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Kinetics and mechanism of acid-catalyzed hydration of 5-hydroxymethyl- and 5-phenoxymethylnorborn-2-enes †

Martti Lajunen * and Esa Latva-Nirva

Department of Chemistry, University of Turku, FIN-20014 Turku, Finland

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The disappearance rate constants for *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**) and *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) were measured in aqueous perchloric acid by a capillary GC method at different temperatures and acid concentrations. The rate constants, activation parameters, excess acidity plots and products (for **3** and **4** only) are in agreement with the rate-determining protonation of the double bond (Ad_E2 mechanism). No proof of *endo* protonation of the double bond *via* the protonated *endo*-5-CH_2OH group was obtained. The excess acidity plots were corrected according to the partial protonation of the hydroxylic or ether oxygen atom. In the case of **3** and **4**, the slope parameter $m^\ddagger$, indicative of the transition state, decreases slightly with increasing temperature, the intercept parameter log (k_o/M^{-1} s^{-1}) depends reasonably on the temperature, and the protonation site parameters of the hydroxymethyl group, m' and $pK_{S'H^+}$, are temperature-independent. The corresponding parameters for **5** and **6** at 303 K are normal except the peculiar $pK_{S'H^+}$ values, *ca.* −2.5.

The excess acidity theory,[1] a versatile tool for investigating acid–base equilibria and reaction rates in aqueous acids of moderate or high acid concentrations, was recently used to study the hydration of 5-methyl-*exo*- and -*endo*-5-hydroxymethylnorborn-2-enes or 5-methyl-*exo*- and *endo*-5-hydroxymethylbicyclo[2.2.1]hept-2-enes (**1** and **2**) in our laboratory.[2] The parameter $m^\ddagger$ of the excess acidity equation [eqn. (1)],

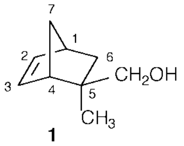
$$\log k_\psi - \log c_{H^+} - \log [c_S/(c_S + c_{S'H^+})] = m^\ddagger m^* X_o + \log k_o \quad (1)$$

derived for the Ad_E2 hydration in the case where a substituent of the substrate S is also protonated to form $S'H^+$ [eqn. (2)],[2]

$$S'H^+ + H_2O \overset{K_{S'H^+}}{\rightleftharpoons} H_3O^+ + S \rightleftharpoons \underset{TS}{[H_2O\cdots H\cdots S]^+} \longrightarrow H_2O + HS^+ \quad (2)$$

obtained somewhat strange values, *i.e.*, 1.05 to 0.90 for **1** and 0.94 to 0.77 for **2**, at different temperatures, 283 to 343 K, respectively. According to Kresge,[3,4] the slope parameter $m^\ddagger$, indicative of the character of the transition state (TS), measures the progress of proton transfer from the hydroxonium ion to the substrate in the transition state of the Ad_E2 mechanism [*i.e.* $0 \le m^\ddagger \le 1$; other parameters of eqn. (1) are explained below]. Thus the $m^\ddagger$ values for the *exo* epimer (**1**) were slightly greater than the upper limit value at the lowest temperature and, in addition, steadily slightly greater than the more normal values for the *endo* epimer (**2**). The decrease of $m^\ddagger$ with increasing temperature was also against our presumption.[5]

Possible reasons for this were considered.[2] The experimental scatter may cause exceptional values, but does not evidently explain the steady variation of $m^\ddagger$ with temperature. The derivation of eqn. (1) was based on the assumption that the substrate **1** or **2** protonated on the hydroxy oxygen [$S'H^+$ in eqn. (2)] did not react in any way. This is probable in the case of the *endo* epimer, in which the Ad_E2 protonation occurs on an olefinic carbon atom, C-2 or C-3, close to the substituent, the hydroxymethyl group. In the case of the *exo* epimer, the reaction center is, however, far from the substituent, thus the formation of two positive charges is more reasonable. The third possible reason is an exceptional *endo* protonation[6] of an olefinic carbon atom *via* the protonated *endo*-5-hydroxymethyl group (Scheme 1).



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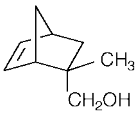

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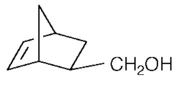

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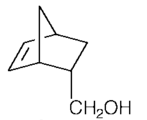

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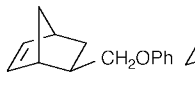

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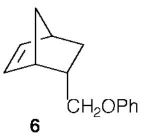

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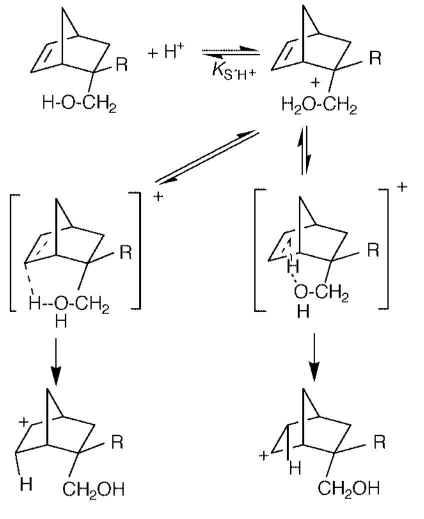
A choice between the three alternatives could not be made,[2] but instead new substrates, *exo*- and *endo*-5-hydroxymethyl-



Scheme 1

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† The IUPAC name for norborn-2-ene is bicyclo[2.2.1]hept-2-ene.

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norborn-2-enes (**3** and **4**) and *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) were synthesized and their rates of disappearance measured in $HClO_4$(aq) at different temperatures and acid concentrations in order to obtain additional experimental data with substrates whose substituents (CH_2OH and CH_2OPh) were assumed to differ significantly in both basicity and size.[2,7,8] The results are presented in this paper.

Experimental

Materials

A commercial mixture (100 g; *exo*:*endo* = 20:80; purity 96%) of norborn-5-ene-2-carbaldehyde from EGA-Chemie was changed to a 54:46 mixture (12.8 g; purity 94%) by distillation in a vacuum (4 mmHg) through an efficient column and the latter reduced by $LiAlH_4$ in anhydrous ether to the corresponding mixture of *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**; 12.1 g; yield 92%).[9] The product was purified by distillation (89.5–90.5 °C/10 mmHg), but no attempt was made to separate the epimers. The purity by GC was 97% and the *exo*:*endo* ratio 53:47.

A mixture of *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) was prepared by the Diels–Alder reaction between 24.1 g (0.18 mol) of allyl phenyl ether[8] and 12.6 g (0.19 mol) of monomerized cyclopentadiene by refluxing in 30 cm^3 of xylene.[10] The reaction was not completed in 22 h, when the solvent and other low-boiling components were distilled off. The residue was distilled through a Vigreux column (*ca.* 101 °C/10 mmHg). The yield was 46%, the purity by GC 98% and the *exo*:*endo* ratio 17:83. The substrates **3**–**6** were identified from their ^1H and ^{13}C NMR,[11] GC-FTIR and/or GC-mass spectra.

Kinetic measurements

The disappearance of the epimers (**3** and **4** or **5** and **6** simultaneously) in $HClO_4$(aq) was followed for *ca.* 3 half-lives by GC (an FFAP capillary column) using nitrobenzene as the internal standard.[2] The initial concentrations of the substrates were *ca.* 6 mM in the case of **3** and **4** and *ca.* 0.2 mM in the case of **5** and **6**. The samples (3 cm^3) of the reaction solution (50 cm^3) were extracted with dichloromethane (2 cm^3) and the CH_2Cl_2 aliquots were neutralized by one drop of concentrated aqueous ammonia. The pseudo-first-order rate constants were calculated from the slopes of the linear correlation ln S_t *vs.* t ($S_\infty = 0$), in which S_t is the ratio of the GC integrals of the substrate and the internal standard at the time t. The plots were strictly linear (r = 0.9993–0.999 99) in the case of **3** and **4**, but at worst only tolerably linear (r = 0.97–0.9996) in the case of **5** and **6**, probably due to their poor solubility in $HClO_4$(aq) and to the small difference between the retention times of the epimers. Each rate constant was measured twice or more in the case of **3** and **4**, their values being equal within 4% at least (av. 1%), and three or more times in the case of **5** and **6**, their values being equal within 22% at least (av. 8%).

Product analysis

Only the hydrolysis products of the 53:47 mixture of *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**) were studied, because the solubility of 5-phenoxymethylnorborn-2-enes (**5** and **6**) was very poor. *ca.* 0.3 g of the substrate mixture was stirred magnetically with 50 cm^3 of 4.4 M $HClO_4$(aq) in a tightly stoppered erlenmeyer bottle at room temperature for 0.5 h (*ca.* 1 $t_{\frac{1}{2}}$) or 4.5 h (*ca.* 10 $t_{\frac{1}{2}}$ for **4**). The reaction solution was extracted with CH_2Cl_2 several times, and the organic phase neutralized and dried by letting it flow through anhydrous K_2CO_3. The solvent was distilled off almost completely and the homogeneous residue analyzed by GC, GC-FTIR and GC-MS, the components being mostly identified by comparing their retention times and spectra with authentic products.

Results and discussion

Rate constants of disappearance for *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**) and *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) in aqueous perchloric acid at different temperatures and acid concentrations are listed in Table 1. The rate constants measured under similar conditions are generally close to each other and also close to those for 5-methyl-*exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**1** and **2**).[2] The activation parameters were calculated from the second-order rate constants ($k_a = k_\psi/c_{H^+}$) for substrates **3** and **4** at different acid concentrations. The entropies of activation decreased regularly from −10 to −20 J K^{-1} mol^{-1} and from −14 to −22 J K^{-1} mol^{-1}, respectively, when the acid concentration increased from 2.0 to 5.5 mol dm^{-3}, and the enthalpies of activation correspondingly decreased from 97 to 84 kJ mol^{-1} and from 96 to 85 kJ mol^{-1} (all values at 298 K). The values are typical of the rate-determining protonation of the carbon double bond (Ad_E2 mechanism).[12]

The activation parameters calculated for the disappearance of **5** and **6** in 3.9 M $HClO_4$(aq), $\Delta S^\ddagger = -68 \pm 11$ and -46 ± 10 J K^{-1} mol^{-1} and $\Delta H^\ddagger = 75 \pm 4$ and 82 ± 3 kJ mol^{-1}, respectively, at 298 K are slightly exceptional, when compared to those for **3** and **4**, and may hint at an *A*-2 hydrolysis of the ether linkage. The disappearance rate constants for **5** and **6** are, however, very much (10^8 times) greater than that for the *A*-2-(carbocation) hydrolysis of propyl phenyl ether and even 10^5 times greater than that for the *A*-1 hydrolysis of isopropyl phenyl ether as extrapolated to 3.9 M $HClO_4$ at 303.2 K.[8,13] Thus, the exceptional activation parameters, which are also rather different from those measured for the hydrolysis of primary alkyl phenyl ethers,[8] are possibly caused by the different solvation of **5** and **6**, as compared to **3** and **4**, in aqueous acids (see later), as well as by the inaccurate rate constants for **5** and **6** (see Experimental section).

It is possible to estimate the Ad_E2 hydration rate constants for substrates **3**–**6** on the basis of the values measured for several *exo*- and *endo*-5-X-substituted norborn-2-enes.[14,15] The logarithms of the rate constants, as extrapolated to 1.00 M $HClO_4$ at 298 K, obey fairly (Fig. 1) the substituent constants σ_I^q.[16] The substituent constant for CH_2OPh is not known, but can be estimated from the value for Ph with the linear correlation (r = 0.9997) between σ_I^q (CH_2OX) and σ_I^q (X), when X = H, CH_3 and $COCH_3$.[16] The log (k_ψ/s^{-1}) values for substrates **3**–**6** [σ_I^q (CH_2OPh) = 0.77], also presented in Fig. 1, are in good agreement with the other data, which indicates that the disappearance reaction dominantly occurs *via* rate-determining protonation of the double bond in all four cases.

The reaction products of *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**; Scheme 2), *i.e.* 3-oxatricyclo-[4.2.1.0^{2,5}]nonane (**7**); possibly even four diols, probably *exo*- and *endo*-6-hydroxymethyl-*exo*-norbornane-2-ols (**8**; minor diols) and/or *exo*- and *endo*-5-hydroxymethyl-*exo*-norbornane-2-ols (**9**; major diols); norbornane-2-carbaldehyde (**10**); and its oxidation product, norbornane-2-carboxylic acid (**11**), accord with the Ad_E2 mechanism, in which the proton attacks on both olefinic carbon atoms, C-2 and C-3, compete.[9,17]

The excess acidity theory[1] was used to examine the dependence of the pseudo-first-order rate constant, k_ψ, upon the acid concentration at three temperatures (283, 303 and 323 K) in the case of *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**) and at one temperature (303 K) in the case of *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) in the form of the nonlinear equation [eqn. (3)].

$$\log k_\psi - \log c_{H^+} = m^\ddagger m^* X_o - \log[1 + (c_{H^+}/K_{S'H^+})10^{m'X_o}] + \log k_o \quad (3)$$

This equation can be derived from the linear equation [eqn. (1)] by the aid of eqn. (4).

Table 1 Rate constants of disappearance for *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**) and *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) in aqueous perchloric acid at different temperatures and acid concentrations

			$k_\psi/10^{-5}$ s^{-1} [c]			
T/K	$c(HClO_4)$/ mol dm^{-3} [a]	X_o [b]	**3**	**4**	**5**	**6**
283.2	2.47	0.642	0.969 ± 0.003	0.775 ± 0.016		
	2.97	0.780	1.985 ± 0.011	1.519 ± 0.009		
	3.49	0.949	4.182 ± 0.011	3.080 ± 0.011		
	3.98	1.128	8.592 ± 0.024	6.071 ± 0.022		
	4.44	1.312	17.57 ± 0.06	12.01 ± 0.07		
	4.96	1.548	38.07 ± 0.12	24.78 ± 0.13		
	5.47	1.805	84.62 ± 0.26	53.01 ± 0.22		
	6.21	2.215	310 ± 6	183 ± 3		
293.2	3.97				24.1 ± 2.8	20.5 ± 1.3
303.2	1.99	0.488	7.956 ± 0.019	6.478 ± 0.020		
	2.45	0.600	15.01 ± 0.11	11.77 ± 0.11	15.4 ± 3.4	12.4 ± 0.8
	2.95	0.729	29.15 ± 0.11	22.12 ± 0.11	26.4 ± 1.3	24.1 ± 1.5
	3.46	0.887	57.5 ± 0.4	42.0 ± 0.5	46.3 ± 3.6	41.6 ± 1.4
	3.94	1.053	114.7 ± 1.6	81.2 ± 1.7	80.5 ± 3.1	71.5 ± 1.8
	4.40	1.225	217.9 ± 0.8	148.2 ± 1.1	151 ± 5	148 ± 5
	4.91	1.446	462 ± 3	306 ± 3	238 ± 17	246 ± 9
	5.41	1.686	951 ± 7	605 ± 5	485 ± 33	411 ± 18
	6.14	2.069			950 ± 40	763 ± 26
313.2	3.93	1.020			204 ± 25	211 ± 12
323.2	0.492	0.134	6.73 ± 0.03	5.97 ± 0.03		
	0.995	0.253	20.33 ± 0.10	17.43 ± 0.09		
	1.433	0.346	41.30 ± 0.13	34.51 ± 0.11		
	1.97	0.457	89.9 ± 0.8	72.3 ± 0.7		
	2.43	0.563	162.6 ± 0.6	126.3 ± 0.6		
	2.92	0.683	299.6 ± 0.9	226.0 ± 0.9		
	3.42	0.832	577 ± 8	420 ± 5		
	3.90	0.988	1027 ± 5	725 ± 5	465 ± 17	504 ± 45

[a] Temperature corrected. [b] Excess acidity,[18] temperature corrected.[1] [c] Error limits are standard deviations.

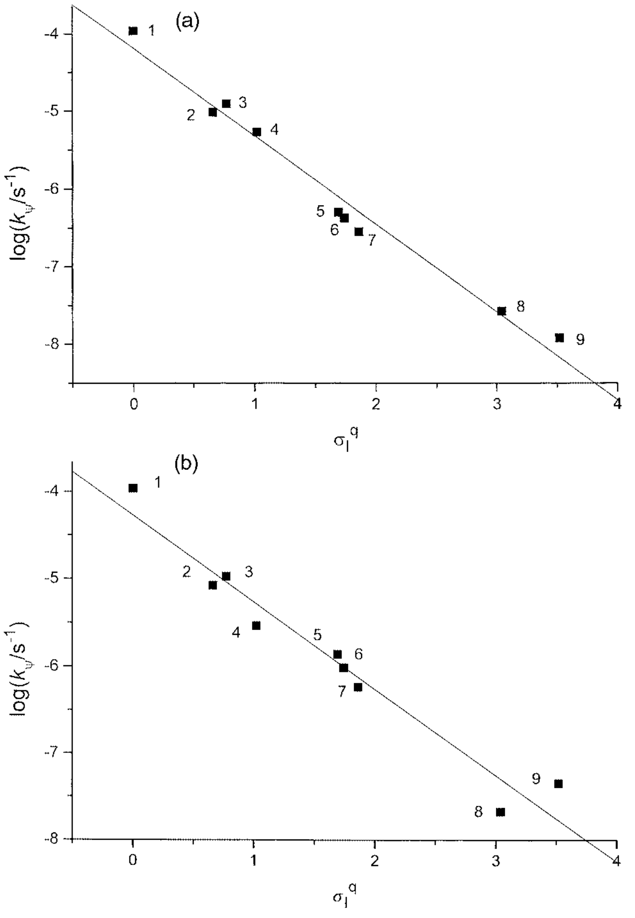
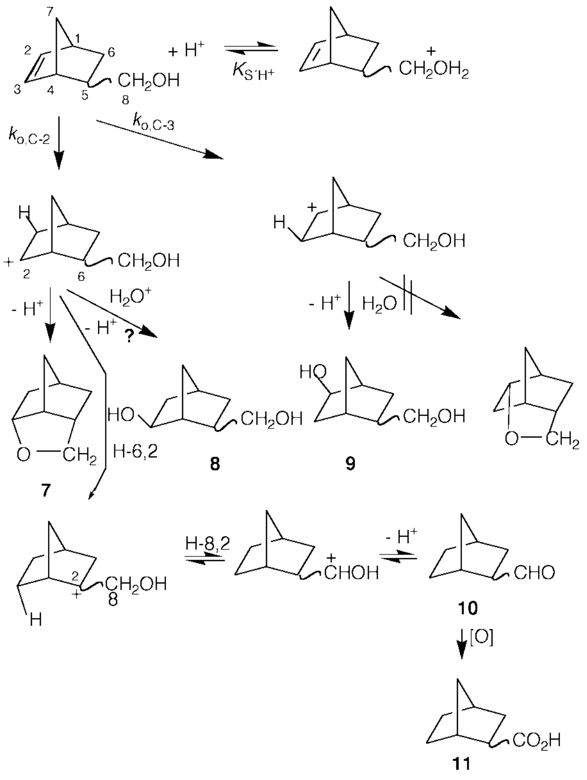


Fig. 1 Logarithms of the rate constants for protonation of the carbon double bond of *exo*-5- (a) and *endo*-5- (b) substituted norborn-2-enes in 1.00 M $HClO_4(aq)$ at 298 K *vs.* substituent constant σ_I^q.[16] Symbols: 1, H; 2, CH_2OH; 3, CH_2OPh; 4, CH_2Cl; 5, $COCH_3$; 6, OH; 7, OCH_3; 8, CN; and 9, NO_2.



Scheme 2

$$\log(c_{S'H^+}/c_S) - \log c_{H^+} = m'X_o + pK_{S'H^+} \qquad (4)$$

In the equations, X_o is the excess acidity[18] of the aqueous acid with a concentration c_{H^+} [= $c(HClO_4)$; c_{H^+} and X_o are corrected according to temperature];[1] $m^\ddagger$ is the slope parameter indicative of the transition state (in this case the measure of the progress of proton transfer; see above); m^* and m' are slope

Table 2 Parameters of the excess acidity equation [eqn. (3)] for the hydration of *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**) and of *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) in $HClO_4$(aq.) (Error limits are standard deviations.)

Substrate	T/K	m'	$pK_{S'H^+}$	$m^{\ddagger a}$	$\log (k_o/M^{-1}\ s^{-1})$
3	283.2	0.96 ± 0.02	−2.03 ± 0.13	1.02 ± 0.02	−6.56 ± 0.04
	303.2	0.95 ± 0.04	−2.01 ± 0.13	0.98 ± 0.05	−5.25 ± 0.05
	323.2	1.11 ± 0.05	−2.01 ± 0.10	0.96 ± 0.02	−4.105 ± 0.008
4	283.2	0.95 ± 0.05	−1.91 ± 0.09	1.00 ± 0.03	−6.62 ± 0.04
	303.2	0.93 ± 0.04	−1.98 ± 0.23	0.93 ± 0.06	−5.25 ± 0.06
	323.2	1.03 ± 0.05	−1.91 ± 0.14	0.89 ± 0.02	−4.145 ± 0.12
5	303.2	0.98 ± 0.04	−2.43 ± 0.18	0.73 ± 0.04	−4.99 ± 0.05
6	303.2	1.06 ± 0.05	−2.48 ± 0.21	0.75 ± 0.05	−5.06 ± 0.07

[a] $m^{\ddagger} = a_A = m^{\ddagger}m^*/1.80$; the divisor (1.80 ± 0.10)[18] is set to be exact in estimation of the error limits.

parameters dependent on the site of proton attack, an olefinic carbon atom in the former case ($m^* = 1.80 \pm 0.10$)[18] and the hydroxylic or ether oxygen in the latter; while k_o stands for the medium-independent rate constant of the rate-determining step of the reaction and $K_{S'H^+}$ for the thermodynamic dissociation constant of the substrate protonated on the hydroxylic or ether oxygen (Scheme 2).

The excess acidity parameters $m^{\ddagger}m^*$, m', $pK_{S'H^+}$ and $\log k_o$ were evaluated from the experimental values of k_ψ, c_{H^+} and X_o with the method of a nonlinear least-squares minimization (iteration) starting from the estimated values of the parameters. The iterated final parameters are shown in Table 2 and, in the main, seem reasonable.

The value of m' (av. 0.99 ± 0.07) evaluated for the protonation of the hydroxymethyl substituent of **3** and **4** is typical for the protonation of hydroxylic oxygen in aqueous perchloric acid,[2] being independent of temperature, as it should be.[5] The corresponding parameter (av. 1.02 ± 0.04) for the protonation of the phenoxymethyl substituent of **5** and **6** is also in agreement with the values (av. 1.01 ± 0.03) measured for the protonation of several ether oxygen atoms.[8,13,15,19–21]

The $pK_{S'H^+}$ values (av. −1.98 ± 0.06) for **3** and **4** are typical for the protonation of hydroxylic oxygen, being independent of temperature in accordance with the earlier measurements.[2,22,23] In many protonation reactions, however, the pK_a value is temperature-dependent.[5] One reason for the present, and the earlier exceptional cases, may be the proton transfer between the rather similar hydroxylic oxygens ($H_3O^+ + ROH \rightleftharpoons H_2O + ROH_2^+$). The $pK_{S'H^+}$ value (av. −2.45 ± 0.21) for **5** and **6** is odd, because much more negative values (−5 to −7)[7,8,13,20,21] have generally been measured for primary and secondary alkyl phenyl ethers and similar values (−1.9 to −3.7)[7,20,21] have been observed where the alkyl group of secondary or tertiary alkyl phenyl ethers is able to form a thermodynamically stable carbocation. Thus, the observed $pK_{S'H^+}$ values for **5** and **6** may be erroneous due to the poor solubility of the substrates in $HClO_4$(aq).

The slope parameters $m^{\ddagger}$ or a_A ("excess acidity a"; Table 2), which indicate the progress of proton transfer ($0 \le a_A \le 1$) in the transition state of the Ad_E2 reaction,[3,4] are very similar to those measured for 5-methyl-*exo*- and -*endo*-5-hydroxymethylnorborn-2-enes (**1** and **2**),[2] *i.e.* exceptionally high at the lowest temperatures used for kinetic measurements, slightly higher for the *exo* than for the *endo* epimer and slightly dependent on temperature (see above). Evidently, the Ad_E2 mechanism is the only one, where the A-1, A-2 and Ad_E2 mechanisms are included, in which the slope parameter $m^{\ddagger}$ depends on temperature,[2,5,13,24] provided that the slope parameter m^* (1.80 ± 0.10)[18] is really temperature-independent. The corresponding $m^{\ddagger}$ values (av. 0.74 ± 0.05) for **5** and **6** seem more normal than those for **1**–**4**.[25]

The intercept parameters ($\log k_o$) for **3** and **4** obey well the Arrhenius equation, *i.e.* $\log (k_o/M^{-1}\ s^{-1})$ *vs.* T^{-1} is linear ($r = -0.999\ 98$ and -0.9996, respectively) giving the following activation parameters: $\Delta S^{\ddagger} = +14 \pm 5$ and $+16 \pm 4$ J K^{-1} mol^{-1} and $\Delta H^{\ddagger} = 109.1 \pm 1.6$ and 110.2 ± 1.2 kJ mol^{-1}, respectively, at 298 K. The parameters are in agreement with the increasing trend of the entropy and enthalpy of activation with decreasing acid concentration (see above), whereas the positive entropies of activation are less typical of the Ad_E2 mechanism.[12,14,15]

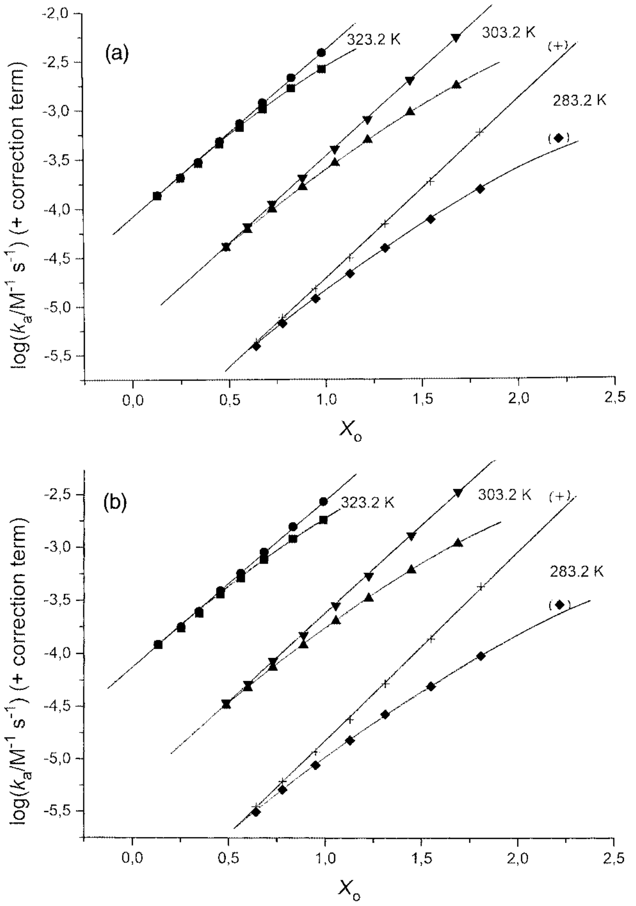


Fig. 2 Excess acidity plots for the hydration of *exo*-5- (a) and *endo*-5- (b) hydroxymethylnorborn-2-enes (**3** and **4**) at different temperatures in $HClO_4$(aq) ($k_a = k_\psi/c_{H^+}$). The straight lines obey eqn. (1) as such whereas for the curved lines the correction term is eliminated. The correction term, $-\log [c_S/(c_S + c_{S'H^+})]$, has been calculated from eqn. (4) with the m' and $pK_{S'H^+}$ values in Table 2.

If eqn. (3) is reverted back to the linear form [eqn. (1)], in which the correction term, $-\log [c_S/(c_S + c_{S'H^+})]$, is calculated with eqn. (4) from the m' and $pK_{S'H^+}$ values in Table 2, the plots (Figs. 2 and 3) are strictly linear ($r = 0.9997$–$0.999\ 94$). They deviate markedly from the nonlinear $\log (k_a/M^{-1}\ s^{-1})$ *vs.* X_o plots showing that the rate-reducing effect of the partial protonation of the hydroxy and ether oxygen atoms is significant at the higher acid concentrations used.

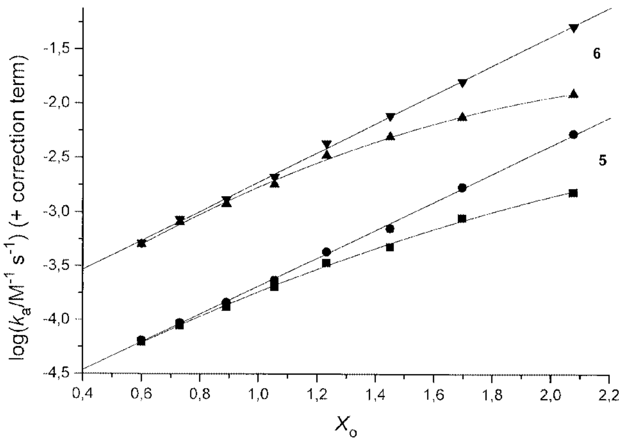


Fig. 3 Excess acidity plots for the hydration of *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) at 303.2 K in $HClO_4$(aq) ($k_a = k_\psi/c_{H^+}$; 1.0 has been added to the log k_a values of **6**, for clarity). The straight lines obey eqn. (1) as such whereas for the curved lines the correction term is eliminated. The correction term $-\log\ [c_S/(c_S + c_{S'H^+})]$, has been calculated from eqn. (4) with the m' and $pK_{S'H^+}$ values in Table 2.

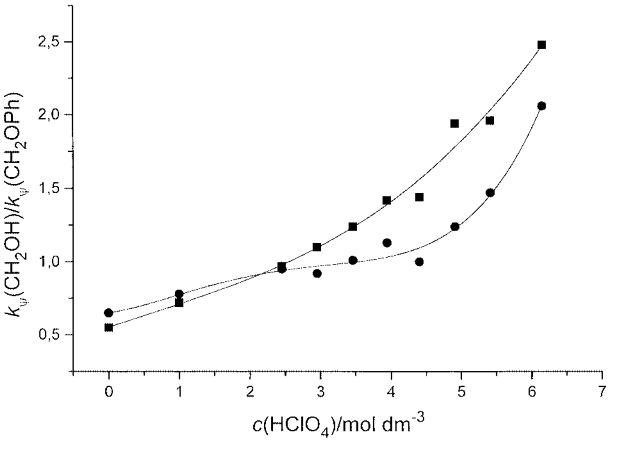


Fig. 4 Rate ratios k_ψ (**3**)/k_ψ (**5**) (■) and k_ψ (**4**)/k_ψ (**6**) (●) for the hydration of *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**) and of *exo*- and *endo*-5-phenoxymethylnorborn-2-enes (**5** and **6**) at different acid concentrations in $HClO_4$ (aq) at 303.2 K. Where the k_ψ values are lacking in Table 1, these have been calculated from eqn. (3) with the excess acidity parameters in Table 2.

All the excess acidity parameters (Table 2) evaluated in this work for *exo*- and *endo*-5-hydroxymethylnorborn-2-enes (**3** and **4**) accord very well with those for 5-methyl-*exo*- and -*endo*-5-hydroxymethylnorborn-2-enes (**1** and **2**).[2] Thus, the slightly peculiar values obtained, especially for **1** and **3**, are evidently not due to experimental scatter.

In order to test the possibility of exceptional *endo* protonation[6] in the case of the *endo*-epimers (**2** and **4**; Scheme 1), in which an intramolecular hydrogen bond has been detected between the hydroxy group and the carbon double bond,[26] the ratios of the rate constants for the hydroxymethyl- and phenoxymethyl-substituted norbornenes are compared with the *exo*- and *endo*-epimers at different acid concentrations (Fig. 4). If the hydroxymethyl group is protonated more easily than the phenoxymethyl group at higher acid concentrations, as was our original presumption, the *exo* protonation of the double bond should become relatively slower in the former case due to the formation of the second positive charge in the transition state and accordingly the rate ratio k_ψ (CH_2OH)/k_ψ (CH_2OPh) should decrease with increasing acid concentration. Fig. 4 shows that this does not occur, the trend, although slight, is exactly opposite. This may be due to a different solvation of **5** and **6**, as compared to **3** and **4**, in the $HClO_4$(aq) solutions used (see above). If the *endo* protonation of the double bond were to take place *via* the protonated *endo*-hydroxymethyl group (Scheme 1), and not *via* the protonated *endo*-phenoxymethyl group (CH_2OPh is less basic and sterically more crowded than CH_2OH), the rate ratio should either decrease less or increase more in the case of the *endo*-epimers than in the case of the *exo*-epimers. Neither is true under the conditions used for the kinetic runs, although the substituents are dominantly protonated (71 to 85%) at the highest acid concentration (6.14 M) as estimated with eqn. (4) from the parameters m' and $pK_{S'H^+}$ in Table 2.

Thus, the results of the present work do not show any evidence of *endo*-protonation in the case of the *endo*-epimers **2** and **4**, although the conditions should be excellent due to the intramolecular hydrogen bond[26] (see above). Therefore, the only remaining explanation among those presented in the introduction for the more peculiar values of the excess acidity parameters for the *exo*-epimers (**1** and **3**) than for the *endo*-epimers (**2** and **4**) is that the protonated *exo*-5-hydroxymethyl substituent does not totally hinder the protonation of the double bond, although its effect on the excess acidity parameters is not known.

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