

Acid-catalyzed Hydrolyses of Bridged Bi- and Tricyclic Compounds.

II. Solvent Effects on the Hydrolysis Rates of Some 2-Norbornyl, 2-Norbornenyl and 3-Nortricycyl Acetates*

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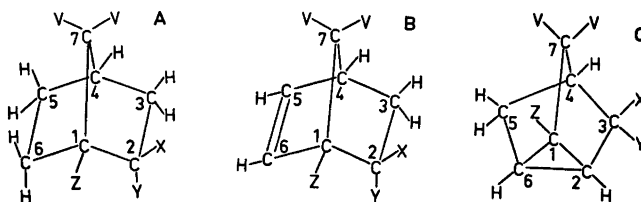
The rates of hydrolysis have been measured for some secondary and methyl-substituted tertiary 2-norbornyl, 2-norbornenyl, and 3-nortricycyl acetates in solutions of 0.25–4.0 M perchloric acid in 60 wt. % dioxane-water and in solutions of 1 M perchloric acid in 0–95.7 wt. % dioxane-water. Linear $\log k_1$ vs. $\log c_{H^+}$ and $(\log k_1 + H_0)$ vs. $(H_0 + \log c_{H^+})$ relationships for the secondary acetates and nonlinear $\log k_1$ vs. H_0 and $(\log k_1 + H_0)$ vs. $(H_0 + \log c_{H^+})$ relationships for the

tertiary acetates were found in the former solutions. The plots for $\log k_a$ vs. H_0 and for $(\log k_a + H_0)$ vs. H_0 ($k_a = k_1/c_{H^+}$) were found to be approximately linear for the tertiary acetates in the latter solutions (0–60 wt. % of dioxane). The slopes of the $(\log k + H_0)$ vs. $(H_0 + \log c_{H^+})$ plots were observed to be equal for the secondary acetates in both kinds of solutions.

* Part 2 of the abridgment of M. Lajunen's Dissertation.¹

In a recent paper² the reaction mechanism of hydrolysis for some secondary and tertiary methyl-substituted 2-norbornyl, 2-norbornenyl,

Table 1. The numbering system and symbols used in this paper for 2-norbornyl (A), 2-norbornenyl^a (B), and 3-nortricycyl (C) acetates and alcohols.



V	X	Y	Z	A	B	C
H	x ^b	H	H	<i>exo</i> -I-x	<i>exo</i> -V-x	X-x ^c
H	H	x	H	<i>endo</i> -I-x	<i>endo</i> -V-x	X-x ^c
H	x	R ^d	H	<i>exo</i> -II-x	<i>exo</i> -VI-x	XI-x ^e
H	R	x	H	<i>endo</i> -II-x	<i>endo</i> -VI-x	XI-x ^e
H	x	H	R	<i>exo</i> -III-x		<i>cis</i> -XII-x
H	H	x	R	<i>endo</i> -III-x		<i>trans</i> -XII-x
R	x	H	R	<i>exo</i> -IV-x		
R	H	x	R	<i>endo</i> -IV-x		

^a The site of the double bond between C(5) and C(6) is not indicated with a number in this paper.
^b x indicates OH or OAc. ^c Enantiomers. ^d R indicates the methyl group. ^e Enantiomers.

and 3-nortricyclyl acetates (Table 1) were dealt with. All secondary acetates were observed to hydrolyze by the $A_{AC}2$ mechanism and tertiary acetates by the $A_{AL}1$ mechanism with the exception of tertiary *endo*-2-norbornenyl acetate, which hydrolyzes simultaneously by both mechanisms in 1 M perchloric acid containing 60 wt. % of dioxane at 10–55 °C. A marked anchimeric increase in the rate was evaluated for tertiary *exo* and tricyclic acetates (the $A_{AL}i$ mechanism; *i.e.* the $A_{AL}1$ mechanism with neighboring group participation).

It is well known that in the $A_{AL}1$ hydrolysis the reaction rate in about fifty-fifty mixtures of acid dioxane-water is distinctly slower than in solutions rich in water or dioxane, but in the $A_{AC}2$ hydrolysis the rate of reaction depends only slightly on the dioxane content.^{3,4} Therefore it is possible that the hydrolysis mechanism of secondary acetates which may produce relatively stable carbocations (*e.g.* nonclassical ions)^{1,2} changes from $A_{AC}2$ to $A_{AL}1$ when the reaction medium is made richer in dioxane or water. The increasing acid concentration may have the same kind of effect owing to the fact that the rate of the $A_{AL}1$ hydrolysis increases much faster than that of the $A_{AC}2$ hydrolysis as the acid concentration becomes greater.^{5,6} The rates of hydrolysis by the $A_{AL}i$ and $A_{AL}1$ mechanisms also may depend differently on the changing reaction medium owing to the different character of the transition states. For the study of these subjects the rates of hydrolysis for several bi- and tricyclic acetates (Table 1) were measured in solutions of 0.25–4.0 M perchloric acid in 60 wt. % dioxane-water and in solutions of 1 M perchloric acid in 0–95.7 wt. % dioxane-water.

EXPERIMENTAL

The syntheses and identification of the acetates (Table 1) have been reported earlier.¹ The reaction media (the percentage, *e.g.* "60 wt. % dioxane-water", indicates the amount of dioxane in dioxane-water mixtures when perchloric acid is excluded) were prepared by weighing the components. The kinetics was studied by titrimetric and gas-chromatographic methods.¹ The results are collected in Tables 2–3.

DISCUSSION

The Zucker-Hammett hypothesis,⁸ despite criticism,⁹ has often been used to identify mechanism A-2 and A-1.^{5,10} According to the hypothesis, for the A-2 hydrolysis, in which the transition state contains water, the logarithm of the first order rate coefficient is a linear function (slope = 1) of the logarithm of the acid concentration, whereas for the A-1 hydrolysis, in which the transition state does not contain water, $\log k_1$ is linearly related (slope = -1) to the Hammett acidity function H_0 .¹¹

According to Table 2 the rates of hydrolysis of secondary acetates increase much more slowly with increasing acid concentration than those of tertiary acetates. A linear correlation exists between $\log k_1$ and $\log c_{H^+}$ in the case of the secondary acetates (the equations are obtained by the method of least squares):

$$\textit{exo-I-OAc}: \log k_1 = (1.19 \pm 0.05) \log c_{H^+} - (4.44 \pm 0.02),$$

$$\textit{exo-V-OAc}: \log k_1 \approx 1.12 \log c_{H^+} - 4.43 \quad (2 \text{ points only}),$$

$$\text{X-OAc}: \log k_1 = (1.337 \pm 0.013) \log c_{H^+} - (4.144 \pm 0.005).$$

The linearity suggests that no remarkable change in mechanism ($A_{AC}2 \rightarrow A_{AL}1$) occurs in the acid concentration range studied although perchloric acid has a greater ability, compared with hydrochloric and sulfuric acids, to increase the rate of the $A_{AL}1$ hydrolysis and a lesser ability to increase the rate of the $A_{AC}2$ hydrolysis.⁵ The hydrolysis rates of the tertiary acetates do not follow the linear correlation. Fig. 1 demonstrates that the $\log k_1$ vs. H_0 plots for secondary acetates are curves of decreasing slope and those for tertiary acetates are lines curving slightly upwards. (Within experimental error the latter plots can also be described as consisting of two straight segments (initial slopes 1.0–1.1 and final slopes 1.4–1.6) linked by a short curved portion.) Thus the rates of the tertiary acetates do not obey the Zucker-Hammett hypothesis.

Bunton *et al.*¹² reported that the rates of hydrolysis of isopropyl acetate and *endo*-2-bornyl acetate (1,7,7-trimethyl-*endo*-2-norbornyl acetate, *endo*-IV-OAc in Table 1) follow the linear $\log k_1$ vs. $\log c_{H^+}$ relationships (the slope is 1.20 for the former at 25 °C and 1.69 for the

Table 2. Rates of hydrolysis of acetates in solutions of perchloric acid in 60 wt. % dioxane-water.

Acetate	Temp./°C	$c_{\text{HClO}_4}/\text{M}$	H_0^a	$10^5 k_1/\text{s}^{-1}$	
<i>exo</i> -I-OAc	25	0.505	1.40	1.53	± 0.03
		0.993	0.75	3.84	0.08
		2.26	-0.49	10.1	0.1
		4.00	-1.84	17.8	0.2
<i>exo</i> -V-OAc	25	0.988	0.75	3.63	± 0.07
		3.23	-1.29	13.6	0.2
X-OAc	25	0.250	1.90	1.09	± 0.01
		0.501	1.40	2.88	0.02
		0.997	0.75	7.42	0.16
		1.49	0.23	12.6	0.7
		2.00	-0.26	18.1	0.2
		3.00	-1.10	30.1	0.3
Hex-II-OAc ^b	25	0.505	1.40	0.853	± 0.009
		1.002	0.75	3.64	0.06
		1.51	0.21	14.3	0.3
		1.98	-0.24	47.3	1.5
		2.51	-0.70	208	4
		2.98	-1.10	755	9
<i>exo</i> -II-OAc	10	0.258	1.90	1.76	± 0.04
		0.503	1.40	5.62	0.08
		0.753	1.05	13.2	0.2
		1.000	0.75	26.6	0.6
		1.25	0.47	59.0	1.2
		1.51	0.21	172	5
		1.59	0.12	212	7
		1.70	0.02	345	14
		1.96	-0.22	615	14
		2.11	-0.35	1070	20
		2.25	-0.48	1530	40
		2.26	-0.48	1450	20
<i>endo</i> -II-OAc	25	1.000	0.75	0.474	± 0.007
		1.50	0.22	1.66	0.06
		1.51	0.21	1.78	0.05
		1.92	-0.19	4.35	0.11
		2.48	-0.69	16.9	0.5
		3.00	-1.10	68.6	1.7
		3.49	-1.48	235	5
		4.00	-1.84	995	26
XI-OAc	10	0.502	1.40	1.44	± 0.01
		0.750	1.05	3.44	0.05
		1.002	0.75	7.86	0.06
		1.24	0.48	15.0	0.2
		1.50	0.22	27.5	0.4
		1.73	-0.01	59.7	2.0
		1.99	-0.25	166	5
		2.24	-0.47	369	5
		2.51	-0.70	760	10
		2.74	-0.91	1680	40
2.74	-0.91	1660	30		

^a Interpolated from H_0 functions at 25 °C presented by Paul and Long.⁷ ^b 1-Methylcyclohexyl acetate.

Table 3. Rates of hydrolysis of acetates in solutions of 1.00 M perchloric acid in different dioxane-water mixtures.

Acetate	Temp./°C	Wt. % of dioxane	H_0^a	$10^5 k_a / M^{-1} s^{-1}$	
<i>exo</i> -I-OAc	25	0	-0.22	4.50	± 0.07
	25	60	0.75	3.90	0.08
	55	60		50.4	0.8
	55	95.7		66.3	0.3
<i>endo</i> -I-OAc	25	0	-0.22	5.15	± 0.13
	25	60	0.75	4.70	0.06
<i>exo</i> -V-OAc	25	0	-0.22	4.16	± 0.07
	25	60	0.75	3.72	0.07
	55	60		47.8	1.2
	55	95.7		53.9	1.0
X-OAc	25	0	-0.22	9.06	± 0.25
	25	19	0.08	8.74	0.18
	25	38.6	0.40	8.60	0.20
	25	60	0.75	7.50	0.16
	25	79.9		5.93	0.16
	25	89.1		5.53	0.11
	25	95.7		6.22	0.19
Hex-II-OAc ^b	25	0	-0.22	65.7	± 1.3
	25	10	-0.06	43.1	0.8
	25	20	0.10	23.5	0.5
	25	40	0.42	9.22	0.05
	25	60	0.75	3.65	0.06
	25	79.2		3.73	0.06
	25	89.1		38.5	0.6
<i>exo</i> -II-OAc	10	0	-0.22	587	± 19
	10	10	-0.06	418	6
	10	19	0.08	213	9
	10	29	0.25	125	4
	10	38.6	0.40	82.2	2.4
	10	48.8	0.57	53.7	1.4
	10	60	0.75	26.5	0.6
	10	68.8		25.5	0.6
	10	79.2		28.1	0.4
	10	89.1		225	6
	<i>endo</i> -II-OAc	45	0	-0.22	48.2
45		10	-0.06	36.5	1.3
45		20	0.10	27.1	0.4
45		30	0.26	19.0	0.5
45		38.6	0.40	13.3	0.4
45		40	0.42	13.1	0.4
45		48.8	0.57	7.80	0.10
45		60	0.75	6.21	0.13
45		79.2		6.49	0.19
45		89.1		34.5	0.9
<i>endo</i> -VI-OAc		45	0	-0.22	11.9
	45	20	0.10	8.34	0.14
	45	40	0.42	6.33	0.15
	45	60	0.75	4.16	0.05
	45	80		3.52	0.09
	45	89.9		11.5	0.3
	45	95.7		919	6

^a Interpolated linearly from H_0 functions at 25 °C presented by Paul and Long.⁷ ^b 1-Methylcyclohexyl acetate.

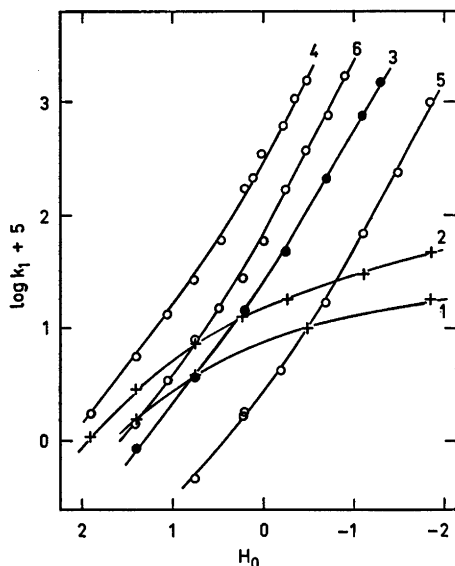


Fig. 1. Plots of $\log k_1$ for hydrolyses of acetates versus H_0 in solutions of perchloric acid in 60 wt. % dioxane-water. 1 = *exo*-I-OAc, 2 = X-OAc, 3 = Hex-II-OAc, 4 = *exo*-II-OAc, 5 = *endo*-II-OAc, and 6 = XI-OAc.

latter at 44.6 °C) and the $\log k_1$ vs. H_0 plot of tertiary butyl acetate is a curve with a slightly increasing slope (or two straight segments linked by a curved portion), whereas the latter plot of *exo*-2-bornyl acetate (1,7,7-trimethyl-*exo*-2-norbornyl acetate, *exo*-IV-OAc in Table 1) is linear (slope = -0.75) in the solutions of perchloric acid in 60 vol. % dioxane-water. They explained the curving $\log k_1$ vs. H_0 plot of tertiary butyl acetate to be an indication of a change in the mechanism ($A_{AC2} \rightarrow A_{AL1}$). The results of this work and Ref. 2, Table 5, imply that the curvature observed for the tertiary acetates cannot be attributed solely to the change of the mechanism since the activation parameters of most tertiary acetates studied were observed to be in accordance with the A_{AL1} mechanism. More probably the ratio of activity coefficients in eqn. (1) does not

$$\log k_1 = -H_0 + \log \frac{y_S y_{BH^+}}{y_{\ddagger} y_B} + \text{constant} \quad (1)$$

remain constant within the acidity scale studied.¹¹ (Symbols y_S , y_{\ddagger} , y_B , and y_{BH^+} indicate the molar activity coefficients of substrate,

transition state, indicator base, and its conjugate acid, respectively.) The same kind of slight curvature can even be seen in the hydrolysis of tertiary butyl acetate in aqueous perchloric acid.⁵ The linear relationship for *exo*-2-bornyl acetate observed by Bunton *et al.*¹² is possibly a fortuitous result of the combined effects of the concurrent A_{AL1} and A_{AC2} mechanisms, which would separately cause the $\log k_1$ vs. H_0 plots to curve upwards and downwards, respectively.

Bunnet and Olsen¹³ studied the relationships between $\log k_1$, $\log c_{H^+}$, and H_0 and found that the value of the coefficient ϕ in eqn. (2) is a better indicator of the different mechanisms of

$$\log k_1 + H_0 = \phi(H_0 + \log c_{H^+}) + \text{constant} \quad (2)$$

acid-catalyzed hydrolyses than the Zucker-Hammett hypothesis. In Fig. 2, eqn. (2) is applied to the rates of hydrolysis of secondary and tertiary acetates. The plots are linear for the secondary acetates and the slopes (ϕ values) have the following values at 25 °C: *exo*-I-OAc: 0.94 ± 0.03 , *exo*-V-OAc: ca. 0.96 (two points), and X-OAc: 0.91 ± 0.01 ($c_{H^+} \geq 1$). They are of the same order of magnitude as the ones that have been obtained for esters hydrolyzing by the A_{AC2} mechanism in aqueous acids ($0.7 \leq \phi \leq 1$).¹³ The plots of eqn. (2) for the tertiary

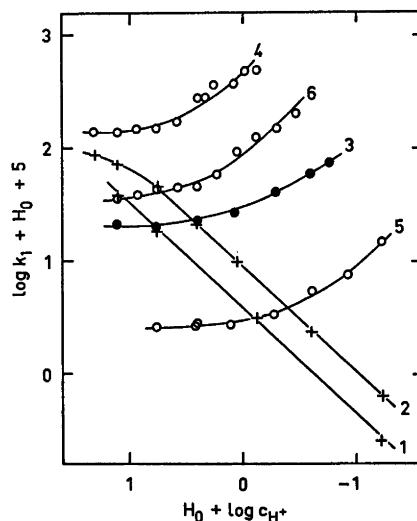


Fig. 2. Plots of $(\log k_1 + H_0)$ for hydrolyses of acetates versus $(H_0 + \log c_{H^+})$ in solutions of perchloric acid in 60 wt. % dioxane-water. The numbering system is the same as in Fig. 1.

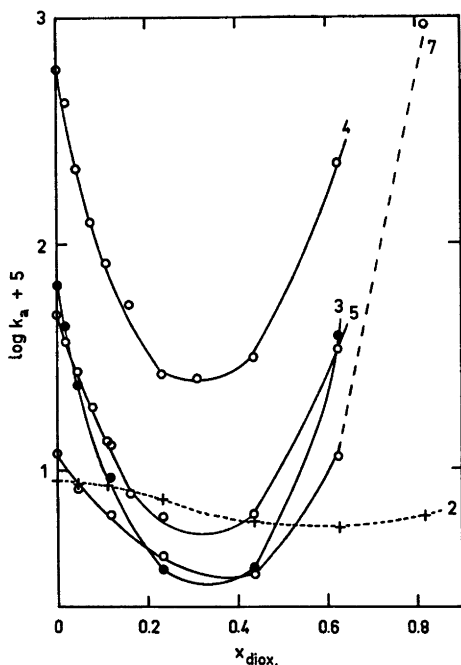


Fig. 3. Plots of $\log k_a$ for hydrolyses of acetates versus the mol fraction of dioxane (x_{diox}) in solutions of 1.00 M perchloric acid in different dioxane-water mixtures. 2 = X-OAc, 3 = Hex-II-OAc, 4 = *exo*-II-OAc, 5 = *endo*-II-OAc, and 7 = *endo*-VI-OAc.

acetates are, however, curves. The results differ from the usually linear relationships observed in aqueous acids for esters which hydrolyze by the $A_{AL}1$ mechanism and for acetals which hydrolyze by the A-1 mechanism.¹³ However, the hydrolysis of tertiary butyl acetate gives a slightly nonlinear correlation in aqueous perchloric acid.⁵

Table 3 and Fig. 3 demonstrate that the rates of hydrolysis of the secondary acetates depend only slightly on the dioxane content of the 1 M perchloric acid solution. Hence, there does not exist any remarkable $A_{AL}1$ hydrolysis of the secondary *exo* and tricyclic acetates even in water and 95.7 wt. % dioxane-water, where the rates of the tertiary acetates are relatively high. The plots of $\log k_a$ vs. mol fraction of dioxane ($k_a = k_1/c_{H^+}$) for 2-methyl-2-norbornyl acetates (*exo*- and *endo*-II-OAc) and 1-methylcyclohexyl acetate (Hex-II-OAc) are very similar, the rate minimum lying at the mol fraction ca. 0.3 (about 70 wt. % of dioxane). The curve of *exo*-2-methyl-*endo*-2-norbornenyl acetate (*endo*-VI-OAc) is, however, somewhat different from those of other acetates, which can probably be attributed to the contribution of two mechanisms of hydrolysis, i.e. $A_{AC}2$ and $A_{AL}1$.^{1,2}

The method based on the observation of the direct formation of unrearranged (by the $A_{AC}2$

Table 4. Rates and intermediate products of acid-catalyzed hydrolyses of *endo*-VI-OAc, *endo*-VI-OH, and XII-OH in solutions of 1.00 M perchloric acid in different dioxane-water mixtures.

Substrate	Temp./°C	Wt. % of dioxane	$10^6 k_a / M^{-1} s^{-1}$	Intermediate ^a products	
<i>endo</i> -VI-OAc	45	0	3.8	± 0.1	<i>endo</i> -VI-OH
	45	0	8.1	± 0.4	XII-OH (+ <i>exo</i> -VI-OH?)
	45	60	2.41	$\pm 0.06^b$	<i>endo</i> -VI-OH
	45	60	1.75	$\pm 0.11^b$	XII-OH (+ <i>exo</i> -VI-OH?)
	45	95.7	919	6	XII-OH (+ <i>exo</i> -VI-OH?)
<i>endo</i> -VI-OH	45	0	3.12	± 0.05	16 % of XII-OH
	45	60	0.403	$\pm 0.005^b$	23 % » »
	45	95.7	410	5	74 % » »
	55	60	1.74	$\pm 0.02^b$	29 % » »
	55	95.7	1670	100	ca. 65 % » »
XII-OH (<i>cis:trans</i> = 1:2)	45	0	18.2	± 0.1	
	45	60	1.49	$\pm 0.01^b$	some unknown subst.
	45	95.7	115	4	
	55	60	5.19	$\pm 0.07^b$	some unknown subst.
	55	95.7	310	8	

^a Final products are norbornanediols. ^b Ref. 2.

mechanism) and rearranged (by the $A_{AL}1$ mechanism) products from the substrate was used to determine the contributions of the mechanisms in the hydrolysis of *endo*-VI-OAc in different acid dioxane-water mixtures.^{1,2} Due to the instability of the hydrolysis products, *exo*-2-methyl-*endo*-2-norbornenol (*endo*-VI-OH) and 1-methyl-3-nortricyclanols (XII-OH, *cis* and *trans* isomers), their disappearance rates were measured in the same solutions and the iteration method^{1,2} was used for estimation of rates of formation. The results, collected in Table 4, demonstrate that the contribution of the $A_{AL}1$ mechanism is 68 % in acid water, 42 % in 60 % dioxane-water, and approximately 100 % in 95.7 % dioxane-water at 45 °C. The dependence of rates on dioxane content is thus similar to those of secondary and tertiary acetates hydrolyzing by either of these mechanisms.

According to Table 4 the rates of acid-catalyzed water addition to the homoallylic double bond of *exo*-2-methyl-*endo*-2-norbornenol (*endo*-VI-OH): $10^5 k_a/M^{-1}s^{-1}$ at 45 °C: 2.62 (aqueous acid), 0.31 (60 % dioxane), and 107 (95.7 % dioxane), and to the three-membered carbon ring of 1-methyl-3-nortricyclanols (XII-OH) depend considerably on the dioxane content of the medium. The hydration of the double bond in the simple olefins has been confirmed to follow the $A-S_E2$ mechanism, in which the addition of a proton to the double bond is the rate-determining step of the reaction.¹⁴ The similar dependence of the rates of hydration of the homoallylic double bond and the three-membered ring upon the dioxane content implies that in both cases the mechanism may be the same, possibly $A-S_E2$. Yet the $A-1$ mechanism (rapid proton exchange between the substrate and the solvent before the unimolecular rate-determining step) cannot be eliminated on this basis, since it has been observed that the dependences of the hydrolysis rates of the reactions proceeding by the $A-S_E2$ and $A-1$ mechanisms upon the dioxane content are very similar.¹⁵ Further investigations on the subject are needed.

According to the results of Harned and Ross⁴ the rate of hydrolysis of methyl acetate (the $A_{AC}2$ mechanism) in solutions of 0.1–0.2 M hydrochloric acid in dioxane-water mixtures mainly depends on the relative activity coefficient ($=1$ in acid water) of the substrate. The

plots of $\log k_a$ vs. mol fraction of dioxane for the secondary bi- and tricyclic acetates are very similar to the corresponding plot for methyl acetate. Thus the deductions of Harned and Ross can also be applied to them. The rates of hydrolysis of the tertiary acetates studied depend on the dioxane content to a so much greater extent that it cannot be explained only by the change of the activity coefficients of the substrates. The plot of the negative Hammett acidity function $-H_0$ vs. dioxane content⁷ is very similar to the plots for the tertiary acetates in Fig. 3. Thus it is natural that fairly linear correlations between $\log k_a$ and H_0 exist in solutions of 1 M perchloric acid in dioxane-water mixtures (0–60 wt. % dioxane, for which the H_0 functions at 25 °C were available⁷):

$$\begin{aligned} \text{Hex-II-OAc: } \log k_a &= -(1.31 \pm 0.03)H_0 - (3.47 \pm 0.01) \text{ at } 25^\circ\text{C}, \\ \text{exo-II-OAc: } \log k_a &= -(1.39 \pm 0.05)H_0 - (2.52 \pm 0.02) \text{ at } 10^\circ\text{C}, \\ \text{endo-II-OAc: } \log k_a &= -(0.96 \pm 0.04)H_0 - (3.50 \pm 0.02) \text{ at } 45^\circ\text{C}, \end{aligned}$$

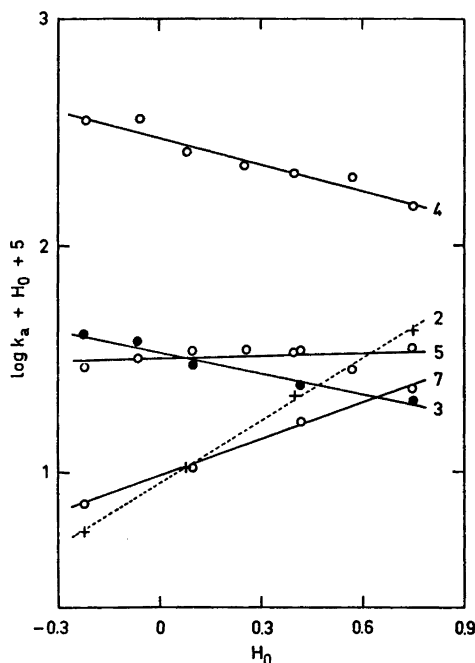


Fig. 4. Plots of $(\log k_a + H_0)$ for hydrolyses of acetates versus H_0 in solutions of 1.00 M perchloric acid in different dioxane-water mixtures. The numbering system is the same as in Fig. 3.

endo-VI-OAc: $\log k_a = -(0.46 \pm 0.02)H_0 - (4.03 \pm 0.01)$, the overall rate, and

endo-VI-OAc: $\log k_a = -0.67H_0 - 4.25$, the $A_{AL}1$ mechanism, at 45 °C.

The discrepancy between the slightly non-linear $\log k_1$ vs. H_0 correlations (0.25–4.0 M acid in 60 wt. % dioxane-water) and fairly linear $\log k_a$ vs. H_0 correlations (1 M acid in 0–60 wt. % dioxane-water) may be due to the narrow H_0 range employed in the latter measurements.

Eqn. (2) has been adapted to the rates of hydrolysis of acetates in acid 0–60 wt. % dioxane-water mixtures in Fig. 4 (in this case $\log c_{H^+} = 0$). The plots are approximately linear and the slopes (ϕ values) have the following values: X-OAc: 0.92 ± 0.02 , other secondary acetates: $0.93 - 0.96$ (two points in each; not plotted in Fig. 4), Hex-II-OAc: $-(0.31 \pm 0.03)$, *exo*-II-OAc: $-(0.39 \pm 0.05)$, *endo*-II-OAc: 0.04 ± 0.04 , and *endo*-VI-OAc: 0.54 ± 0.02 (the total rate; the $A_{AC}2$ mechanism: ca. 0.8 and the $A_{AL}1$ mechanism: ca. 0.3, two points in both of them). The slopes of eqn. (2) obtained by changing the acid concentration and the dioxane content of the medium are equal for the secondary acetates (*cf.* above). The latter slopes for the tertiary acetates are typical of the A-1 hydrolyses in aqueous acids ($-1 \leq \phi \leq 0$)¹³ with the exception of that for *exo*-2-methyl-*endo*-2-norbornenyl acetate (*endo*-VI-OAc; the value for the $A_{AL}1$ mechanism is abnormal, possibly due to the experimental errors). Distinct differences in the $\log k$ vs. H_0 and $(\log k + H_0)$ vs. $(H_0 + \log c_{H^+})$ plots between the acetates, *exo*-II-OAc and XI-OAc, which can produce the non-classical or semionclassical transition states, and the acetates, Hex-II-OAc, *endo*-II-OAc, and *endo*-VI-OAc, the transition states of which are probably classical, cannot be seen. The slopes of the plots may, however, be more negative for the former acetates (compared in Ref. 1).

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REFERENCES

1. Lajunen, M. *Kinetics and Product Analyses of the Acid-Catalyzed Hydrolyses of Some Secondary and Tertiary 2-Norbornenyl, 2-Norbornenyl, and 3-Norbornenyl Acetates*, Diss., University of Turku, 1973.
2. Lajunen, M. *Acta Chem. Scand. A* 28 (1974) 919.
3. Sadek, H. and Khalil, F. Y. Z. *Phys. Chem. (Frankfurt am Main)* a. 57 (1968) 306; b. 61 (1968) 63.
4. Harned, H. S. and Ross, A. M. *J. Amer. Chem. Soc.* 63 (1941) 1993.
5. Bunton, C. A., Crabtree, J. H. and Robinson, L. *J. Amer. Chem. Soc.* 90 (1968) 1258.
6. Salomaa, P. *Suom. Kemistilehti B* 32 (1959) 81, 145.
7. Paul, M. A. and Long, F. A. *Chem. Rev.* 57 (1957) 1, with refs.
8. Zucker, L. and Hammett, L. P. *J. Amer. Chem. Soc.* 61 (1939) 2791.
9. Bunnett, J. F. *J. Amer. Chem. Soc.* 83 (1961) 4956, with refs.
10. Euranto, E. K. In Patai, S., Ed., *The Chemistry of Carboxylic Acids and Esters*, Interscience, London 1969, pp. 549–569, with refs.
11. Long, F. A. and Paul, M. A. *Chem. Rev.* 57 (1957) 935.
12. Bunton, C. A., Khaleeluddin, K. and Whittaker, D. *J. Chem. Soc.* (1965) 3290.
13. Bunnett, J. F. and Olsen, F. P. *Can. J. Chem.* 44 (1966) 1917.
14. Kresge, A. J., Chiang, Y., Fitzgerald, P. H., McDonald, R. S. and Schmid, G. H. *J. Amer. Chem. Soc.* 93 (1971) 4907.
15. Kankaanperä, A. and Merilähti, M. *Acta Chem. Scand.* 26 (1972) 685.

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