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Acid-Catalyzed Hydrolysis of Some Primary Alkyl Phenyl Ethers

Martti Lajunen,* Riitta Laine and Marika Aaltonen

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

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Products were analyzed and rate constants of disappearance and hydrolysis, alkylation and/or rearrangement were measured for methyl, ethyl, propyl and allyl phenyl ethers by GC in concentrated aqueous perchloric acid solutions. Chlorination of the substrate and possibly of the product, phenol, was observed beside the hydrolysis of methyl phenyl ether and a slight chlorination of phenol beside the hydrolysis of ethyl phenyl ether. A marked Claisen rearrangement to isopropylphenols and alkylation to propyl isopropylphenyl ethers were observed in addition to the hydrolysis of propyl phenyl ether. The Claisen rearrangement to *o*-allylphenol was estimated to be quantitative in the case of allyl phenyl ether. The change of the reaction mechanism from *A*-2 (MeOPh and EtOPh) possibly via *A*-2(carbocation)(PrOPh?) to *A*-1 (allyl phenyl ether and possibly PrOPh) was deduced from the products, reaction rates, activation parameters, solvent deuterium isotope effect and parameters of excess acidity plots.

Primary alkyl phenyl ethers, especially methyl and ethyl phenyl ethers (anisole and phenetole, respectively), are useful solvents and reagents in organic syntheses. They are very resistant to acid hydrolysis,[1,2] this being at least partly due to their strongly negative pK_a values (-6.5 to -6.0).[3–5] Their *ortho* and *para* hydrogens exchange rather easily in acid media, but this does not generally lead to further reactions.[2] Some substituents in the aromatic ring, however, cause a facile rupture of the ether linkage, but in these cases the cleavage is evidently caused by an initial acid reaction of the substituent or the aromatic ring.[6] The protonation and fragmentation of higher primary alkyl phenyl ethers, e.g. 1-propyl phenyl ether, in the gas phase have recently been of interest.[7]

It seems to us that studies concerning the acid-catalyzed hydrolysis of the most simple primary alkyl phenyl ethers have so far been very rare.[8] Therefore, the present work concentrates on the first three members of this group, i.e. methyl, ethyl and 1-propyl phenyl ethers. For comparison, allyl (2-propen-1-yl) phenyl ether is also included, although its acid-catalyzed Claisen rearrangement is rather a well known reaction.[9–12] This work is an enlargement of our recent studies of secondary and tertiary alkyl phenyl ethers.[13–17]

* To whom correspondence should be addressed.

Experimental

Methyl and ethyl phenyl ethers were commercial products from Merck AG and Aldrich, respectively, and were used without further purification (purities by GC $\geqslant$ 99%). Also *o*-allylphenol was a commercial product from Aldrich (98%).

Syntheses. 1-Propyl phenyl ether was prepared from 1-propyl iodide and sodium phenoxide and allyl phenyl ether from allyl bromide and sodium phenoxide.[18] The yields were good (74–79%) and the purities after fractional distillations 99.9% (by GC). The structures were checked from the FTIR, mass, ^1H and ^{13}C NMR spectra.

Product analyses. 0.3 g of the substrate was stirred with 50 cm^3 of aqueous perchloric acid (10.0 and 11.6 M for MeOPh, 10.0 M for EtOPh and PrOPh, and 7.4 M for allyl phenyl ether) in a tightly stoppered bottle at an elevated temperature (ca.75 °C for MeOPh, EtOPh and PrOPh and ca. 45 °C for allyl phenyl ether) for ca. one and ten half-lives. The reaction solutions were extracted with CH_2Cl_2 and the organic phases were neutralized by letting them flow through anhydrous K_2CO_3. The solvent was evaporated off and the residues analyzed by GC, GC-FTIR and GC-MS, the components being mainly identified by comparing their retention times and spectra with those of authentic compounds or with the spectra collected in the memories of the spectrometers.

A marked amount of solid material was formed in the hydrolysis of methyl phenyl ether and smaller amounts in the cases of ethyl and propyl phenyl ethers. The precipitates were filtered, washed with water, dried and analyzed by IR.

Kinetic measurements. The disappearance rate constants of the substrates were measured by a GC method using an FFAP capillary column, dichloromethane as the extracting solvent and norcamphor or nitrobenzene as the internal standard.[13] Because of the high acid concentrations used in the runs, the CH_2Cl_2 phases remained acidic after the extractions. To eliminate its marked effect on the GC analyses, the phases were neutralized either by washing with 1 M $NaHCO_3$(aq) or by adding one drop of concentrated ammonia. The pseudo-first-order rate constants (k_ψ) were calculated from the slopes of the linear ($r=0.999$–0.9999) plots $\ln S_t = -k_\psi t + \ln S_0$ ($S_\infty = 0$), where S is the ratio of integrals of the substrate and the internal standard and t is the time. The final samples were taken after estimated ten half-lives. Each rate constant was measured twice or more and the values were equal at least within 8% (av. 2%).

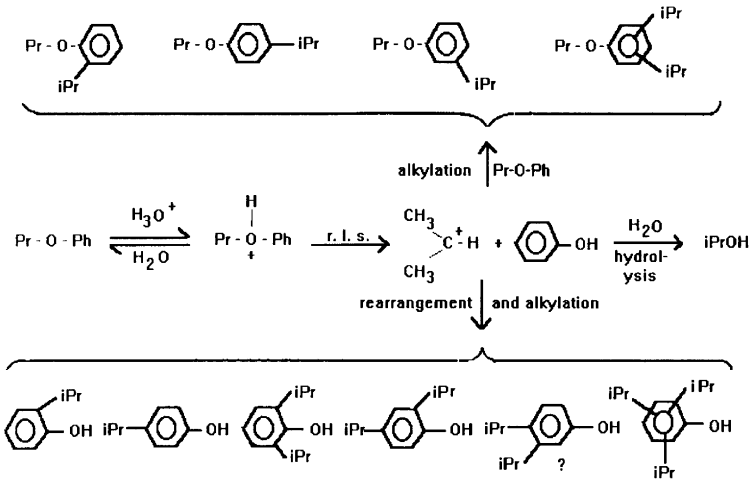
An unexpected chlorination of the substrate was observed in the case of methyl phenyl ether (anisole; see later). Therefore the estimated rate constants of formation of chloroanisoles were subtracted from the rate constants of disappearance of anisole in order to obtain its rate constants of hydrolysis.

An isopropylation of the substrate was observed in the case of propyl phenyl ether (see later) and this caused a small increase ($15\pm3\%$) of the rate constants of disappearance in the course of the runs. The addition of the GC integrals of propyl isopropylphenyl ethers to the integrals of the substrate and the recalculation of the rate constants with the above equation gave estimates of rate constants of hydrolysis, alkylation and/or rearrangement which were approximately equal to the initial rate constants of disappearance (the estimation of the rate constants at the beginning of the runs, when propyl isopropylphenyl ethers were not yet formed, was rather approximate).

Results and discussion

According to the product analyses (see Experimental), methyl phenyl ether (anisole) yields in concentrated aqueous perchloric acid solutions, in addition to the main products, phenol and probably methanol (the latter was not observable by the method used), also the following chlorinated anisoles and phenols: 2-chloroanisole (not observable in the final sample), 4-chloroanisole and 2,4-dichloroanisole, as well as 4-chlorophenol and 2,4-dichlorophenol, the amounts of which evidently increase with increasing substrate concentration. Some 4-chlorophenol, but no (or possibly only traces of) chlorinated phenetoles were formed in the case of ethyl phenyl ether (phenetole), the main products of which were phenol and probably ethanol (not observable by the method used). The products show that there are, besides hydrolysis, some chlorination reactions, which also have an increasing effect on the rate constants of disappearance (see later) in the case of methyl phenyl ether. This kind of chlorination is unexpected in perchloric acid and may be the consequence of a reduction of $HClO_4$, e.g. to Cl_2, which causes a substitution of the chlorine atom for the *ortho* and/or *para* hydrogen(s) in the benzene ring. No chlorination was observed in the case of propyl and allyl phenyl ethers, the hydrolysis products of which are discussed in the following chapters.

Propyl phenyl ether yields (Scheme 1) phenol (32%; the amounts are approximate) and possibly 2-propanol (not observable by the method used); 2-isopropylphenol (16%) and 4-isopropylphenol (9%), which are typical products of the acid-catalyzed Claisen rearrangement;[9] 2,6-diisopropylphenol (small quantity), 2,4-diisopropylphenol (8%) and a third diisopropylphenol (small quantity); probably n-propyl 2-isopropylphenyl ether (15%),

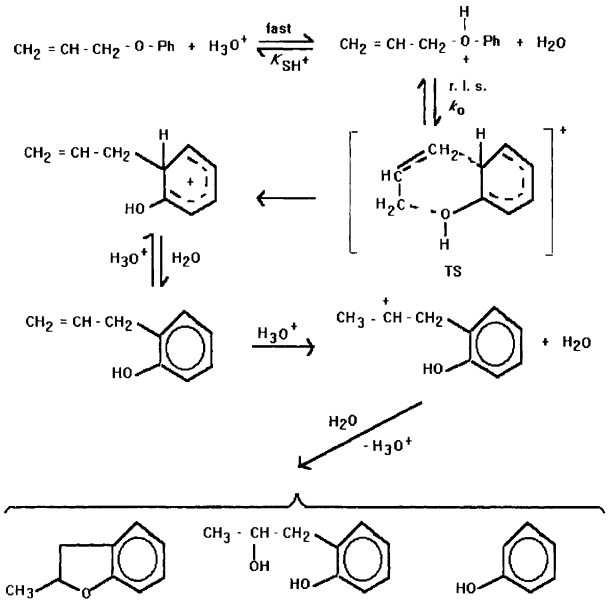


Scheme 1.

n-propyl 3-isopropylphenyl ether (small quantity) and n-propyl 4-isopropylphenyl ether (10%); as well as one n-propyl diisopropylphenyl ether (trace) and two triisopropylphenols (traces). The products indicate the formation of the isopropyl cation in the cleavage of the ether linkage (Scheme 1). The formation of the Claisen rearrangement products, 2- and 4-alkyl-substituted phenols, has been generally observed in the acid-catalyzed hydrolysis of secondary and tertiary alkyl phenyl ethers,[13–15] but were not found, in this work, among the hydrolysis products of methyl and ethyl phenyl ethers (see above). The formation of the isopropylated substrates indicates that propyl phenyl ether is almost as effective a trap of the isopropyl cation as phenol (Scheme 1).

Formation of polymeric phenols was also observed and their amounts decreased in the order: MeOPh > EtOPh > PrOPh.

Allyl phenyl ether yields (Scheme 2) in concentrated perchloric acid 2-methyl-2,3-dihydrobenzofurane (54%), probably 2-(2-hydroxy-1-propyl)phenol (40%) and phenol (6%). The same hydrolysis products in approximately the same ratio were also formed in the case of *o*-allylphenol.



Scheme 2.

The rate constants of disappearance (k'_ψ) and hydrolysis, alkylation and/or rearrangement [k_ψ; separate rate constants for the hydrolysis, alkylation and rearrangement (e.g. Scheme 1) were not measured, because the products are formed in the stages after the rate-limiting step (r.l.s.)] for four primary alkyl phenyl ethers in aqueous perchloric acid at different temperatures and acid concentrations are listed in Table 1. The rate constants k'_ψ and k_ψ are different in the case of methyl phenyl ether because of a chlorination of the substrate and in the case of propyl phenyl ether because of an isopropylation of the substrate (see Experimental). The activation parameters were calculated from both rate constants (k_ψ and k'_ψ), but they were rather similar. The parameters calculated from the rate constants of hydrolysis, alkylation and/or rearrangement are given in Table 2, together with the solvent deuterium isotope effect measured only for allyl phenyl ether.

The hydrolysis rate of methyl phenyl ether in aqueous perchloric acid is very low ($t_{1/2}$ = 38.5 h at 348 K in 9.6 M or 64 wt. % $HClO_4$; the total disappearance rate is ca. 4% higher owing to chlorination of the substrate). Ethyl and propyl phenyl ethers hydrolyze, alkylate or rearrange ca. 8 and 25 times faster, respectively, under these conditions. This order is unexpected for the bimolecular mechanism of hydrolysis (*A*-2; Scheme 3), in which water participates in the rupture of the ether linkage, because the ethyl and propyl groups should be sterically more crowded than the methyl group.

The amount of protonation of the substrate also has an effect on the disappearance rate of the alkyl phenyl ethers, because the oxygen protonation occurs in the fast pre-equilibrium before the rate-limiting stage in both the *A*-1 and *A*-2 mechanisms (Scheme 3). The pK_{SH^+} of the substrate has the following literature values at 273 K: −6.54 for MeOPh, −6.44 for EtOPh and −6.40 for PrOPh.[3] Thus, the ether oxygen becomes more basic and the amount of protonation increases in the order Me < Et < Pr, but this effect on the rate is rather small (≤40%). The pK_{SH^+} values at 348 K are probably not identical with those at 273 K, but the present estimations (Table 2) are too approximate to make corresponding comparisons.

A more fruitful way to explain the rate order $k_{Me} < k_{Et} < k_{Pr}$ is in a change of the reaction mechanism from bimolecular (*A*-2) to monomolecular (*A*-1;

Table 1. Rate constants of disappearance (k'_ψ) and hydrolysis, alkylation and/or rearrangement (k_ψ, if different from k'_ψ) for primary alkyl phenyl ethers (R–O–Ph) in aqueous perchloric acid at different temperatures and acid concentrations.

T/K	$c(HClO_4)$/[a] mol dm^{-3}	X_0[b]	a_w[c]	$k'_\psi/10^{-5}$ s^{-1}	$k_\psi/10^{-5}$ s^{-1}
			R = Me		
348.2	9.60			0.52(2)	0.50(2)
348.2	9.60			0.513(14)[d]	0.496(6)[d]
358.2	9.54			1.54(6)	1.48(6)
368.2	9.47			4.61(7)	4.43(7)
			R = Et		
338.2	9.68			1.274(7)	
348.2	9.60			4.37(2)	
348.2	9.60			4.34(3)[d]	
358.2	9.54			13.77(6)	
348.2	8.21	3.16	0.167	0.479(4)	
348.2	8.66	3.44	0.134	0.938(10)	
348.2	9.18	3.82	0.096	2.03(4)	
348.2	9.60	4.13	0.074	4.37(2)	
348.2	9.62	4.14	0.073	5.23(8)	
348.2	10.07	4.48	0.056	10.56(12)	
348.2	10.15	4.54	0.054	11.2(3)	
348.2	10.55	4.89	0.040	27.4(8)	
348.2	10.56	4.91	0.040	27.8(6)	
348.2	11.13	5.36	0.029	77(3)	
348.2	11.16	5.42	0.028	81.8(14)	
			R = Pr		
338.2	9.68			4.65(7)	3.91(7)
348.2	9.60			15.74(8)	12.9(2)
348.2	9.60			15.66(10)[d]	13.1(2)[d]
358.2	9.54			49.2(3)	41.4(3)
348.2	8.22	3.18	0.166	0.934(17)	0.776(14)
348.2	8.66	3.44	0.134	2.01(4)	1.67(4)
348.2	9.18	3.82	0.096	5.87(9)	4.87(9)
348.2	9.30	3.91	0.089	7.96(6)	6.66(7)
348.2	9.55	4.08	0.076	14.1(3)	11.7(3)
348.2	9.60	4.13	0.074	15.74(8)	12.9(2)
348.2	10.07	4.48	0.056	45.6(4)	37.3(4)
348.2	10.15	4.54	0.054	45.8(4)	38.0(4)
348.2	10.55	4.89	0.040	137.7(11)	114.5(9)
348.2	10.56	4.91	0.040	143(2)	118.5(17)
348.2	11.13	5.36	0.029	452(9)	375(8)
348.2	11.16	5.42	0.028	514(4)	425(6)
			R = allyl		
318.2	6.71			10.64(4)	
328.2	6.67			35.38(11)	
338.2	6.62			110.5(6)	
348.2	6.58			319.4(14)	
348.2	6.58			320(1)[d]	
318.2	6.09	1.97	0.452	3.23(4)	
318.2	6.37	2.13	0.412	5.26(2)	
318.2	6.71	2.31	0.365	10.64(4)	
318.2	7.23	2.65	0.292	29.7(2)	
318.2	7.49	2.82	0.258	54.9(2)	
318.2	7.53	—	—	98.1(19)[e]	
318.2	7.85	3.05	0.217	104.8(17)	
318.2	8.09	3.23	0.189	207.5(17)	
318.2	8.43	3.47	0.157	436(4)	
318.2	8.71	3.67	0.134	954(15)	

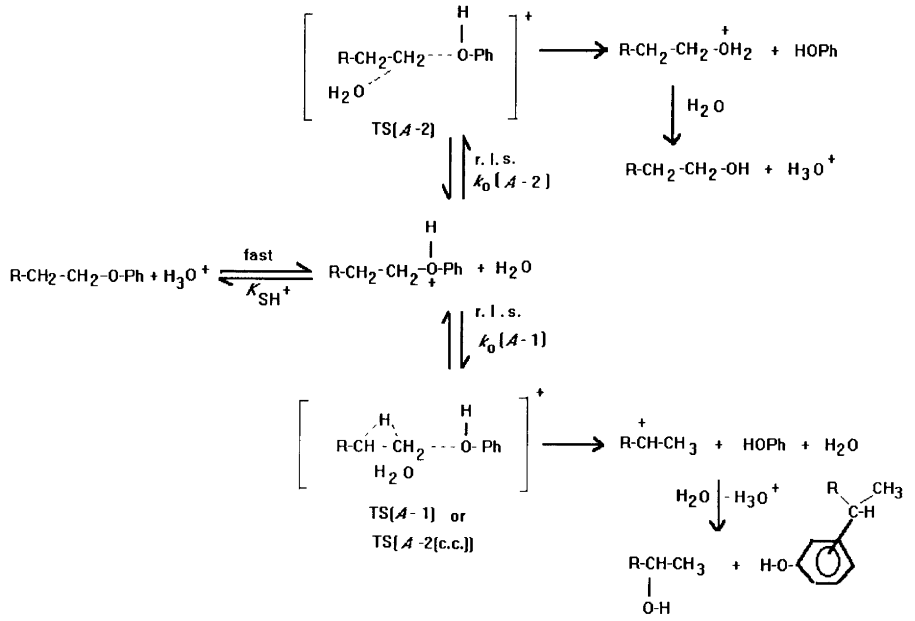
[a]Temperature corrected. [b]Excess acidity,[24] temperature corrected.[22] [c]Activity of water,[25] temperature corrected.[26] [d]Calculated from the activation parameters (Table 2). [e]Measured in $DClO_4(D_2O)$.

Table 2. The activation parameters, the solvent deuterium isotope effect and the parameters of the excess acidity eqns. (1) and (2) at 348 K (if not otherwise noted) for the hydrolysis, alkylation and/or rearrangement of primary alkyl phenyl ethers (R–O–Ph) in $HClO_4$(aq).

R	$\Delta H^{\neq}$/ kJ mol^{-1}	$\Delta S^{\neq}$/ J mol^{-1} K^{-1}	k_H/k_D
Me	111.9(9)[a]	−45(3)[a]	
Et	117.7(5)[a]	−11(2)[a]	
Pr	116.5(11)[a]	−5(3)[a]	
Allyl	102.2(2)[b]	−16.0(4)[b]	0.61[c]

R	Mechanism	$m^{\neq}$	m^*	$\log(k_0/K_{SH^+})$	pK_{SH^+}
Et	*A*-1	0.99(4)	0.998(5)	−9.38(8)	−7.1(3)
	A-2	1.31(1)	0.998(8)	−9.57(5)	−7.5(2)
Pr	*A*-1	1.24(3)	1.002(12)	−10.01(11)	−6.8(2)
	A-2	1.56(2)	1.001(5)	−10.18(7)	−7.0(2)
Allyl[c]	*A*-1	1.35(2)	0.999(1)	−7.94(5)	—[d]
	A-2	1.66(2)	0.999(1)	−8.22(5)	—[d]

[a] 9.6 M $HClO_4$. [b] 6.6 M $HClO_4$. [c] 318 K. [d] Uncertain owing to the excellent linearity of eqn. (2), when the correction term $\log[c_S/(c_S+c_{SH^+})] \approx 0$.



Scheme 3.

Scheme 3) in the order Me, Et and Pr, which is in agreement with the entropies of activation ($\Delta S^{\neq}$/J mol^{-1} K^{-1}: −45, −11 and −5; Table 2) and with the products of hydrolysis (see above).

The disappearance of allyl phenyl ether was also studied in aqueous perchloric acid in order to obtain the kinetic parameters typical of the Claisen rearrangement.[9–12] Its disappearance rate is ca. 8×10^3 and 4 times greater than that for 1-propyl and 2-propyl[16] phenyl ethers, respectively, in 6.6 M $HClO_4$(aq) at 348 K. Its negative entropy of activation, −16 J mol^{-1} K^{-1}, is in agreement with the *A*-1 rearrangement through a cyclic transition state to *o*-allylphenol (Scheme 2), and the solvent deuterium isotope effect ($k_H/k_D = 0.61$) disagrees with a possible protonation of the carbon–carbon double bond,[19] which starts the acid-catalyzed hydrolysis of allyl alcohol (ca. 22 times slower than that for allyl phenyl ether).[20] *o*-Allylphenol is not stable in the acid solutions used, but rapidly disappears [$k_\psi = (1.568 \pm 0.004) \times 10^{-3}$ s^{-1} in 7.49 M $HClO_4$ at 318.2 K and $k_H/k_D = 2.0$; the values measured in the present work are typical of the protonation of a carbon double bond][19] yielding the same products in approximately the same ratio as were observed to form in the case of allyl phenyl ether. Thus, allyl phenyl ether is rearranged quantitatively into *o*-allylphenol (Scheme 2), which was confirmed by using the rate equations for the consecutive reactions[21] [k_ψ(formation of *o*-allylphenol) = 99 ± 2% of k_ψ(disappe-

arance of allyl phenyl ether) according to six measurements in $HClO_4(H_2O)$ and $DClO_4(D_2O)$].

The excess acidity theory[22] was applied to the rate constants measured for ethyl, propyl and allyl phenyl ethers at constant temperatures but at varying acid concentrations (Table 1) according to eqn. (1),[15,23]

$$\log k_\psi - \log c_{H^+}(-\log a_w) = m^{\neq} m^* X_0 - \log[1 + (c_{H^+}/K_{SH^+})10^{m^* X_0}] + \log(k_0/K_{SH^+}) \quad (1)$$

which can be formed from the original eqn. (2)[22]

$$\log k_\psi - \log c_{H^+} - \log[c_S/(c_S + c_{SH^+})](-\log a_w) = m^{\neq} m^* X_0 + \log(k_0/K_{SH^+}) \quad (2)$$

via eqn. (3):[22]

$$\log(c_{SH^+}/c_s) - \log c_{H^+} = m^* X_0 + pK_{SH^+} \quad (3)$$

In the above equations, which express the dependence of the reaction rate [eqns.(1) and (2)] and of the amount of protonation of the substrate [eqn. (3)] upon the acidity of the medium,[22] k_ψ is a pseudo first-order rate constant; c_S and c_{SH^+} are the concentrations of the unprotonated and protonated substrate S ($pK_a = pK_{SH^+}$) in aqueous acid of concentration c_{H^+}, of excess acidity X_0,[24] and of activity of water a_w;[25,26] $m^{\neq}$ and m^* are slope parameters (the former depends on the structure of the transition state and the latter on the site of protonation); and k_0 stands for the solvent-independent rate constant of the rate-limiting step. The term water activity is included in the case of an *A*-2 mechanism and excluded in the case of an *A*-1 mechanism (Scheme 3).[22]

Eqn. (1) was used to evaluate the most probable values for parameters $m^{\neq}$, m^*, K_{SH^+} and $\log(k_0/K_{SH^+})$ from the experimental values of k_ψ, c_{H^+} [$=c(HClO_4)$], a_w and X_0 with the aid of a nonlinear least-squares minimization.[15,23] The values of the parameters are given in Table 2 and the linear excess acidity plots, which obey eqn. (2), in Figs. 1 and 2. The equations were used both in the case of the *A*-1 mechanism ($-\log a_w$ excluded) and the *A*-2 mechanism ($-\log a_w$ included).

The slope parameter m^* always obtains the value of unity (av. 1.000 ± 0.002) which is typical of the proton attack on the ether oxygen.[13–17,23] The kinetic slope parameter $m^{\neq}$ obtains in the case of the *A*-1 mechanism the following values: 0.99 for EtOPh, 1.24 for PrOPh and 1.35 for allyl phenyl ether, of which the first does not accord with the *A*-1 mechanism,[22] but the last is normal being equal to that measured for the hydrolysis of isopropyl phenyl ether at the same temperature, 318 K.[16] The middle value is slightly smaller than normal (ca. 1.30) when the temperature (348 K) of the kinetic measurements is taken into account.[16] In the case of the *A*-2 mechanism, all the values are abnormal, for which reason the mechanistic conclusions are less sure. However, the value of $m^{\neq}$ for ethyl phenyl ether (1.31), although not unity as generally,[22,23] is close to the preliminary values (1.2–1.3) evaluated for the *A*-2

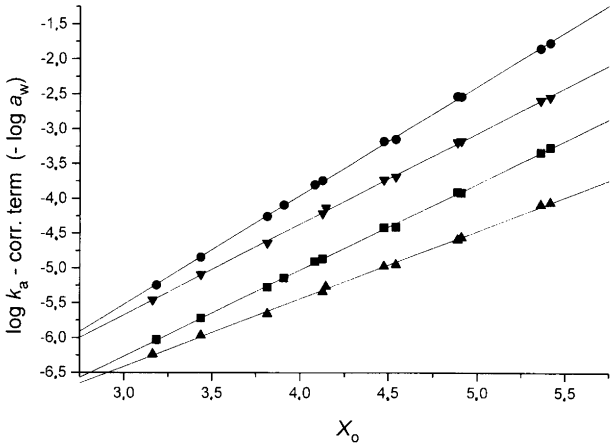


Fig. 1. Excess acidity plots [eqn. (2)] for the hydrolysis, alkylation and/or rearrangement of propyl and ethyl phenyl ethers in $HClO_4$(aq) at 348 K with inclusion (● and ▼, respectively) and exclusion (■ and ▲, respectively) of the activity of water ($k_a = k_\psi/c_{H^+}$). The parameters m^* and pK_{SH^+} in Table 2 were used to calculate [eqn. (3)] the correction term $\log[c_S/(c_S + c_{SH^+})]$.

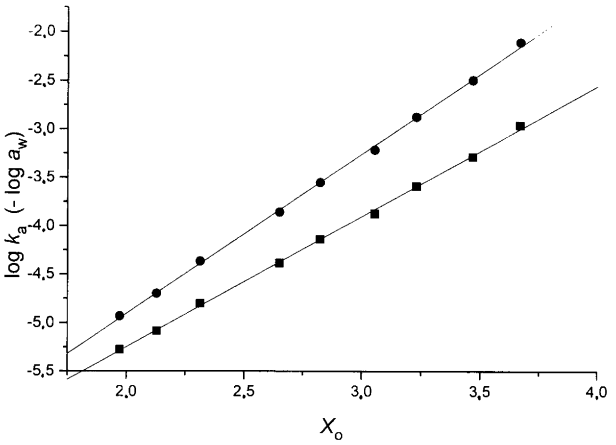


Fig. 2. Excess acidity plots [eqn. (2)] for the rearrangement of allyl phenyl ether in $HClO_4$(aq) at 318 K with inclusion (●) and exclusion (■) of the activity of water ($k_a = k_\psi/c_{H^+}$). The correction term $\log[c_S/(c_S + c_{SH^+})] \approx 0$.

hydrolysis of unsubstituted, 1-methyl- and 1,6-dimethyl-substituted 3-tricyclo[2.2.1.$0^{6,2}$]heptanones at the same temperature 348 K.[27] Thus, it seems possible that the $m^{\neq}$ value for the *A*-2 mechanism depends slightly on temperature, but in the opposite direction than that for the *A*-1 and Ad_E2 mechanisms.[16,28] Further studies are required.

To summarize, one can conclude that methyl and ethyl phenyl ethers hydrolyze in aqueous concentrated perchloric acid very slowly obeying the *A*-2 mechanism (Scheme 3), but have a side reaction which causes a partial chlorination of the benzene ring. Propyl phenyl ether hydrolyzes, alkylates and rearranges (the Claisen rearrangement) somewhat faster than those above via the *A*-1 mechanism [or possibly via an *A*-2(carbocation) mechanism][29] (Schemes 1 and 3) producing, in addition to phenol and isopropylphenols, also propyl isopropyl-

phenyl ethers. Its rate of hydrolysis is somewhat greater than that expected for the *A*-2 mechanism, the kinetic parameters being between those typical of the *A*-2 and *A*-1 mechanisms and the products are typical of the *A*-1 mechanism. Allyl phenyl ether reacts ca. 10^4 times faster than the saturated primary alkyl phenyl ethers and produces quantitatively unstable *o*-allylphenol (the Claisen rearrangement; the *A*-1 mechanism; Scheme 2).

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References

1. Staude, E. and Patat, F. In: Patai, S., Ed., *The Chemistry of the Ether Linkage*, Interscience Publishers, London 1967, Chap. 2.
2. Cox, R. A. *J. Phys. Org. Chem. 4* (1991) 233 and references cited therein.
3. Arnett, E. M. and Wu, C. Y. *J. Am. Chem. Soc. 82* (1960) 5660.
4. Arnett, E. M., Wu, C. Y., Anderson, J. N. and Bushick, R. D. *J. Am. Chem. Soc. 84* (1962) 1674.
5. Lambrechts, H. J. A. and Cerfontain, H. *Recl. Trav. Chim. Pays-Bas 102* (1983) 299.
6. Cox, R. A., Onyido, I. and Buncel E. *J. Am. Chem. Soc. 114* (1992) 1358 and references cited therein.
7. Kondrat, R. W. and Morton, T. H. *J. Org. Chem. 56* (1991) 952; *Org. Mass Spectrom. 26* (1991) 410.
8. Satchell, D. P. N. *J. Chem. Soc.* (1956) 3911.
9. Dalrymple, D. L., Kruger, T. L. and White, W. N. In: Patai, S., Ed., *The Chemistry of the Ether Linkage*, Interscience Publishers, London 1967, Chap. 14.
10. Svanholm, U. and Parker, V. D. *J. Chem. Soc., Chem. Commun.* (1972) 645.
11. Svanholm, U. and Parker, V. D. *J. Chem. Soc., Perkin Trans. 2* (1974) 169.
12. Widmer, U., Hansen, H.-J. and Schmid, H. *Helv. Chim. Acta 56* (1973) 2644.
13. Lajunen, M. and Himottu, M. *Acta Chem. Scand. 43* (1989) 957.
14. Lajunen, M. and Kähkönen, M. *Acta Chem. Scand. 46* (1992) 726.
15. Lajunen, M. and Tanskanen-Lehti, K. *Acta Chem. Scand. 48* (1994) 861.
16. Lajunen, M. and Setälä, J. *Acta Chem. Scand. 51* (1997) 334.
17. Lajunen, M. Himottu, M. and Tanskanen-Lehti, K. *Acta Chem. Scand. 51* (1997) 515.
18. Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed., Longman, London 1956, p. 671.
19. Chwang, W. K., Nowlan, V. J. and Tidwell, T. T. *J. Am. Chem. Soc. 99* (1977) 7233.
20. Herlihy, K. P. *Aust. J. Chem. 35* (1982) 2221; *42* (1989) 1345.
21. Daniels, F. and Alberty, R. A. *Physical Chemistry,* 3rd ed., Wiley International, New York 1967, p. 336.
22. Cox, R. A. *Acc. Chem. Res. 20* (1987) 27.
23. Lajunen, M. and Koskinen, J.-M. *Acta Chem. Scand. 48* (1994) 788.
24. Cox, R. A. and Yates, K. *Can. J. Chem. 59* (1981) 2116.
25. Wai, H. and Yates, K. *Can. J. Chem. 47* (1969) 2326.
26. Attiga, S. A. and Rochester, C. H. *J. Chem. Soc., Perkin Trans. 2* (1978) 466.
27. Lajunen, M. and Wiksten, P. *Finn. Chem. Lett.* (1980) 17. The $m^{\neq}$ parameters were calculated by using eqn. (1) of this work.
28. Lajunen, M., Virta, M. and Kylliäinen, O. *Acta Chem. Scand. 48* (1994) 122.
29. Lajunen, M., Kaitaranta, E. and Dahlqvist, M. *Acta Chem. Scand. 48* (1994) 399.

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