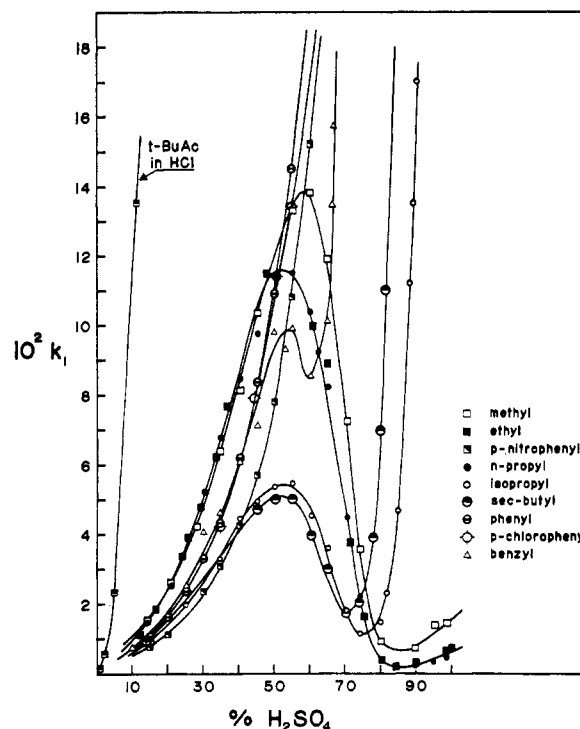(11) J. T. Edward and S. C. R. Meacock, *ibid.*, 2000 (1957).

Table I. Ester Hydrolysis Rates in Sulfuric Acids at 25°

% H_2SO_4	$10^2 k_1{}^a$	% H_2SO_4	$10^2 k_1$	% H_2SO_4	$10^2 k_1$
Methyl acetate		n-Propyl acetate		Isopropyl acetate	
14.1	1.50	14.1	1.47	14.1	0.890
20.7	2.61	20.7	2.52	25.3	1.99
28.3	4.22	30.2	5.23	34.8	3.30
34.8	6.41	34.8	6.78	40.4	4.21
40.4	8.14	40.4	8.47	45.4	4.96
45.4	10.4	45.4	9.76	50.2	5.38
50.2	11.4	50.2	11.4	55.2	5.48
55.2	13.3	55.2	11.5	60.4	4.54
60.4	13.8	60.4	10.4	65.2	3.60
65.2	11.9	65.2	8.23	70.4	1.80
70.4	7.25	70.4	4.48	74.1	1.14
74.1	3.83	74.1	2.20	80.0	1.48
80.0	0.931	89.7	0.205	81.7	2.30
		95.0	0.323	84.7	4.69
		98.6	0.450	88.2	11.2
				89.7	13.5
				90.8	17.0
sec-Butyl acetate		Benzyl acetate		Phenyl acetate	
14.1	0.964	10.1	0.740	15.1	1.08
45.4	4.72	25.3	2.52	20.1	1.62
50.2	5.00	30.2	4.04	25.3	2.38
55.2	5.02	34.8	4.61	30.2	3.30
60.4	3.96	40.4	6.08	34.8	4.34
65.2	2.99	45.4	7.13	40.4	6.20
70.4	1.71	50.2	9.81	45.4	8.36
74.1	2.03	52.8	9.30	50.2	10.9
77.7	3.90	55.2	9.91	55.2	14.5
80.0	7.00	60.4	8.52	60.4	19.2
81.7	11.00	62.5	9.24	65.2	22.6
84.7	23.6	65.2	10.1	70.4	27.2
88.2	63.2	66.8	13.7	74.1	29.3
		67.3	15.7		
		69.0	22.3		
p-Chlorophenyl Acetate				p-Nitrophenyl acetate	
15.1	0.922			15.1	0.751
34.8	4.25			20.1	1.12
45.4	7.90			25.3	1.52
55.2	13.4			30.2	2.36
65.2	22.7			34.8	3.09
70.4	27.3			40.4	4.27
74.1	38.2			45.4	5.71
				50.2	7.81
				55.2	10.8
				60.4	15.2
				65.2	21.3
				70.4	36.1
				74.1	70.5
				75.3	93.3
				77.7	161
				78.5	158
				80.0	222

^{a} Pseudo-first-order rate constants in l. mole^{-1} min^{-1}.

Figure 1. Rate–acidity dependence for the hydrolysis of acetates in aqueous sulfuric acid at 25° (k_1 is the pseudo-first-order rate constant in min^{-1}).
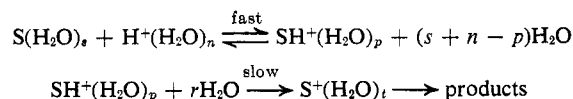
servable rate maximum, the rate increasing monotonically with acid concentration until the reaction is too rapid to follow by conventional methods even at moderate acidities. The three phenyl esters exhibit this type of behavior as shown in Figure 1, as well as t-butyl acetate. The reported data based on hydrolysis in HCl solutions[12] has been plotted for the t-butyl ester since as yet we have not been able to obtain satisfactory or reproducible results for any tertiary alkyl esters in sulfuric acid, partly because of their high reactivities and partly because of solubility problems.

It seems clear from the above diversity of behavior that all these esters cannot be reacting by the same mechanism, and further that changes in mechanism are

(12) P. Salomaa, Suomen Kemistilehti, B32, 145 (1959).

occurring for individual esters at different acidities. This raises three questions. First, can all of these rate profiles be explained in a way consistent with the types of mechanism previously mentioned? Second, can all these different rate–acidity dependences be treated quantitatively by some uniform approach, and finally can this be used to obtain any detailed information about the possible transition states?

We have shown previously[13] that rates of organic reactions in concentrated acids can be treated quantitatively as a function of the acidity and water activity of the reaction medium by an approach which is essentially a modification of the Bunnett hydration parameter treatment.[4,14] The modification involves basing the acidity of the reaction medium on an acidity function which is strictly appropriate to the type of substrate whose mechanism is being considered. For example, if we write the general rate scheme for ester hydrolysis in terms of fully hydrated species as

$$S(H_2O)_s + H^+(H_2O)_n \underset{}{\overset{fast}{\rightleftharpoons}} SH^+(H_2O)_p + (s + n - p)H_2O$$

$$SH^+(H_2O)_p + rH_2O \overset{slow}{\longrightarrow} S^+(H_2O)_t \longrightarrow products$$

the following simple relationship between rate, acidity, and water acitivity can be derived from transition-state theory

$$\log k_1 + H_S = r \log a_{H_2O} + (\text{constant}) \qquad (1)$$

(where k_1 is the pseudo-first-order rate constant) providing H_S is an acidity function based on the ionization of indicators which are esters of the type whose hydrolysis reaction is being considered. The approxima-

(13) K. Yates and J. B. Stevens, Can. J. Chem., 43, 529 (1965); K. Yates and J. C. Riordan, ibid., 43, 2328 (1965).
(14) J. F. Bunnett, J. Am. Chem. Soc., 83, 4968, 4973, 4978 (1961).

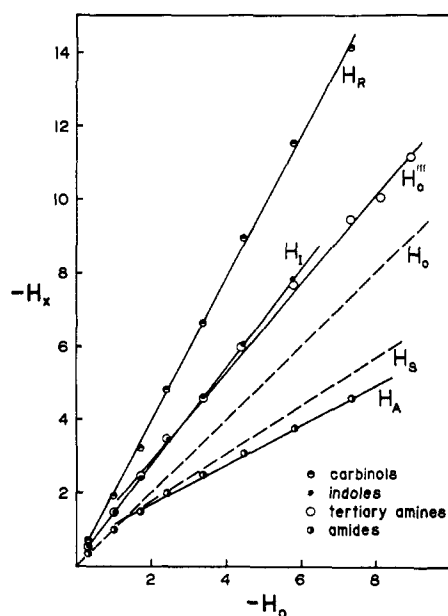Figure 2. Approximate linear dependence of H_x acidity functions on the Hammett acidity function H_0.

Figure 3. Log k_1 + mH_0 vs. log a_{H_2O} for methyl, ethyl, and n-propyl acetates.

tions and assumptions involved in obtaining eq 1 are then much less drastic than in the Bunnett hydration parameter treatment[4,14] and have been discussed previously.[13] If eq 1 is valid for ester hydrolysis, plots of (log k_1 + H_S) should be linear in log a_{H_2O} with a slope r which would give information about the involvement of water in the rate-determining step, and hence about the mechanism.

An equation like (1) has been found to give linear plots with uniform slopes for a number of amide hydrolyses[13] for which an amide-based acidity function is available[15] but as yet no ester-based acidity function such as H_S has been established. It would clearly be tedious and in some cases difficult if not impossible to establish an acidity scale strictly appropriate to each substrate type which is of interest, but fortunately this is not necessary, at least for acetate esters. Theoretically, the relationship between measured ionization ratios for esters and some suitable function H_S is given by

$$\log [SH^+]/[S] = -H_S + pK_{SH^+}$$

We have measured ionization ratios spectrophotometrically for several acetates whose rates of hydrolysis are not too fast in the acid range of interest and find that these closely obey the linear relationship

$$\log [SH^+]/[S] = -mH_0 + (\text{constant})$$

using available[16] H_0 data. The slopes m are approximately 0.62 for simple acetates, which correspond closely to Lane's reported[5] value of 0.65 for the indicator slope of ethyl acetate. Therefore, we can use available H_0 data to approximate to H_S by means of the relationship H_S = mH_0 + (constant) and thus modify eq 1 to give

$$\log k_1 + mH_0 = r \log a_{H_2O} + (\text{constant}) \quad (2)$$

(15) K. Yates, J. B. Stevens, and A. R. Katritzky, Can. J. Chem., 42, 1957 (1964).
(16) M. J. Jorgenson and D. R. Hartter, J. Am. Chem. Soc., 85, 878 (1963).

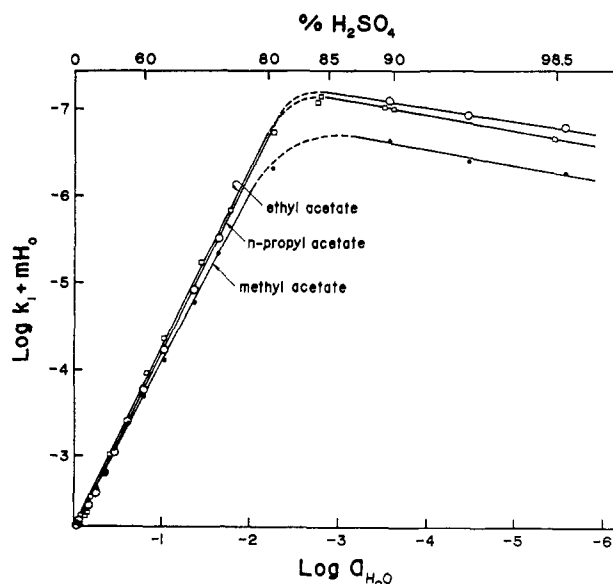That this is a valid approximation to H_S can be shown by plotting all available acidity functions for sulfuric acid, namely the H_R,[17] H_A,[15] H_0''',[18] and H_I[19] functions, against the H_0 function. Over a very wide range of acidity (more than eight logarithmic units) each of these functions is linear in H_0 as shown in Figure 2, and, therefore, from the measured ionization behavior of the esters it is reasonable to conclude that the H_S function will vary with acid concentration approximately as shown in Figure 2.

We have tested the relationship in eq 2 using all of the rate data listed in Table I along with independently measured values of H_0, m, and log a_{H_2O}.[20] This is shown in Figure 3 for methyl, ethyl, and n-propyl acetates. Excellent linearity is obtained over a very wide range (0–80% acid) with an almost identical slope (r = 2.1) for the ethyl and n-propyl esters and a very similar slope (r = 1.92) for methyl acetate. In each case, a break occurs at about 80–85% acid, followed by an equally linear relationship, but with a small negative slope ($r \simeq$ −0.02) which extends to very high acidities[21] or very low water activities. The same treatment of the data for the secondary alkyl acetates is shown in Figure 4. Again a linear relationship with r = 2.1 is found for each ester over almost as wide a range of acid (0–70%) followed by a change to a different linear dependence with negative slope in the high acidity region. However, the break occurs earlier, and the final negative slope is steeper (r = −0.6) for the secondary esters than for the primary. Very similar behavior to that of the

(17) N. C. Deno, J. J. Jaruszelski, and A. Schrieshein, ibid., 77, 3044 (1955).
(18) E. M. Arnett and G. W. Mach, ibid., 86, 2671 (1964).
(19) R. L. Hinman and J. Lang, ibid., 86, 3796 (1964).
(20) W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, ibid., 82, 62 (1960).
(21) At the higher acidities the fraction of total ester protonated becomes significant and the function plotted against log a_{H_2O} is actually log ($h_0{}^m/h_0{}^m$ + $K^m_{SH^+}$). Values of K_{SH^+} have been estimated from spectrophotometric measurements for methyl, n-propyl, and isopropyl acetates. Since these and the previously reported[8] value for ethyl acetate show little variation with structure and the slopes r are not sensitive to small changes in K_{SH^+} a value of K_{SH^+} = −7.2 was adopted for the other esters.
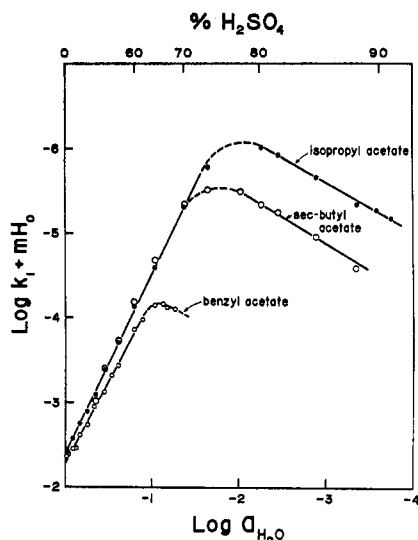
Figure 4. Log $k_i + mH_0$ vs. log a_{H_2O} for isopropyl, sec-butyl, and benzyl acetates.

secondary esters is obtained for benzyl acetate, also shown in Figure 4. The initial slope is about the same ($r = 2.0$), but the break occurs even earlier, at about 60% acid. There are insufficient data to obtain the final slope for benzyl acetate, but comparison with the curves for the secondary acetates shows this is probably very similar in its water activity dependence. Finally, the data for the three phenyl esters are plotted in Figure 5. This time the initial linear portion is shorter (0–50% acid) but again with initial slope approaching 2, followed by a fairly wide change-over region (50–70%), and finally a small negative slope ($r = -0.2$) for p-nitrophenyl acetate at higher acidities. The unsubstituted phenyl ester cannot be studied at higher acidities because of sulfonation. Thus, each ester obeys eq 2 with a large positive slope initially, which extends over a wide range of acidity. This is followed by a marked change in water acitivity dependence at some higher acidity and presumably a change in mechanism. Since the position and type of
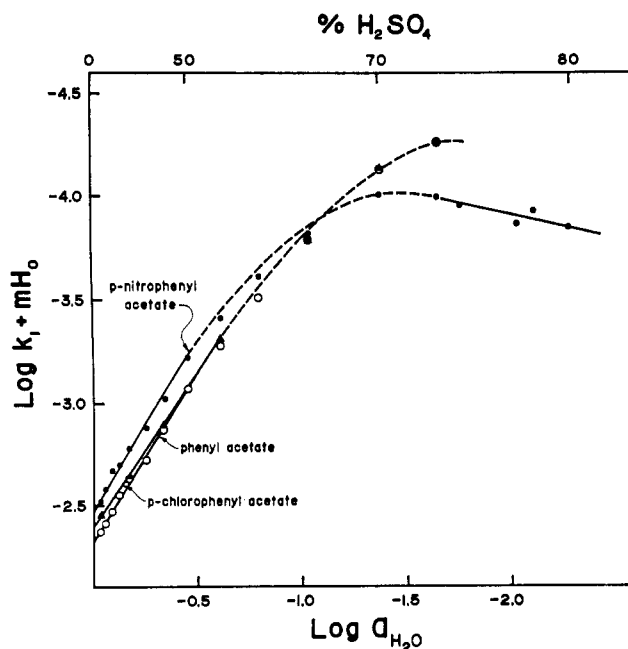

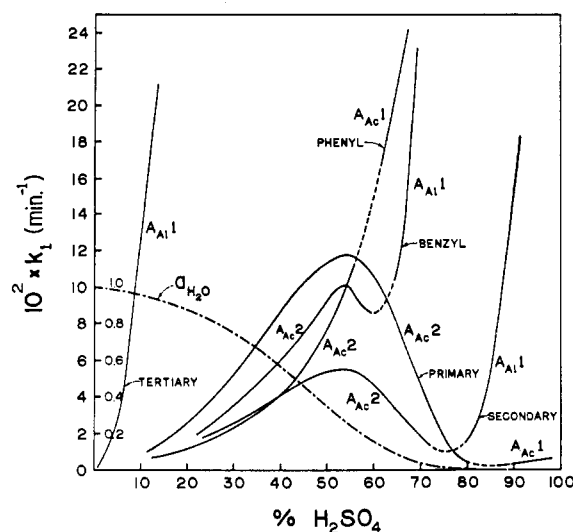Figure 5. Log $k_i + mH_0$ vs. log a_{H_2O} for phenyl, p-chlorophenyl, and p-nitrophenyl acetates.

Figure 6. Schematic representation of typical rate–acidity dependences for primary, secondary, tertiary, benzyl, and phenyl acetate hydrolyses.

change is not the same in every case, the new mechanism operating at high acidities is different for the primary alkyl and phenyl esters from that for the secondary alkyl and benzyl esters. However, the close similarity of the water activity dependence for all esters at low acidities strongly suggests that the same mechanism is operating in all cases. However, one clear exception to this kind of behavior is shown, not surprisingly, by t-butyl acetate. The limited data available for HCl solutions show that the water activity dependence for this ester is decidedly negative even in the most dilute acids. The few points available for this ester give $r \sim -1.5$.

The calculated hydration parameters are summarized in Table II. The least-squares correlation coefficients and σ_y values show that the statistical fit of the data to eq 2 is surprisingly good. This indicates strongly that

Table II. r Values for Ester Hydrolysis in Sulfuric Acid

Acetate	r value	Acid range, % H_2SO_4	c^a	$\sigma_y{}^b$	n^c	Mechanism
Methyl	1.92	0–80	0.9997	0.026	13	$A_{Ac}2$
	−0.2	>80	...	...	3	
Ethyl	2.10	0–80	0.9995	0.04	19	$A_{Ac}2$
	−0.18	>85	0.9999	0.004	5	$A_{Ac}1$
n-Propyl	2.06	0–80	0.9998	0.024	12	$A_{Ac}2$
	−0.2	>85	...	...	3	$A_{Ac}1$
Isopropyl	2.11	0–75	0.9994	0.037	11	$A_{Ac}2$
	−0.57	>80	0.998	0.024	6	$A_{Al}1$
sec-Butyl	2.18	0–70	0.9992	0.040	7	$A_{Ac}2$
	−0.66	>75	0.997	0.027	5	$A_{Al}1$
Benzyl	1.9	0–60	0.996	0.035	11	$A_{Ac}2$
	$\simeq$−0.5	>65	...	...	3	$A_{Al}1$
Phenyl	1.6	0–50	0.998	0.016	8	$A_{Ac}2$
	<0	>70	...	...	..	$A_{Ac}1$
p-Nitrophenyl	1.6	0–50	0.996	0.055	8	$A_{Ac}2$
	$\simeq$−0.2	>70	0.893	0.055	5	$A_{Ac}1$
p-Chlorophenyl	1.5	0–55	0.999	0.014	4	$A_{Ac}2$

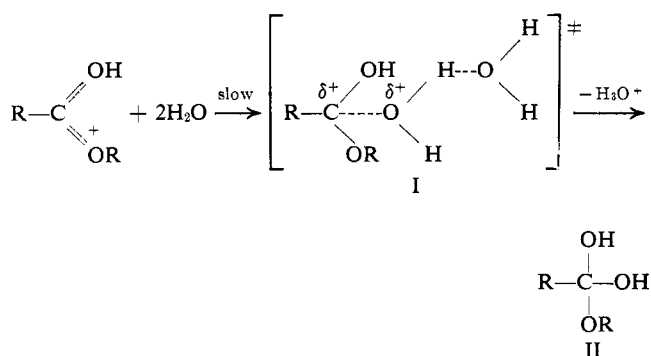^{a} Least-squares correlation coefficient. ^{b} Standard deviation on the y (log a_{H_2O}) axis. ^{c} Number of points.

the assumptions and approximations involved in the present hydration parameter treatment are reasonably valid. The concentration ranges over which linearity is obtained are also surprisingly wide, particularly since average hydration numbers for all species involved must be steadily decreasing as the water available for hydration is decreasing with acid concentration.

The values of r obtained in different acid regions can be reasonably interpreted in terms of hydrolysis mechanism as follows. Regions where $r \simeq 2$ (low acidities for all esters except t-butyl) correspond to hydrolysis by an $A_{Ac}2$ type of mechanism in which a protonated ester molecule is attacked in the rate-determining step by two water molecules, one acting as a nucleophile and the second assisting in dispersing the positive charge developing on oxygen in the transition state I as progress is made toward the tetrahedral intermediate II

$$R\text{—}C\overset{OH}{\underset{OR}{\diagdown}}{}^{+} + 2H_2O \xrightarrow{slow} \left[R\text{—}C\overset{OH}{\underset{OR}{\diagdown}}\cdots O\diagup\overset{H\cdots O}{\underset{H}{\diagdown}}{}^{H} \right]^{\ddagger} \xrightarrow{-H_3O^+}$$

I

$$R\text{—}\underset{\underset{OR}{|}}{\overset{\overset{OH}{|}}{C}}\text{—}OH$$

II

The second water molecule is then in a position to accept a proton in the formation of the intermediate II. Lane has previously suggested[8] that two water molecules are involved in the transition state for ethyl acetate hydrolysis, but possibly in a cyclic structure III rather than that shown in I, but there appears to be no compelling reason to prefer either structure. On the basis of theoretical calculations of medium effects on

$$\left[\begin{array}{c} C_2H_5 \\ | \\ O \\ CH_3\text{—}C \quad H \\ HO \diagup \quad | \\ O \quad O\text{—}H \\ \diagup \quad \diagdown \\ H \quad H \end{array} \right]^{+}$$

III
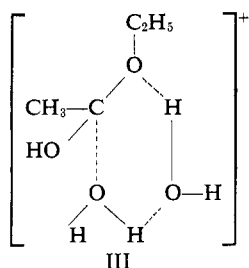
hydrolysis rates Laidler[22] has concluded that for simple esters the transition state contains a molecule of ester, a hydronium ion, and a water molecule. This is consistent with either I or III in that over-all two water molecules plus a proton plus ester are involved. However, Laidler suggests a transition-state structure which differs in detail from either of the above.
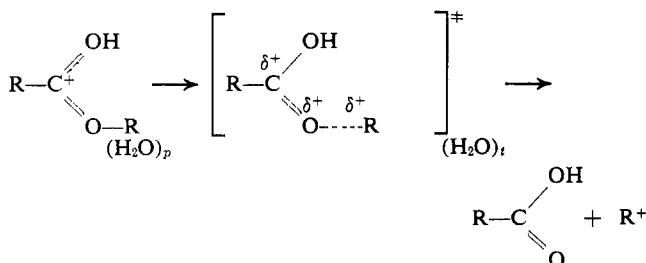
Regions where r becomes negative but is fairly close to zero (i.e., $r \simeq -0.2$) correspond to changes from the $A_{Ac}2$ to the $A_{Ac}1$ mechanism, in which ester conjugate acid undergoes unimolecular fission to acylium ion and alcohol. Water is essentially not involved in the rate-determining step, hence the water activity dependence is effectively zero.[23] This behavior occurs for the

primary alkyl and phenyl esters. Although the methyl, ethyl, n-propyl, phenyl, and p-nitrophenyl esters must all form the same acylium ion if they react via the $A_{Ac}1$ mechanism the change in water activity dependence occurs much earlier for the three phenyl esters. This is reasonable since cleavage to form acylium ion would be assisted more by the electron-withdrawing phenyl groups than by alkyl groups, so that this new mechanism can occur before the available water has been as drastically depleted as in the very high acid concentrations required before the primary alkyl acetates change mechanism. In agreement with this is the fact that at low acidities the rates of hydrolysis are in the order phenyl $>$ p-chlorophenyl $>$ p-nitrophenyl, but by about 75% acid (where $A_{Ac}1$ predominates) this order is exactly reversed. Although the data are limited, the log σ values for the phenyl esters give reasonably good linearity with σ in each of the acid ranges studied. Below 55% acid the ρ value is close to -0.2 in each of several acids, but above 70% acid it becomes $+0.5$. This change in both the sign and magnitude of ρ is consistent with a changeover from an $A_{Ac}2$ to $A_{Ac}1$ type of mechanism.

Regions where r is negative but significantly less than zero ($r \sim -0.5$) also correspond to a "unimolecular" fission of protonated ester, but by the $A_{Al}1$ mechanism. The strong negative water activity dependence indicates that water is actually being released in the rate-determining step, which is reasonable for decomposition of a strongly hydrated ester conjugate acid to give a weakly hydrated carbonium ion, especially since t-butyl acetate is known to hydrolyze $A_{Al}1$ and also has a substantial negative water activity dependence in HCl. It has already been pointed out[24] that r values obtained in very concentrated acids cannot be interpreted too quantitatively but it seems reasonable that $t < p$ for a reaction leading to a carbonium ion and a neutral molecule.

$$R\text{—}C\overset{OH}{\underset{O\text{—}R}{\diagdown}}{}^{+} \longrightarrow \left[R\text{—}C\overset{\overset{OH}{\diagup}}{\underset{O\text{----}R}{\diagdown}} \right]^{\ddagger} \longrightarrow$$

$$(H_2O)_p \qquad\qquad (H_2O)_t$$

$$R\text{—}C\overset{OH}{\underset{O}{\diagdown}} + R^+$$

This behavior is shown by the isopropyl, sec-butyl, and benzyl esters in the higher acid regions. The regions where r becomes negative for these esters are also consistent with the expected order of stability of the carbonium ions formed in $A_{Al}1$ hydrolysis, i.e., t-butyl (dilute) $>$ benzyl (65%) $>$ sec-butyl (75%) $>$ isopropyl (80%).

That the sign of r should actually change in going from an $A_{Ac}2$ to an $A_{Al}1$ or $A_{Ac}1$ mechanism is in general agreement with Whalley's[24] conclusions based on the pressure dependence of hydrolysis rates. For A2 type hydrolyses, $\Delta V^{\ddagger}$ is found to be significantly negative, whereas for A1 type hydrolyses $\Delta V^{\ddagger}$ is either zero or has a small positive value.

(22) K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, **52**, 200 (1956).
(23) That r is not actually zero probably reflects the fact that a_{H_2O} slopes in the higher acid regions cannot be interpreted as quanti-

tatively as those for lower acidities since the approximations inherent in eq 2 will be less valid at higher acidities.
(24) E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959); A. R. Osborn and E. Whalley, *Can. J. Chem.*, **39**, 1094 (1961).

The reasons for the characteristic rate–acidity profiles obtained for various types of ester can now be summarized in terms of structure, acidity, and water activity. These are shown schematically in Figure 6 for primary, secondary, tertiary, benzyl, and phenyl esters with the water activity variation of the medium superimposed. Primary alkyl esters show an initial rate increase due to protonation of an increasing fraction of substrate, until reduction of available water slows down the "bimolecular" process. Eventually the rate → 0 as a_{H_2O} → 0, until at extremely high acidities acylium ions can be formed. Despite the fact that the new mechanism does not require water, this final rate increase is modest owing to the difficulty of forming the acetylium ion. Secondary alkyl esters show an initial rate increase passing through a maximum at intermediate acidities for similar reasons. However, before a_{H_2O} → 0 and V → 0 a new mechanism can occur which does not require available water. As this carbonium ion mechanism predominantes the rate increases sharply since secondary carbonium ions are less difficult to form than acylium ions. For tertiary alkyl esters the rate rises rapidly with acidity even in the dilute acid region due to the ease of formation of tertiary carbonium ions. The benzyl ester resembles the secondary alkyl type, except that the mechanism changes from $A_{Ac}2$ to $A_{Ac}1$ earlier because of the intermediate stability of benzyl carbonium ion. The phenyl esters are somewhat unusual in showing no rate maximum at intermediate acidity, after an initial rate increase resembling those for primary and secondary esters. Since the rate continues to increase sharply even at very low values of a_{H_2O} a unimolecular mechanism must be taking over. Since phenyl carbonium ions are extremely unlikely, the new mechanism must be $A_{Ac}1$. The reason this occurs as low as 70% sulfuric acid has been discussed previously.

In conclusion it seems clear that even simple esters can hydrolyze by a variety of mechanisms and that extreme acidities are not necessary before A1 type mechanisms can occur. The present quantitative treatment of ester hydrolysis rates appears promising. It would be interesting to apply this treatment to other acid-catalyzed reactions whose detailed mechanisms are less well understood. The r values could then become established as a useful indicator of mechanism, in addition to those already available from O^{18}-exchange studies, kinetic isotope effects, and stereochemical studies, particularly since taken individually these criteria do not always allow unambiguous conclusions to be drawn.

Experimental Section

Reagents. Commercially available acetates were either distilled immediately before use or recrystallized from methanol–water. Sulfuric acids below 95% (w/w) were prepared by diluting CIL reagent grade acid (95% min) and more concentrated acids by mixing this acid with Fisher reagent fuming (30%) acid. Acid concentrations were determined by titrating weighed samples against standard base. The H_0 values of these solutions were obtained by interpolation from a graph of the data of Jorgenson and Hartter.[16]

Kinetic Methods. The method chosen for each ester depended on the ultraviolet absorption characteristics of the ester itself and the sulfuric acid solution of interest. In some cases both methods were found suitable.

For methyl, n-propyl, isopropyl, and sec-butyl acetates in sulfuric acids above 25%, and for phenyl, p-chlorophenyl, and p-nitro-

phenyl acetates in all acids, the change in ultraviolet absorption was measured using a Perkin-Elmer Model 350 spectrophotometer with either repeated scanning attachment or external recorder. The wavelength range 182–195 mμ (1-mm cells, N_2 purging) was used for the alkyl acetates and the range 260–280 mμ (1-cm cells) for the phenyl acetates. This method could not be used below 200 mμ for solutions in the low acidity range because of the background absorption due to hydrogen sulfate ion.[25] The cell compartment was thermostated at 25 ± 0.2°. Concentrations of ester used depended on solubility and extinction coefficient and were generally in the range 0.02–0.2 M for the alkyl and 10^{-3} to 10^{-4} M for the phenyl esters. Excellent linear plots of log A vs. time were obtained in all cases (correlation coefficients ≥ 0.999), and the pseudo-first-order rate constants obtained using different wavelengths near the maximum for a given ester were in good agreement. The results of a typical run using this technique are given in Table III.

Table III. Kinetic Data for the Hydrolysis of Isopropyl Acetate at 25°; Sulfuric Acid Concentration, 65.2%; Initial Ester Concentration, 0.238 M.

Time, min	A_t[a]	$A_t - A_\infty$	Log $(A_t - A_\infty)$ $+ 1$
0	1.700	1.360	1.134
2	1.594	1.254	1.098
4	1.504	1.164	1.066
6	1.398	1.058	1.024
8	1.312	0.972	0.988
10	1.268	0.928	0.968
12	1.204	0.864	0.937
14	1.150	0.810	0.909
16	1.072	0.732	0.865
18	1.016	0.676	0.830
20	0.970	0.630	0.799
22	0.932	0.592	0.772
24	0.900	0.560	0.748
26	0.868	0.528	0.723
28	0.828	0.480	0.681
30	0.790	0.450	0.653
32	0.750	0.410	0.613
34	0.720	0.380	0.580
36	0.686	0.346	0.539
90	0.370		
130	0.342		
190	0.340		
	$A_\infty = 0.340$	$k_1 = 3.69 \times 10^{-2}$ min^{-1}	

[a] Absorbance measured at 191 mμ using 1-mm cells.

For benzyl acetate, and for the alkyl acetates in acids below 25% and n-propyl acetate above 85% acid, the following modification of the method of Jaques[10] was used. Sulfuric acid (50 ml) of known concentration and ester (0.02–0.04 ml) were mixed in a reaction vessel thermostated at 25.0 ± 0.1°. At suitable time intervals, 5-ml samples were withdrawn and poured onto crushed ice. These were then neutralized, first with concentrated, then with 0.1 N sodium hydroxide to exactly pH 7. This neutral solution was made up to 100 ml with distilled water and a 20-ml aliquot added to 10 ml of 2 M hydroxylamine hydrochloride and 10 ml of 2.5 N sodium hydroxide. After 10 min, 5 ml of 5.6 N HCl was added followed by an excess of 15% ferric chloride in 0.2 N HCl. The optical density of this solution at 540 mμ was measured within 2 on a Bausch and Lomb Model 505 spectrophotometer using 10-cm cells. Accurate pH control (1.0–1.4) is required in the above procedure to prevent hydrolysis of the ferric chloride complex of the acethydroxamic acid formed from unreacted ester. This method also gave good linear plots of log (ester) vs. time from which the pseudo-first-order rate constants were obtained.

pK Determinations. The indicator behavior of methyl, n-propyl, and isopropyl acetates was investigated by measuring the zero-time extinction coefficient at 190 mμ as a function of sulfuric acid concentration. The data were treated by standard methods and for methyl acetate fitted the equation log [BH$^+$]/[B] = 0.63($-H_0$ −

(25) J. T. Edward and I. C. Wang, *Can. J. Chem.*, **43**, 2867 (1965).

Table IV

$\frac{\%}{H_2SO_4}$	$-H_0$	$\epsilon_{obsd}{}^a$	$\epsilon_{calcd}{}^b$
15.1	0.67	79	75
30.2	1.73	89	90
40.4	2.44	94	101
50.2	3.40	115	117
55.2	3.94	127	128
60.4	4.51	146	141
65.2	5.10	167	162
67.3	5.40	186	177
70.4	5.86	221	210
72.6	6.18	245	241
74.1	6.40	279	270
75.3	6.60	294	297
78.5	7.11	367	373
80.0	7.34	424	410
81.7	7.61	446	450
84.7	8.08	535	510
88.2	8.65	567	554
89.7	8.90	577	566
94.5	9.75	585	588
98.6	10.5	595	595

^{a} Zero-time extinction coefficient measured at 190 mμ. ^{b} Calculated from the equation log [BH$^+$]/[B] = 0.62($-H_0$ $-$ 7.16) with ϵ_B = 65, ϵ_{BH^+} = 598, g_B = -14.7, g_{BH^+} = 0.^{26}

7.25), and for n-propyl acetate the equation log [BH$^+$]/[B] = 0.62·($-H_0$ $-$ 7.18). A typical set of experimental data for n-propyl acetate is given in Table IV. This was treated by a previously described[26] method to obtain the best fit of the experimental points

to a calculated curve based on the equation log [BH$^+$]/[B] = m-($-H_0$ $-$ pK). The above method of obtaining m values was preferred over the more conventional logarithmic plots for two reasons. First, the log [BH$^+$]/[B] $vs.$ H_0 plots only utilize data obtained within a narrow range, usually 1.5-2.0 H_0 units either side of pK, whereas the previously described kinetic treatment using m involves data obtained over a much wider acidity range (15-98% sulfuric acid). Second, both the linearity and slopes of these log plots can be influenced by medium effects on the spectra of the base and conjugate acid forms. The present method reduces the seriousness of this possibility by correcting for medium effects. Unfortunately the rate of hydrolysis of isopropyl acetate is too high in acids above 90% to obtain reliable zero-time extinction coefficients. However, below this acidity, plots of log ϵ for isopropyl and n-propyl acetates against H_0 are strikingly similar, and it is reasonable to assume that the ionization behavior of isopropyl acetate closely resembles that of the n-propyl ester. Lane,[5] using a similar method, found the ionization behavior of ethyl acetate in sulfuric acid followed the equation log [BH$^+$]/[B] = 0.65($-H_0$ $-$ 6.93). The close similarity of the indicator slopes and "pK" values for methyl, n-propyl, and ethyl acetates indicates that the protonation behavior of acetate esters is reasonably independent of structure. For the other acetates studied no reliable protonation data could be obtained either because of too rapid hydrolysis or because sulfonation interfered at the high acidities required to measure ϵ_{BH^+}. Therefore, in cases where no indicator slope could be measured, a value of m = 0.62 was assumed, and an approximate pK of -7.2 was used to correct for fraction protonated, where necessary.[21]

(26) A. R. Katritzky, A. J. Waring, and K. Yates, *Tetrahedron*, **19**, 465 (1963).

Stable Carbonium Ions. XXXIV.[1]
The 1-Methylcyclopentyl Cation[2]

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Abstract: 1-Methyl-1-chlorocyclopentane, cyclopentylcarbinyl chloride, and cyclohexyl fluoride (chloride, bromide) in SbF$_5$–SO$_2$ solutions at $-60°$ gave a stable solution of the 1-methylcyclopentyl cation. The same ion is also formed when 1-methylcyclopentanol or cyclohexanol were dissolved in FSO$_3$H–SbF$_5$ solutions. 1-Methylcyclopentene and cyclohexene are protonated in HF–SbF$_5$–SO$_2$ or FSO$_3$H–SbF$_5$–SO$_2$ solution to the 1-methylcyclopentyl cation, which is also formed by hydride abstraction from methylcyclopentane and cyclohexane in FSO$_3$H–SbF$_5$ solution. The structure of the 1-methylcyclopentyl cation was investigated based on its nmr spectrum.

The acid-catalyzed isomerization of methylcyclopentane and cyclohexane has long been recognized and studied and has provided much useful information concerning the carbonium ion chain mechanism for hydrocarbon isomerization.[4,5] In terms of product stability, cyclohexane is favored. The equilibrium mixture at 25° consists of 77% cyclohexane and 23% methylcyclopentane.[6] In terms of carbonium ion stability, however, the tertiary methylcyclopentyl cation I should be favored over the secondary cyclohexyl cation II. No good estimate is available concerning either the relative energy differences between these two

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(5) For reviews see (a) H. Pines and N. E. Hoffman, "Friedel–Crafts and Related Reactions," Vol. II, Part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 28; (b) F. E. Condon

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