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Acid-catalyzed hydrolysis of bridged bi- and tricyclic compounds. XXXIX—Kinetics and mechanisms of the hydration reactions of 1- and 3-acetylnortricyclanes

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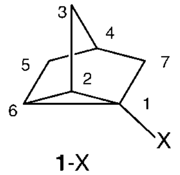
ABSTRACT: The disappearance of 1- and 3-acetylnortricyclanes (**1-Ac** and **2-Ac**) in aqueous perchloric acid was followed by capillary gas chromatography at different temperatures and acid concentrations. **1-Ac** is much less reactive than **2-Ac**. The activation parameters, solvent deuterium isotope effects and parameters of excess acidity equations were measured and the products studied. 1-Acetylnortricyclane is hydrated according to the *A*-2 mechanism, i.e. the carbonyl oxygen is protonated in the fast pre-equilibrium and one water molecule attacks at the rate-limiting stage the partially open cyclopropane ring, producing 6-acetyl-2-norborneols. 3-Acetylnortricyclane is hydrated according to the Ad_E2 mechanism, i.e. the cyclopropane ring is slowly protonated and opened, with subsequent fast attack of water producing 3-, 5- and 7-acetyl-2-norborneols. Copyright © 2002 John Wiley & Sons, Ltd.

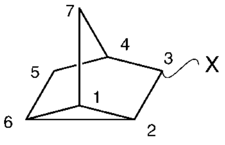
KEYWORDS: nortricyclanes; kinetics; acid catalysis; excess acidity; hydration; reaction mechanisms

INTRODUCTION

The acid-catalyzed hydrolysis of 1- and 3-acetoxynortricyclanes (**1-OAc** and **2-OAc**) was recently studied in our laboratory and the reaction mechanisms were observed to be very similar, although the former is a tertiary and the latter a secondary acetate.[1] In both cases the reaction changes from the $A_{AC}2$ ester hydrolysis,[2] dominant at lower acid concentrations, to the Ad_E2 or A-S_E2 hydration of the cyclopropane ring[3] at higher acid concentrations [dominant when $c(HClO_4)$ $\geq 6\ \mathrm{mol\ dm^{-3}}$]. The next substrates studied were 1- and 3-nortricyclanols (**1-OH** and **2-OH**), both of which react via the rate-determining protonation and subsequent opening of the cyclopropane ring (Ad_E2 mechanism), although **1-OH** is ca 1000 times more reactive than **2-OH**.[4]



1-X



2-X

X = OAc, OH, Ac *etc.*

These studied initiated our efforts to compare the acid-catalyzed hydrations of 1- and 3-substituted nortricyclanes or tricyclo[2.2.1.0^{2,6}]heptanes (**1-X** and **2-X**). The latter isomers have been objects of interest for a long time,[3,5–14] whereas the former have been less studied.[15–20] The similarity of the mechanisms and rates in the case of **1-OAc** and **2-OAc** and the similarity of the mechanisms, but the differences in rates, in the case of **1-OH** and **2-OH** inspired us to investigate tricyclic isomer pairs with different types of substituents, of which 1- and 3-acetylnortricyclanes or 1- and 3-acetyltricyclo-[2.2.1.0^{2,6}]heptanes (**1-Ac** and **2-Ac**) were studied in the present work, and in this case the isomers are hydrated in different ways.

EXPERIMENTAL

Materials. The syntheses of 1- and 3-acetylnortricyclanes (**1-Ac** and **2-Ac**) have been presented previously.[12,15] The purities by gas chromatography (GC) were 98 and 99%, respectively. The substrates were identified from their ^{13}C NMR spectra [**1-Ac** ($CDCl_3$, TMS) tentative assignments: C-1, 36.6; C-2 and C-6, 25.3; C-3 and C-5, 33.7; C-4, 27.2; C-7, 33.1; C=O, 207.2; and CH_3, 31.1; and **2-Ac**[13]] and from GC–Fourier transform (FT) IR and GC–mass spectra.

Kinetic measurements. The disappearance of the substrates in aqueous perchloric acid was followed by GC (with an FFAP capillary column) using norcamphor or nitrobenzene as the internal standard and dichloromethane as the extracting solvent. The dichloromethane

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solution ($2\,\mathrm{cm}^3$) was neutralized with one drop of concentrated aqueous ammonia. The pseudo-first-order rate constants were calculated from the slopes of the linear [r(**1-Ac**) = 0.994–0.9999 and r(**2-Ac**) = 0.999–0.9999] correlation $\log(S_t - S_\infty)$ vs t, where S_t is the ratio of the GC integrals of the substrate and the internal standard at the time t. Each rate constant was measured twice or more, the values being equal within 8% at least (average 2.5%) in the case of **1-Ac** and within 2.3% at least (average 1.2%) in the case of **2-Ac**.

pK_{SH^+} measurements. $\mathrm{p}K_{SH^+}$ was measured only for 1-acetylnortricyclane (**1-Ac**) in aqueous perchloric acid (0–11.0 M) at 293.2 K by the spectrophotometric method described earlier.[21] Exactly $0.25\,\mathrm{cm}^3$ of a 0.15 M methanolic stock solution of **1-Ac** was diluted to $25\,\mathrm{cm}^3$ with an appropriate acid solution, shaken and the UV spectrum rapidly recorded on a Perkin-Elmer Lambda 12 UV/Vis spectrometer using a solution of methanol ($0.25\,\mathrm{cm}^3$) in the corresponding acid (to $25\,\mathrm{cm}^3$) as a blank reference. Maximum absorbances $A_{\max}$ were measured and baseline corrections ($A_{320\ \mathrm{nm}}$) were made by substituting $A_{\max} - A_{320\ \mathrm{nm}}$ for $A_{\max}$ in order to reduce scatter.

Product analyses. About 0.3 g (**1-Ac**) or 0.2 g (**2-Ac**) of the substrate was stirred magnetically with $50\,\mathrm{cm}^3$ of 5 M $HClO_4$(aq.) for 70 min at ca 328 K (ca 1 $t_{1/2}$) and for 90 min at ca 348 K (ca 10 $t_{1/2}$) in the case of **1-Ac** and with the same volume of 1 M $HClO_4$(aq.) for 40 min at ca 341 K (ca 1 $t_{1/2}$) and for 4.5 h at ca 347 K (>10 $t_{1/2}$) in the case of **2-Ac** in a tightly stoppered Erlenmeyer flask. The solutions were extracted several times with CH_2Cl_2, the combined organic solutions being neutralized and dried by allowing them to flow through anhydrous K_2CO_3. The solvent was evaporated and the residues analyzed by GC and by GC–FTIR and GC–mass spectrometry.

RESULTS AND DISCUSSION

Rate constants, activation parameters and solvent isotope effects

The rate constants of the disappearance of 1- and 3-acetylnortricyclanes (**1-Ac** and **2-Ac**) in aqueous perchloric acid at different temperatures and acid concentrations and in $DClO_4(D_2O)$ are listed in Table 1. The rate constants measured for **2-Ac** are in good agreement with those[12] measured earlier under similar conditions. **1-Ac** is ca 80 times less reactive than **2-Ac** in 5 M $HClO_4$(aq.) at 318 K. The activation parameters and solvent deuterium isotope effects calculated from the second-order rate constants [$k_a = k_\psi/c(HClO_4)$] are presented in Table 2. The entropies of activation, −41 and $-12\ \mathrm{J\,K^{-1}\,mol^{-1}}$, the enthalpies of activation, 95 and $103\ \mathrm{kJ\,mol^{-1}}$, and the isotope effects, $k_H/k_D = 0.56$ and 1.35,[12] for **1-Ac** and **2-Ac**, respectively, are so different (measured under different conditions; see Table 1) that they hint at different reaction mechanisms: A-2 for **1-Ac** and Ad_E2 for **2-Ac**.[13,14,22] The reaction products (see later), 6-acetyl-2-norborneols (**3** and **4**, Scheme 1) for **1-Ac** and 7- and 3- and 5-acetyl-2-norborneols (**5**–**7**, Scheme 2) for **2-Ac**, show that the hydration of the cyclopropane ring occurs in both cases, but do not give any other useful information regarding the reaction mechanisms.

Identification of the reaction mechanisms by the excess acidity method

Identification of the two mechanisms can be made by applying the excess acidity theory,[23,24] according to which the pseudo-first-order rate constant, k_ψ, obeys the equation

$$\log k_\psi - \log[c_S/(c_S + c_{SH^+})] - \log c_{H^+} - n_w \log a_w = m^{\neq}{}_1 m^*{}_1 X_0 + \log(k_{0,1}/K_{SH^+}) \qquad (1)$$

in the case of the A-2 mechanism and the equation[1]

$$\log k_\psi - \log[c_S/(c_S + c_{SH^+})] - \log c_{H^+} = m^{\neq}{}_2 m^*{}_2 X_0 + \log k_{0,2} \qquad (2)$$

in the case of the Ad_E2 mechanism. In the latter reaction, partial protonation of the carbonyl oxygen causes a curvature of the ideally linear plot, $\log k_\psi - \log c_{H^+}$ vs X_0.[23,24] This 'protonation side reaction' is taken into account in Eqn. (2).[1] The correction term, $-\log[c_S/(c_S + c_{SH^+})]$, can be calculated with the equation[23,24]

$$\log(c_{SH^+}/c_S) - \log c_{H^+} = m^*{}_1 X_0 + \mathrm{p}K_{SH^+} \qquad (3)$$

In these equations, c_S and c_{SH^+} are the concentrations of the unprotonated and protonated (on the carbonyl oxygen) substrate in the aqueous acid with concentration c_{H^+} [$= c(HClO_4)$], excess acidity X_0[24] and water activity a_w (c_{H^+}, X_0,[23,24] and a_w[25] were corrected according to temperature; the recent molarity-based $\log a_w$ values by Cox[24] were used because of their correct standard state), and n_w is the number of water molecules in the transition state.[23,24] The slope parameters $m^{\neq}{}_1$ and $m^{\neq}{}_2$ are indicative of the transition states of the two mechanisms, A-2 and Ad_E2, and the slope parameters $m^*{}_1$ and $m^*{}_2$ depend on the site of proton attack, the carbonyl oxygen in the former and the cyclopropane ring ($m^*{}_2 = 1.80 \pm 0.10$)[24,26] in the latter case, and $k_{0,1}$ and $k_{0,2}$ are the medium-independent rate constants of the rate-limiting steps (r.l.s. in Schemes 1 and 2) of the two reactions. K_{SH^+} is the thermodynamic dissociation constant of the substrate protonated on the carbonyl oxygen.

Non-linear least-squares minimizations (NLSM) were

Table 1. Rate constants of disappearance for 1- and 3-acetylnortricyclanes (**1-Ac** and **2-Ac**) in aqueous perchloric acid at different temperatures and acid concentrations, and in $DClO_4(D_2O)$

Substrate	T (K)	$c(HClO_4)^a$ (mol dm^{-3})	X_0 ^{b}	Log a_w ^{c}	k_ψ (10^{-4} s^{-1})^d
1-Ac	318.2	4.881	1.381	1.257	0.559 ± 0.017
	318.2	5.567	1.703	1.155	0.820 ± 0.012
	318.2	5.964	1.907	1.087	0.928 ± 0.012
	318.2	6.300	2.090	1.024	1.054 ± 0.014
	318.2	6.836	2.401	0.914	1.262 ± 0.015
	318.2	7.355	2.723	0.796	1.455 ± 0.020
	318.2	7.856	3.054	0.670	1.598 ± 0.017
	318.2	8.406	3.436	0.517	1.620 ± 0.019
	318.2	8.759	3.694	0.410	1.570 ± 0.011
	318.2	9.360	4.152	0.211	1.341 ± 0.010
	318.2	9.840	4.537	0.037	1.158 ± 0.010
	318.2	10.312	4.931	−0.146	0.946 ± 0.011
	318.8	10.778	5.338	−0.339	0.753 ± 0.008
	328.2	4.848			1.66 ± 0.07
	338.2	4.824			5.07 ± 0.08
	348.2	4.792			13.2 ± 0.4
	348.2	4.792			13.3 ± 0.5^e
	338.2	4.328			3.62 ± 0.04
	338.2	4.340			6.53 ± 0.08^f
2-Ac	298.2	1.000			0.0141 ± 0.0004^e
	318.2	0.994	0.254	1.659	0.202 ± 0.004^g
	318.2	0.996	0.255	1.659	0.201 ± 0.05^e
	318.2	1.488	0.358	1.615	0.4616 ± 0.0023
	318.2	1.938	0.453	1.575	0.887 ± 0.011
	318.2	1.996	0.466	1.570	0.950 ± 0.008^g
	318.2	2.376	0.553	1.536	1.581 ± 0.025
	318.2	2.961	0.701	1.480	3.42 ± 0.07
	318.2	2.990	0.709	1.477	3.46 ± 0.03^g
	318.2	3.442	0.842	1.432	6.41 ± 0.05
	318.2	3.489	0.856	1.427	6.70 ± 0.04
	318.2	3.844	0.974	1.388	10.56 ± 0.11
	318.2	3.932	1.004	1.378	12.26 ± 0.08
	318.2	3.961	1.015	1.375	12.5 ± 0.2^g
	318.2	4.397	1.179	1.323	22.20 ± 0.27
	318.2	4.921	1.399	1.254	44.9 ± 0.8
	318.2	4.950	1.412	1.250	46.8 ± 0.5^g
	328.2	0.990			0.680 ± 0.004
	338.2	0.984			2.080 ± 0.012
	348.2	0.978			6.28 ± 0.15
	348.2	1.000			6.20 ± 0.10^e
	348.2	0.982			6.36 ± 0.12^g
	348.2	0.982			$4.71 \pm 0.12^{f,g}$
	358.2	0.972			17.08 ± 0.18

[a] Temperature corrected.
[b] Excess acidity,[24] temperature corrected.[23,24]
[c] Logarithm of water activity,[24] temperature corrected.[25]
[d] Error limits are standard deviations.
[e] Calculated from the activation parameters (Table 2).
[f] Measured in $DClO_4(D_2O)$.
[g] Ref. 12.

made according to the equation[1]

$$\log k_\psi(A\text{-}2) - \log c_{H^+} - n_w \log a_w = m^{\neq}{}_1 m^*{}_1 X_0 - \log[1 + (c_{H^+}/K_{SH^+})10^{m^*{}_1 X_0}] + \log(k_{0,1}/K_{SH^+}) \quad (4)$$

where the values of parameters $m^{\neq}{}_1$, $m^*{}_1$, pK_{SH^+} and $\log(k_{0,1}/K_{SH^+})$ for the A-2 hydration were obtained by iteration. NLSM iterations according to the equation[1,27]

$$\log k_\psi(Ad_E2) - \log c_{H^+} = m^{\neq}{}_2 m^*{}_2 X_0 - \log[1 + (c_{H^+}/K_{SH^+})10^{m_1^* X_0}] + \log k_{0,2} \quad (5)$$

were also made in order to estimate the values of parameters $m^{\neq}{}_2$ $m^*{}_2$, $m^*{}_1$, pK_{SH^+} and $\log k_{0,2}$ for the Ad_E2

Table 2. Parameters of activation at 348.2 K, solvent deuterium isotope effects at 338 or 348 K and the parameters of excess acidity equations [Eqns (4) and (5)] at 318 K for the hydrolysis of 1- and 3-acetylnortricyclanes (**1-Ac** and **2-Ac**) in $HClO_4$(aq.) (error limits are standard deviations)

Substrate	$c(HClO_4)$ (mol dm^{-3})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	k_H/k_D
1-Ac	4.79	95.3 ± 1.3	-41 ± 4	0.556 ± 0.012
2-Ac	0.978	103.0 ± 0.7[a]	-12 ± 2[a]	1.35 ± 0.06[b]

Substrate	Mechanism	m^*_1	pK_{SH^+}	$m^{\neq}$[c]	$\text{Log}(k_{0,1}/K_{SH^+})$	$\text{Log}[k_{0,2}$ (M^{-1} s^{-1})]
1-Ac	A-2 ($n_w = 1$)	0.48 ± 0.02	-2.79 ± 0.13	1.15 ± 0.07	-6.91 ± 0.06	
	A-2 ($n_w = 2$)	0.71 ± 0.03	-4.98 ± 0.18	1.10 ± 0.05	-8.45 ± 0.03	
	A-2 ($n_w = 3$)	0.97 ± 0.07	-6.92 ± 0.34	1.21 ± 0.08	-10.28 ± 0.03	
	Ad_E2[d]	0.72 ± 0.07	-2.48 ± 0.13	0.55 ± 0.08[e]		-5.67 ± 0.13
2-Ac	A-2 ($n_w = 1$)[d]	0.98 ± 0.06	-1.62 ± 0.08	2.34 ± 0.13	-6.90 ± 0.02	
	Ad_E2	0.98 ± 0.08	-1.79 ± 0.24	1.02 ± 0.11[e]		-5.13 ± 0.02

[a] M. Lajunen and M. Susi, unpublished results, 1999.

[b] Ref. 12.

[c] $m^{\neq}_1$ or $m^{\neq}_2$ depending on the mechanism.

[d] The iterations have been executed, although this mechanism is not probable.

[e] $m^{\neq}_2 = m^*_2\, m^{\neq}_2/1.80$.[24,26]

hydration. The final best values of the parameters are given in Table 2.

The iterative procedures worked almost as well when the number of water molecules in the transition state of the A-2 hydration of 1-acetylnortricyclane (**1-Ac**) was fixed to one, two or three [i.e. $n_w = 1,2$ or 3 in Eqns (1) and (4); standard deviations 0.019, 0.030 and 0.024, respectively], giving different values for the parameters (Table 2). For the slope parameter m^*_1, indicative of the site of protonation, the values obtained were 0.48, 0.71 and 0.97, of which the middle one is that most typical of the protonation of carbonyl oxygen, although the other two are not very exceptional.[14,28–30] The corresponding pK_{SH^+} values, −2.79, −4.98 and −6.92, also differ markedly from each other. The first of these is in good agreement with that (−3.27 at 298 K) for the protonation of methyl cyclopropyl ketone,[31] and where $m^*_1 \approx 1 - \Phi$ [Φ is the slope of the linear plot of $\log(c_{SH^+}/c_S) + H_0$ vs $H_0 + \log c_{H^+}$],[32] also the first value for m^*_1 (0.48) and that for methyl cyclopropyl ketone (ca 0.45) are in good agreement. The middle values of m^*_1 and pK_{SH^+} are, however, in harmony with those (0.74 and −5.33 at 318.2 K) measured recently for the A-2 hydration of 3-nortricyclanone.[14] Moreover, there is a structural similarity in 3-nortricyclanone and 1-acetylnortricyclane: both have a carbonyl group next to the cyclopropane ring, although the carbonyl group of the former ($\nu_{C=O} = 1780$ cm^{-1})[14] is much more strained than that of the latter ($\nu_{C=O} = 1705$ cm^{-1}, both in the gas phase).[33,34] The last m^*_1 and pK_{SH^+} values are evidently exceptional and thus the alternative $n_w = 3$ can be rejected. The $m^{\neq}$ values indicative of the transition state, 1.15, 1.10 and 1.21, are all fairly close to unity, typical of the A-2 mechanism.[14,23,24] Hence the kinetic excess acidity method used in this work does not alone give a reliable number of water molecules in the transition state. However, the mechanism is evidently A-2, as the parameter $m^{\neq}_2$ (0.55; Table 2) evaluated for the hypothetical Ad_E2 mechanism is too small for the relatively slow hydration and as the other kinetic parameters also disagree with this mechanism (see above).

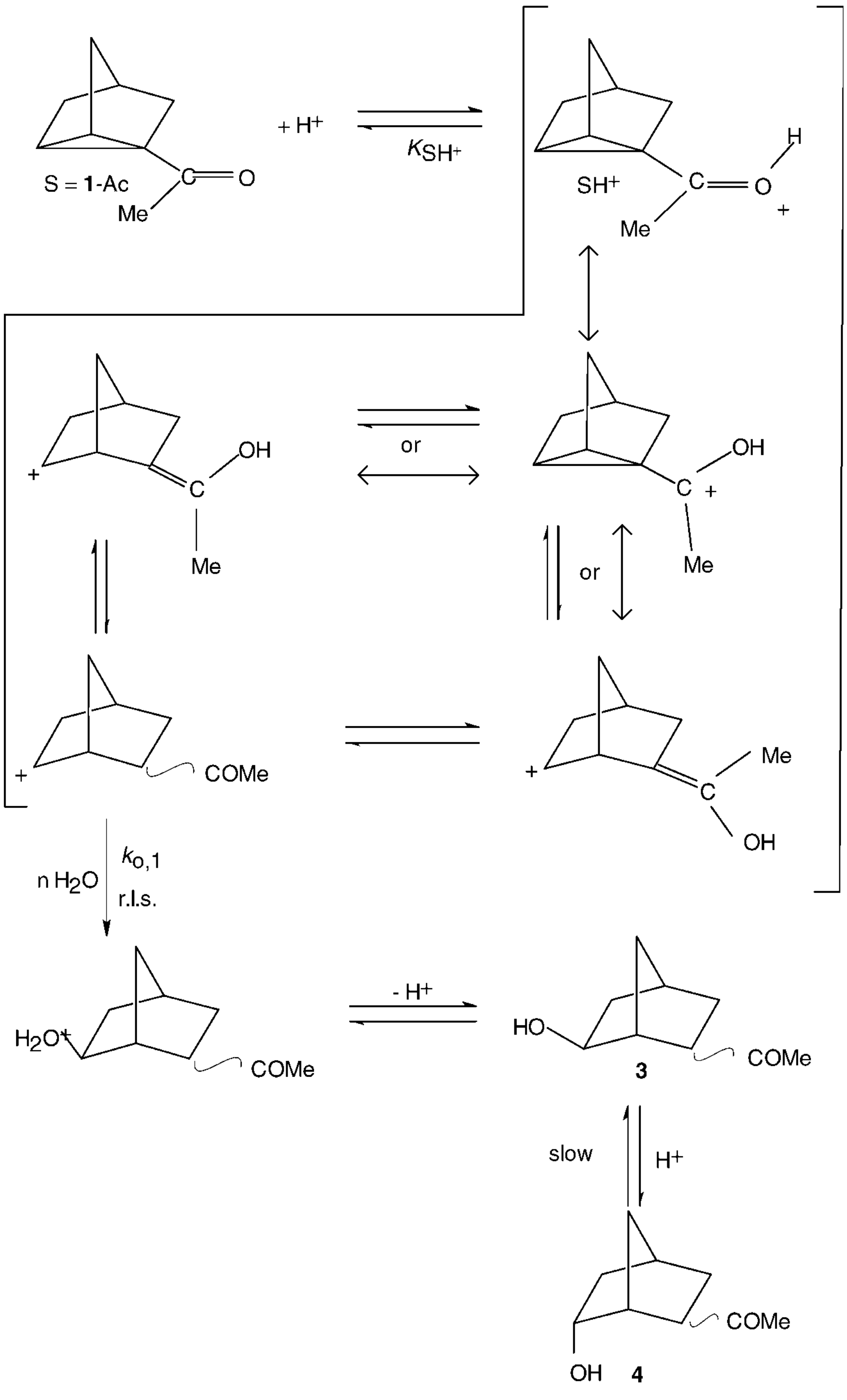
A static spectrophotometric method[21] was used to evaluate the m^*_1 and pK_{SH^+} values for **1-Ac**, owing to its slow hydrolysis. The method applies Eqns (3) and (6):

$$c_{SH^+}/c_S = (A_S - A_{max})/(A_{max} - A_{SH^+}) \qquad (6)$$

as combined to Eqn. (7)

$$A_{max} = (A_S - A_{SH^+})/[1 + (c_{H^+}/K_{SH^+})10^{m^*_1 X_0}] + A_{SH^+} \qquad (7)$$

to the UV absorbances (A_{max}) of S and SH^+ at several acid concentrations (0 to 11.3 M) at appropriate wavelengths (Fig. 1). The NLSM iterations gave the following values for the parameters: A_S (absorbance of the unprotonated substrate) = 0.189 ± 0.003, A_{SH^+} (absorbance of the protonated substrate) = 0.610 ± 0.003, $m^*_1 = 0.65 \pm 0.05$ and $pK_{SH^+} = -2.08 \pm 0.10$ at 293.2 K. The values of A_S and A_{SH^+} seem reasonable (Fig. 1), but those of m^*_1 and pK_{SH^+} are strange. However, when these are compared with the corresponding values evaluated kinetically for three A-2 mechanisms in Table 2, they are in the best agreement with those for the A-2 mechanism with one water molecule in the transition state, i.e. $n_w = 1$. The spectrophotometric values of pK_{SH^+} (ca − 1.92 as corrected to 318.2 K)[29] and m^*_1 are, however, in fair agreement with those evaluated for the Ad_E2 mechanism (Table 2). This

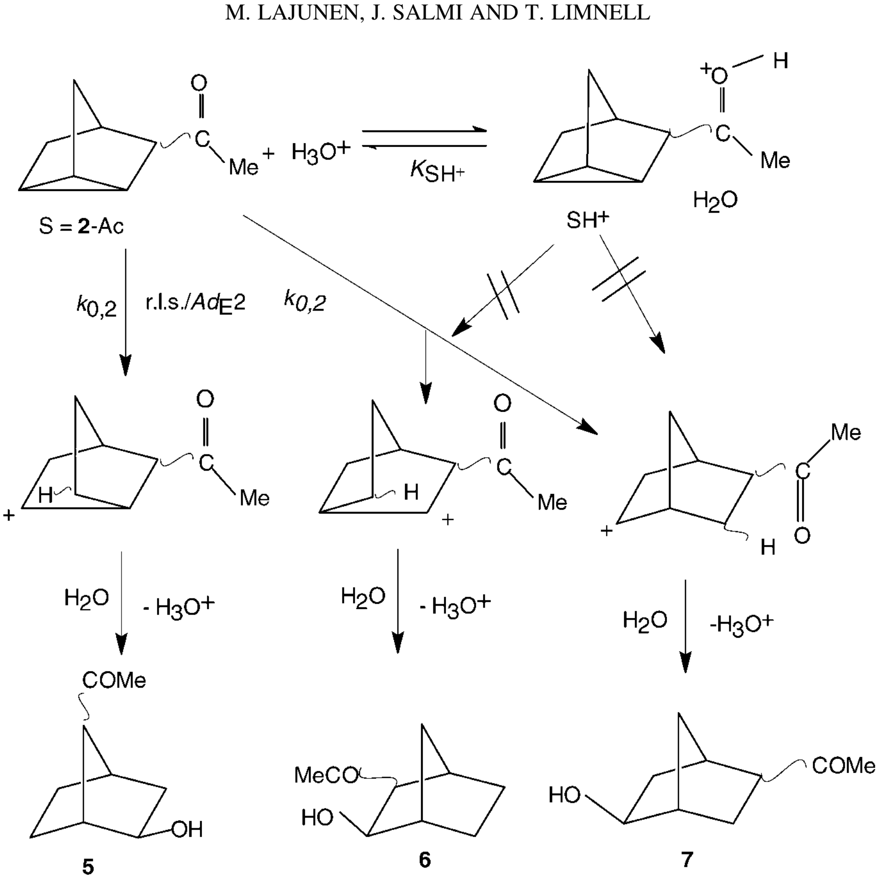


Scheme 1

mechanism is not possible according to the kinetic parameters (see above).

The iterative procedures also worked well in the hydration of 3-acetylnortricyclane (**2-Ac**), in which both mechanisms, *A*-2 and Ad_E2, were tested. The excess acidity parameters (Table 2) for the hypothetical *A*-2 mechanism do not seem normal (especially $m^{\neq} = 2.34$, which should be close to unity; see above), but those for the Ad_E2 mechanism ($m^*_1 = 0.98$, $pK_{SH^+} = -1.79$ and $m^{\neq}_2 = 1.02$), although somewhat exceptional, are in fair agreement with those ($m^*_1 = 0.79$; $pK_{SH^+} = -2.19$ and $m^{\neq}_2 = 1.02$ at 298 K) recently evaluated for the Ad_E2 hydration of 3-acetoxynortricyclane (**2-OAc**).[1] Additionally, the rate constant of disappearance for **2-Ac** as extrapolated to 1.0 M $HClO_4$(aq.) and 298.2 K is in good agreement with the rate constants of the Ad_E2 hydration (protonation) for several 3-substituted nortricyclanes (**2-X**) under similar conditions.[1]

The excess acidity plots according to Eqns (1) and (2) for the *A*-2 hydration (with one water molecule) of **1-Ac**



Scheme 2

and for the Ad_E2 hydration of **2-Ac** are presented in Figs 2 and 3 without (curved lines) and with (straight lines) ($r = 0.9997$ and 0.99995, respectively) the protonation correction term, $-\log[c_S/(c_S + c_{SH^+})]$, calculated with Eqn. (3) from the m^*_1 and pK_{SH^+} values in Table 2. The differences between the curved and straight lines show that the correction term, and hence also the protonation of the carbonyl group, are significant in both the A-2 and Ad_E2 mechanisms at the acid concentrations used in this work (Table 1).

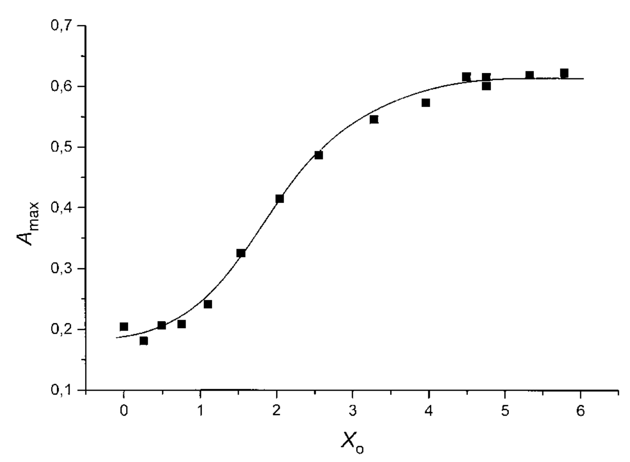


Figure 1. Excess acidity plot [Eqn. (7)] for the protonation of 1-acetylnortricyclane (**1-Ac**) in aqueous perchloric acid at 293.2 K. Maximum absorbances (A_{max}) at varyious wavelengths (238–273 nm) were measured spectrophotometrically

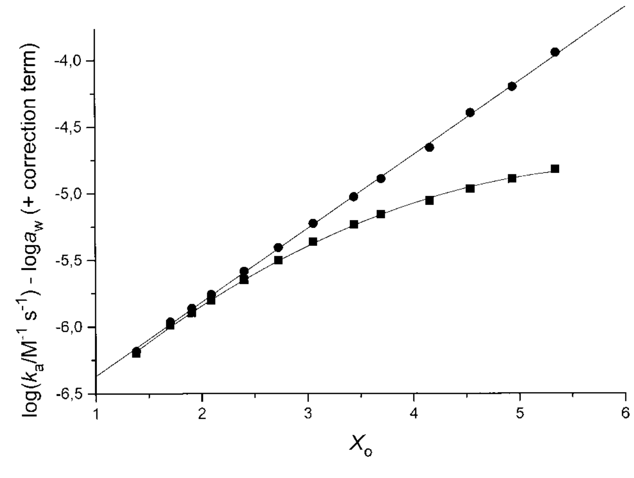


Figure 2. Excess acidity plots [Eqn. (1); $n_w = 1$] for the A-2 hydration of 1-acetylnortricyclane (**1-Ac**) in $HClO_4$(aq.) at 318.2 K: (■) without the correction term and (●) with the correction term. $k_a = k_\psi/c(HClO_4)$. The correction term, $-\log[c_S/(c_S + c_{SH^+})]$, was calculated with Eqn. (3) from the m^*_1 and pK_{SH^+} values in Table 2

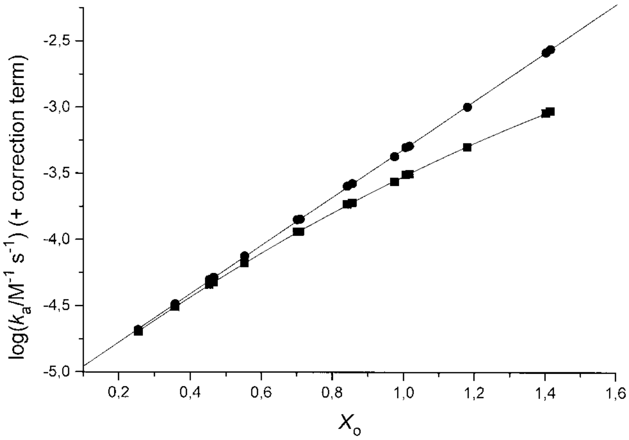


Figure 3. Excess acidity plots [Eqn. (2)] for the Ad_E2 hydration of 3-acetylnortricyclane (**2-Ac**) in $HClO_4$(aq) at 318.2 K: (■) without the correction term and (●) with the correction term. $k_a = k_\psi/c(HClO_4)$. The correction term, $-\log[c_S/(c_S + c_{SH^+})]$, was calculated with Eqn. (3) from the m^*_1 and pK_{SH^+} values in Table 2

Hydrolysis products

According to the product analyses (see Experimental), 1-acetylnortricyclane (**1-Ac**; GC retention time $t_R = 6.0$ min; $M = 136$; $\nu_{\Delta H} = 3075\ cm^{-1}$ and $\nu_{C=O} = 1705\ cm^{-1}$) yields in $HClO_4$(aq.) as main products (ca 90%) four acetyl-substituted 2-norborneols (**3** and **4**; Scheme 1), the t_Rs for the three being very similar (14.4–15.0 min), with one being clearly shorter (11.5 min). The last mentioned is probably *endo*-6-acetyl-*endo*-2-norborneol and the first three other isomeric 6-acetyl-2-norborneols ($M = 154$; $\nu_{OH} = 3654\ cm^{-1}$ and $\nu_{C=O} = 1726\ cm^{-1}$). An acetyl-2-norbornene ($\leq$5%; $t_R = 4.4$ min; $M = 136$; $\nu_{C=CH} = 3125$ and $1616\ cm^{-1}$; and $\nu_{C=O} = 1680\ cm^{-1}$) and a lactone ($\leq$5%; $t_R = 13.1$ min; $M = 138$; and $\nu_{C=O} = 1813\ cm^{-1}$; possibly *endo*-6-hydroxynorbornane-*endo*-2-carboxylic lactone) were observed as minor products (the extraction method used for the product analysis may overestimate these amounts compared with those of the very water-soluble acetylnorborneols).

3-Acetylnortricyclane (**2-Ac**; $t_R = 4.8$ min; $M = 136$; $\nu_{\Delta H} = 3079\ cm^{-1}$ and $\nu_{C=O} = 1721\ cm^{-1}$) yields in $HClO_4$ (aq.) as main products ($\geq$95%) possibly as many as eight acetyl-2-norborneols ($t_R = 11.3$–14.9 min), the identification of which was not possible. Probably these are epimeric 7-, 3- and 5-acetyl-2-norborneols (**5**–**7**; Scheme 2; the routes of formation of the products are presented as briefly as possible and can be more complicated; $M = 154$; $\nu_{OH} = 3653\ cm^{-1}$ and $\nu_{C=O} = 1721\ cm^{-1}$). An acetyl-2-norbornene ($t_R = 4.0$ min; $M = 136$; $\nu_{C=CH} = 1613\ cm^{-1}$ and $\nu_{C=O} = 1684\ cm^{-1}$) was also observed as a minor product (ca 4%) as in the case of **1-Ac** (see above), hence it may be formed by deprotonation of an acetylnorbornyl cation or by dehydration of an acetyl-2-norborneol.

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