

Acid-Catalyzed Hydrolysis of Bridged Bi- and Tricyclic Compounds. XXVII. An Application of the Excess Acidity Method to the Norbornyl Cation Problem

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Hydrolysis rates and products of *exo*- and *endo*-2-phenoxy-norbornanes have been studied in concentrated aqueous perchloric acid solutions. The activation parameters, solvent deuterium isotope effects, dependences of the reaction rates on acid concentration, products of hydrolysis and the high *exo/endo* rate ratio (2570) are all in agreement with the A-1 mechanism, in which the norbornyl cation is formed in the rate-limiting stage. The excess acidity method was used to determine first the pK_a value (-5.56) and the slope parameter ($m^* = 1.01$) for the oxygen protonation of the *endo* epimer, and then the slope parameters for the rate-limiting stages of the *exo* and *endo* hydrolyses ($m^* = 1.37$ and 1.55 , respectively). The slope parameters are somewhat exceptional, and may hint at a more delocalized charge in the transition state of the *exo* hydrolysis.

Characterization of transition states and subsequent carbocations in the solvolyses of *exo*- and *endo*-2-norbornyl esters, e.g. sulfonates, has been of great interest up to the present time.¹⁻⁴ There are, however, two serious problems in these investigations, namely internal return (i. r.) in the *exo* solvolysis [eqn. (1)] and the possibility of solvent participation [bimolecular solvolysis, S_N2 , eqn. (2)] in the *endo* solvolysis. Both reactions are medium-dependent.

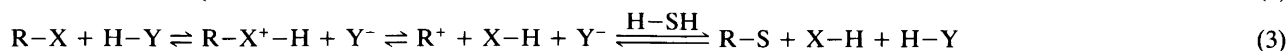
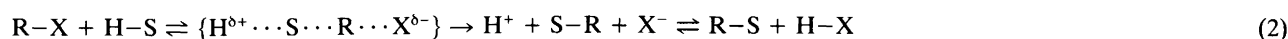
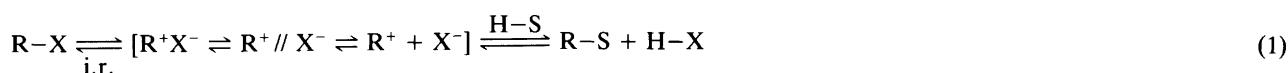
The effect of the internal return can be seen, for instance, in the *exo/endo* rate ratios of acetolysis of 2-norbornyl brosylates measured by different methods: $k_{t,exo}/k_{t,endo} = 350$ when measured titrimetrically, and $k_{a,exo}/k_{a,endo} = 1600$ when measured polarimetrically under similar conditions.^{5,6} The difference is caused by the different rate constants (k_t and k_a) of the *exo* epimer. Some investigations support the view that there is a slight solvent participation in the *endo* solvolysis.¹⁻⁴ Agreement concerning the unimolecular mechanism of the *exo* solvolysis is, however, general,^{1-4,7} as is the opinion that the intermediate carbocation is non-classical in character¹⁻³ (with rare exceptions).⁴

Each of the difficulties mentioned above can, however, be avoided by protonating the leaving group [eqn. (3)], which makes its departure as an uncharged molecule (XH)

easier and the formation of the intimate ion pair (R^+X^-) impossible. The possible formation of an ion pair between the carbocation (R^+) and the anion of the proton donor (HY) can also be reduced by using water as solvent (high permittivity), and attack of the anion (Y^-) on the carbocation (R^+) can be hampered by selecting a poor nucleophile, e.g. the perchlorate ion, as the anion of the proton donor.

If the protonation of the leaving group takes place in a fast pre-equilibrium, and if the departure of the protonated leaving group is the rate-limiting stage of the hydrolysis, the reaction mechanism is an acid-catalyzed unimolecular hydrolysis (A-1).⁸ The formation of a sufficiently stable carbocation is a necessary condition for this mechanism; however, the 2-norbornyl cation evidently fulfils this requirement.¹⁻⁷ The pre-equilibrium protonation is, of course, an additional stage of the solvolysis [cf. eqns. (1) and (3)] and may cause new problems, but the acid-catalyzed hydrolysis has such an advantage that the dependence of the reaction rate upon the acid concentration of the solution gives a method of estimating the relative solvation of the transition state and thus of investigating its character.⁸⁻¹⁰

Our first suggested choices of substrates are *exo*- and *endo*-2-phenoxy-norbornanes (1 and 2), which as *sec*-alkyl



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Table 1. Tentative assignments of ^{13}C NMR chemical shifts for *exo*- and *endo*-2-phenoxy-norbornanes (**1** and **2**) and 2- and 4-(*exo*-2-norbornyl)phenols (**3** and **4**) in CDCl_3 (TMS).

Substrate	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13
1	41.2	79.9	40.0	35.5	28.5	24.3	35.2	157.9	115.5	129.3	120.2	129.3	115.5
2	40.6	77.9	37.5	36.9	29.4	20.8	37.3	158.7	115.4	129.4	120.2	129.4	115.4
3	41.0	36.9	40.4	38.2	30.3	29.1	36.2	133.4	153.2	115.3	126.4	120.6	126.1
4	41.0	43.1	39.2	38.2	30.5	29.1	35.9	140.1	128.1	115.1	152.8	115.1	128.1

aryl ethers probably hydrolyze by an A-1 mechanism in aqueous mineral acids.¹¹ In order to prove that the mechanism is A-1 and that the bond between the norbornyl moiety and the oxygen atom is broken in the rate-limiting stage of the reaction, the *exo/endo* rate ratio, activation parameters, solvent deuterium isotope effects and products of hydrolysis have been studied in aqueous perchloric acid solutions. Then the excess acidity method of Cox and Yates⁸ is applied to the dependences of the hydrolysis rates on acid concentration.

Experimental

Synthesis. Mixtures of *exo*- and *endo*-2-phenoxy-norbornanes were prepared from (a) *exo*-2-bromonorbornane and sodiumphenoxide and (b) potassium-*endo*-2-norbornylate and bromobenzene.^{12,13} In case (a), ethanol or DMSO was used as solvent when the *exo/endo* product ratio was 90/10 and 69/31, respectively, but the yields were poor (9–12%, in agreement with an earlier study).¹² The product was distilled *in vacuo* through an efficient column (b.p. 123–127°C/5 Torr when ethanol was used as solvent). The residue of distillation was distilled without a column (b.p. 145–161°C/4 Torr) and it was found that it consisted of 2- and 4-(*exo*-2-norbornyl)phenols (**3** and **4**) in the ratio 89/11.

In case (b), where hexamethylphosphoric triamide was used as solvent,¹³ the yield was much better (52%) and the product contained more (58%) *endo* epimer than when method (a) was used. The *endo* epimer was separated from the mixture by hydrolyzing the *exo* epimer into norbornanol and phenol by stirring the mixture efficiently in 6M $\text{HClO}_4(\text{aq})$ at 75°C for 27 h. The product was extracted with ethyl ether and fractionated by distillation through an efficient column (b.p. 107–112°C/0.7 Torr). The yield was 94% and the purity 93% (7% was diphenyl ether).

The products were analyzed by capillary GLC and ^1H and ^{13}C NMR spectroscopy.^{14,15} The ^{13}C NMR chemical shifts are listed in Table 1.

Kinetic measurements. The disappearance of *exo*-2-phenoxy-norbornane and the formation of phenol in $\text{HClO}_4(\text{aq})$ was followed spectrophotometrically with a Cary 17D instrument at 222 nm. Efforts to measure the hydrolysis rates of the *endo* epimer in the same way were not successful. Therefore its disappearance was followed by GLC using Perkin Elmer 8500 chromatograph equipped with a BP 1

silicon capillary column, with 3-nitrotoluene as internal standard. Samples taken after appropriate intervals were extracted with CH_2Cl_2 , and the organic phase was washed with aqueous NaHCO_3 (1 M) and analyzed by GLC.

Owing to the poor solubilities of the substrates their initial concentrations were ca. 1×10^{-4} M. The disappearance rate constants were calculated from the slopes of linear correlations ($r \geq 0.999$), $\ln(A - A_\infty)$ vs. t , where A is the absorbance in the spectrophotometric measurements and an integral of the substrate divided by that of the internal standard in the GLC measurements, and t is time. Each measurement under a given set of conditions was repeated at least once, and the rate constants obtained were generally equal within 5% (av. 2.5%) in the spectrophotometric method and within 10% (av. 5%) in the GLC method. The average rate constants obtained by each method were equal within 2% in the case of *exo*-2-phenoxy-norbornane (Table 2).

Product analyses. The hydrolysis products of the substrates were analyzed by GLC using a Carbowax 20 M, XE 60 or NB-225 capillary column. The retention times of the components were compared with those of *exo*- and *endo*-2-norbornanols, phenol, and 2- and 4-(*exo*-2-norbornyl)phenols (**3** and **4**). The low concentrations of the product components in the homogeneous hydrolysis made their quantitative analyses difficult because of their very different retention times.

The epimeric norbornanols are known to isomerize into each other in aqueous mineral acids.¹⁶ Therefore their isomerization rate was measured in 7.03 M HClO_4 at 308.2 K by GLC with *endo*-2-norbornanol as the starting material (a 1×10^{-3} M solution). The reaction of *exo*-2-norbornanol and phenol was also followed by GLC in 5.97 M HClO_4 at 348.2 K using 1×10^{-3} M solutions. The formation of phenoxy-norbornane, which is hydrolyzed very rapidly, was proved by using sufficiently high reagent concentrations that the phenoxy-norbornane formed separated as insoluble and could be detected by GLC.

The pK_a value of the protonated form of *endo*-2-phenoxy-norbornane. This was measured by a spectrophotometric method. 0.1 cm^3 of a methanolic stock solution of the *endo* ether was injected as accurately as possible into 25 cm^3 of 7.0–10.34 M aqueous HClO_4 solutions thermostatted at 288.2 K. The UV spectra of the obtained solutions were

Table 2. Disappearance rate constants of *exo*- and *endo*-2-phenoxybornanes (**1** and **2**) in aqueous perchloric acid at different temperatures and acid concentrations, activation parameters at 298 K, and solvent deuterium isotope effects.

Epimer	[HClO ₄]/mol dm ⁻³	X ₀ ^a	T/K	k _ψ ^b 10 ⁻⁴ s ⁻¹	Activation parameters and isotope effects
<i>exo</i>	5.96		298.2	4.20(12)	ΔH [‡] = 100.9(12) kJ mol ⁻¹
	5.96		298.2	4.12(7) ^c	
	5.96		298.2	4.28(8) ^d	ΔS [‡] = 14(4) J mol ⁻¹ K ⁻¹
	5.91		298.2	8.85(4) ^e	
	5.96		303.2	8.53(30)	k _{H+} /k _{D+} = 0.471(16)
	5.96		308.2	16.9(5)	
	5.96		314.7	38.4(1)	
	5.96		318.2	56.8(3)	
	4.03	1.06	308.2	0.565(2)	
	4.52	1.24	308.2	1.259(5)	
	5.01	1.46	308.2	2.92(13)	
	5.96	1.92	308.2	16.9(5)	
	6.55	2.26	308.2	46.5(21)	
	7.05	2.57	308.2	119(7)	
<i>endo</i>	7.98		288.2	0.0217(7)	ΔH [‡] = 111.6(12) kJ mol ⁻¹
	7.98		298.2	0.114(1)	
	7.98		298.2	0.110(3) ^d	ΔS [‡] = 17(4) J mol ⁻¹ K ⁻¹
	7.97		308.2	0.497(5)	
	7.98		318.2	1.86(4)	k _{H+} /k _{D+} = 0.465(32)
	7.98		328.4	7.67(11)	
	8.48		308.2	1.449(2)	
	8.46		308.2	3.11(20) ^e	
	6.47	2.22	308.2	0.0141(2)	
	7.03	2.55	308.2	0.0463(7)	
	7.49	2.86	308.2	0.150(2)	
	7.97	3.17	308.2	0.497(5)	
	8.51	3.55	308.2	1.41(5)	
	9.06	3.95	308.2	6.56(8)	
	9.51	4.29	308.2	22.4(3)	
	9.96	4.66	308.2	62.3(14)	

^aRef. 18. The excess acidities are corrected to 308.2 K. ^bMeasured spectrophotometrically in the case of the *exo* epimer and by GLC in the case of the *endo* epimer, unless otherwise noted. ^cMeasured by GLC. ^dCalculated from the activation parameters.

^eMeasured in DClO₄(D₂O).

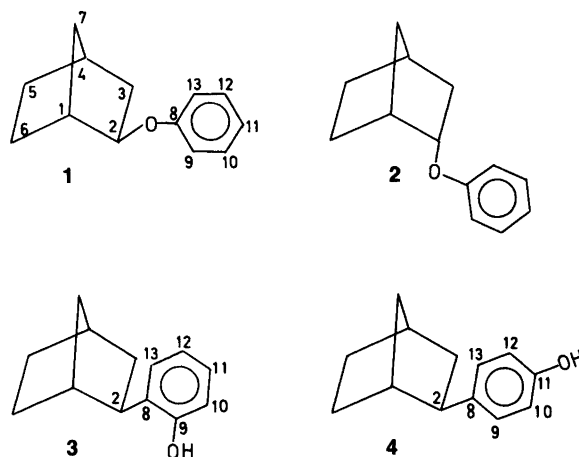
recorded rapidly three times successively between 250 and 280 nm on a Cary 17D spectrophotometer at 288.2 K using a solution of methanol (0.1 cm³) and each HClO₄(aq) solution (25 cm³) as a blank reference. There was only one maximum in the spectrum, and its wavelength varied slightly with the acid concentration. The differences in the absorbances at 266.5 nm (an average maximum) and at 280 nm (no marked absorbance) were measured, and the mean value at each acid concentration was used for evaluation of the pK_a value (see later). In the case of high acid concentrations (> 10 M), the hydrolysis rate of the *endo* ether was significant. Therefore the absorbances were extrapolated to the time of mixing the stock solution and the acids. The series of measurements was repeated once.

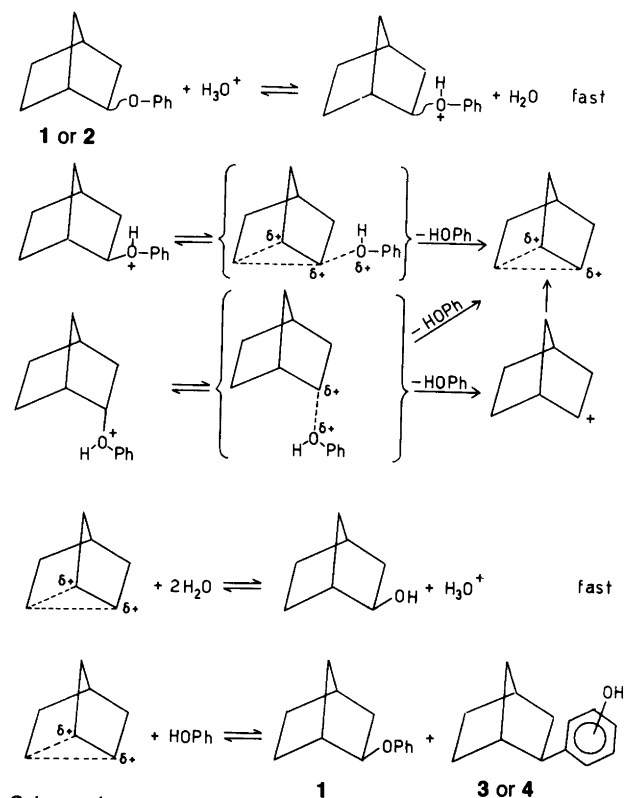
The hydrolysis rate of the *exo* ether was so great that measurements of its pK_a value could not be made, even at 273 K.

Results and discussion

The mechanism of hydrolysis. Disappearance rate constants of *exo*- and *endo*-2-phenoxybornanes (**1** and **2**)

were measured in aqueous perchloric acid solutions at different temperatures and acid concentrations, and in deuterio-perchloric acid. The rate constants, excess acidities,¹⁸ activation parameters and solvent deuterium isotope effects are listed in Table 2. The hydrolysis rates were slow, therefore rather concentrated acids (4–10 M) were used.





The activation entropies of hydrolysis of the epimeric ethers are positive (14 and 17 J mol⁻¹ K⁻¹ at 298 K) and thus typical of the A-1 mechanism, as are also the isotope effects ($k_{\text{H}}/k_{\text{D}} = 0.471$ and 0.465).^{19,20} The similarity of the values (the experimental conditions were, however, different) speaks strongly for a similar reaction mechanism (Scheme 1) in the case of the epimers. The measured *exo/endo* rate ratio, 2570, is very high (cf. Table 2 of Ref. 1) and thus shows that the formation of the norbornyl cation is the rate-limiting stage and that no internal return occurs (see above).

The hydrolysis products of *exo*-2-phenoxynorbornane were identified to be *exo*-2-norbornanol and phenol, which is in agreement with the A-1 mechanism. In the case of the *endo* ether, *endo*-2-norbornanol and 2- and 4-(*exo*-2-norbornyl)phenols (3 and 4 in the approximate ratio of 75:25) were formed in addition. The measured isomerization rate constant of the epimeric norbornanols, $k_1 = (1.06 \pm 0.11) \times 10^{-5} \text{ s}^{-1}$ in 7.0 M HClO₄ at 308 K, is, however, greater than the rate of disappearance of the *endo* ether ($4.63 \times 10^{-6} \text{ s}^{-1}$) under the same conditions; thus the formation of *endo*-2-norbornanol is probably due to the acid-catalyzed epimerization of the initially formed *exo*-2-norbornanol (Scheme 1).

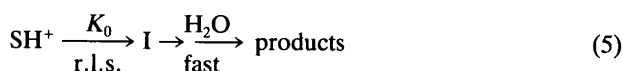
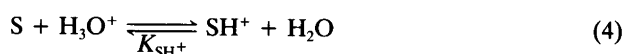
The formation of the norbornyl phenols (3 and 4) is possibly due to the reaction of the 2-norbornyl cation with phenol¹³ and/or to the reaction of *exo*-2-norbornanol with phenol, which probably also takes place via the norbornyl cation (Scheme 1). The latter reaction was observed to

occur separately, and the rate constant of formation of the norbornyl phenols, $k_1 = (2.6 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$ in 6.0 M HClO₄ at 348 K, is roughly one third of the rate of disappearance of *endo*-2-phenoxynorbornane under the same conditions. The ratio of the *ortho* and *para* isomers was in agreement with the ratio of the isomers formed from the hydrolysis of *endo*-2-phenoxynorbornane. The ratio was changed slightly during the reaction in favour of the *para* isomer. This thermodynamic control accords with the observation that the reaction of *exo*-2-norbornanol and phenol did not proceed completely to the norbornyl phenols: part of the reagents remained unchanged.

The formation of 2-phenoxynorbornane (probably the *exo* form) was also observed in the reaction of *exo*-2-norbornanol and phenol, but its concentration was very low at its highest, and was undetectable in the final samples. This formation reaction is the reverse of the hydrolysis of *exo*-2-phenoxynorbornane. Thus the hydrolysis is a reversible reaction, but the proportion of ether formation is so small (<0.1% of that of its hydrolysis) that it does not hamper the investigation of the transition state of hydrolysis.

The kinetic data above are in full agreement, and the product-analytic data are not in disagreement with the A-1 mechanism in the acid-catalyzed hydrolyses of *exo*- and *endo*-2-phenoxynorbornanes. The large *exo/endo* rate ratio (2570), however, indicates that there must be a marked difference in the energies of the transition states. Whether or not a difference can also be found in the characters of the transition states will be studied in the following section.

Application of the excess acidity method.^{8,21} For the acid-catalyzed unimolecular hydrolysis (A-1) of substrate S [eqns. (4) and (5)] which is protonated moderately in an aqueous acid solution, eqn. (6) can be derived. In eqn. (6),



$$\log k_{\psi} - \log \frac{c_{\text{S}}}{c_{\text{S}} + c_{\text{SH}^+}} - \log c_{\text{H}^+} = m^* m^{\ddagger} X_0 + \log \frac{k_0}{K_{\text{SH}^+}} \quad (6)$$

k_{ψ} is an observed pseudo first-order rate constant for the hydrolysis of S; k_0 is a medium-independent rate constant of the rate-limiting stage (5); K_{SH^+} ($= K_{\text{a}}$) represents an acid dissociation constant of the protonated substrate; c_i stands for the concentration of component i ; m^* is a slope parameter of eqn. (7), which is derived for the pre-equilibrium protonation (4); m^{\ddagger} is a slope parameter which depends on the character of the transition state of the rate-limiting stage (5); and X_0 is a so-called excess acidity.

$$\log \frac{c_{\text{SH}^+}}{c_{\text{S}}} - \log c_{\text{H}^+} = m^* X_0 + pK_{\text{SH}^+} \quad (7)$$

In the case of *endo*-2-phenoxybornane, the hydrolysis was sufficiently slow that the parameters m^* and pK_{SH^+} could be evaluated by measuring the absorbances (A) of acid solutions of the ether at 288 K and by using eqns. (7) and (8).¹⁷ In eqn. (8), A_S and A_{SH^+} are absorbances of the

$$\frac{c_{SH^+}}{c_S} = \frac{A_S - A}{A - A_{SH^+}} \quad (8)$$

unprotonated and totally protonated substrate. It was not possible to measure the values of A_S and A_{SH^+} directly, but they could be computed together with the parameters m^* and pK_{SH^+} by fitting the experimental A values to the c_{H^+} and X_0 values of the solutions [eqn. (9)] via a non-linear least-squares minimization (Fig. 1).²²

$$A = \frac{A_S - A_{SH^+}}{1 + \frac{c_{H^+}}{K_{SH^+}} 10^{m^* X_0}} + A_{SH^+} \quad (9)$$

The calculated values of A_S (0.120) and A_{SH^+} (0.273) seem reasonable, and the pK_{SH^+} value, -5.56 , is in agreement with the values for oxygen protonation of 2-propyl and 2-butyl phenyl ethers (-5.80 and -5.36 , respectively, at 273 K), which were evaluated from eqn. (10) by the iterative method of Arnett and Wu.¹⁷ This acidity function

$$\log \frac{A_S - A}{A - A_{SH^+}} = -H_0 + pK_{SH^+} \quad (10)$$

method gives a value of -5.72 ± 0.07 (H_0 values from Ref. 23) in the case of *endo*-2-phenoxybornane, a value which accords rather well with that obtained above by the excess acidity method. The slope parameter m^* of eqn. (7) takes a value of 1.006, which is exceptional (see later).

If the pK_{SH^+} value measured at 288 K is approximated to be temperature-independent within the rather narrow range of 20 K,²⁴ and if the c_{H^+} and X_0 values are corrected to the temperature of the kinetic measurements, 308.2 K,⁸ the protonation correction term, eqn. (11), of eqn. (6) can be calculated from eqn. (7) at each acid concentration used, and then the parameters m^* , m^* and $\log(k_0/K_{SH^+})$ can be evaluated from the experimental rate constants, k_ψ (Table 2), by eqn. (6) using the method of linear least squares (Fig. 2). Eqn. (6) can also be used for *exo*-2-phenoxybornane, because the protonation correction term is insignificant at the acid concentrations employed.

$$\log \frac{c_S}{c_S + c_{SH^+}} = -\log \left(1 + \frac{c_{SH^+}}{c_S} \right) \quad (11)$$

The correlations are fairly linear: $r = 0.998$ ($n = 6$) for the *exo* ether and $r = 0.9999$ ($n = 8$) for the *endo* ether, and

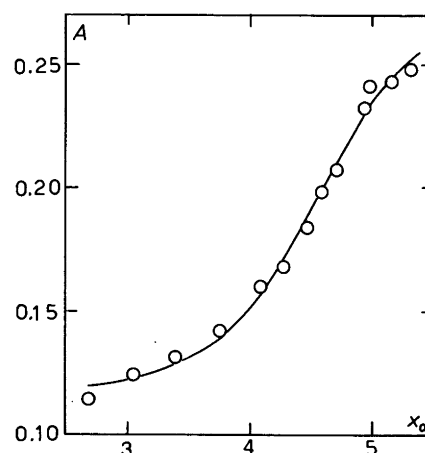


Fig. 1. Correlation of the absorbances with excess acidities for *endo*-2-phenoxybornane (2) in aqueous $HClO_4$ at 288 K.

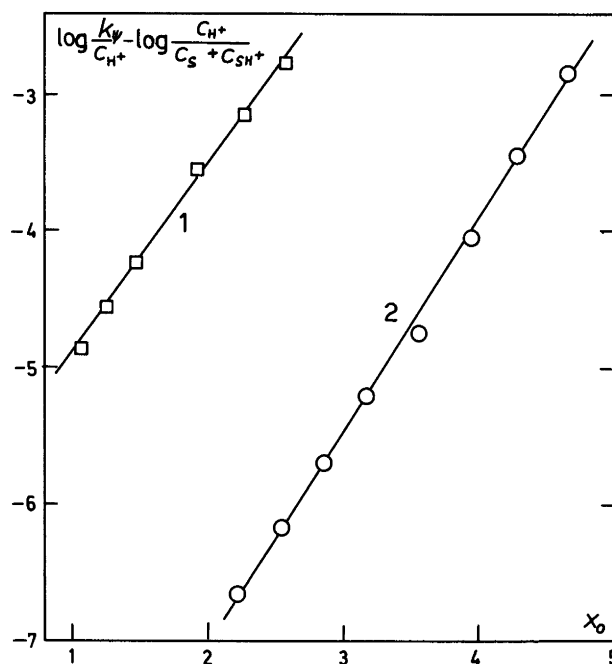


Fig. 2. Excess acidity plots for the hydrolyses of *exo*- and *endo*-2-phenoxybornanes (1 and 2) in aqueous $HClO_4$ at 308 K.

the following values are obtained for the parameters: $m^* m^* = 1.38 \pm 0.04$ (*exo*) and 1.56 ± 0.03 (*endo*) and $\log(k_0/K_{SH^+}) = -6.26 \pm 0.07$ (*exo*) and -10.15 ± 0.10 (*endo*). If the values of m^* (1.006) and pK_{SH^+} (-5.56) are assumed to be equal in the case of the epimeric phenoxybornanes, the following values of m^* can be calculated: 1.37 for the *exo* epimer and 1.55 for the *endo* epimer, and the ratio of the medium-independent rate constants, $k_{0,exo}/k_{0,endo}$, takes an approximate value of $(7.6 \pm 3.0) \times 10^3$, which is still greater than that measured experimentally (2570).

The $m^* m^*$ values above are of the same magnitude as those measured by Cox and Yates²¹ for the acid-catalyzed hydrolyses (depolymerization) of 2,4,6-trimethyl-1,3,5-trioxane (1.45) and 1,3,5-trioxane (1.16), the A-1 reactions of which are also initiated by the pre-equilibrium protonation of the ether oxygen. Our m^* value does not, however, agree with those (0.4–0.6) generalized by these authors for a typical oxygen protonation on the basis of the protonation of carbonyl compounds.²¹ Thus our m^* values are also smaller than those (2–3) estimated to be “normal” for the rate-limiting formation of a carbocation or oxocarbenium ion via the A-1 mechanism.^{21,25} The number of experimentally determined m^* values is, however, so small that no decisive conclusions can be drawn from their magnitude with regard to the hydrolysis of alkyl aryl ethers. More investigations are needed.

The difference between the m^* values of the *exo* and *endo* ethers is small. The value measured for the hydrolysis of the *exo* epimer, which probably produces directly the non-classical 2-norbornyl cation,^{1–6} is slightly smaller and thus more exceptional than that for the *endo* epimer, which evidently produces first the classical 2-norbornyl cation or at least the classical transition state (Scheme 1).^{1–6,26} Thus the lower value of m^* may hint at a more delocalized charge in the transition state. The results of the present work support the opinion² that it is difficult to find other clear differences than those in energy in the transition states of solvolysis of the *exo*- and *endo*-2-norbornyl esters.

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