

Acid-Catalyzed Hydrolysis of Some Secondary Alkyl Phenyl Ethers in Perchloric Acid: Kinetics and Mechanism

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Hydrolysis rates and products of isopropyl, cyclopentyl and cyclohexyl phenyl ethers were studied in concentrated aqueous perchloric acid solutions. The activation parameters, solvent deuterium isotope effects, dependences of the reaction rates on acid concentration, substituent effects and products were in agreement with the A-1 mechanism. The pK_{SH^+} values (-6.13 to -5.76) and the slope parameters m^* (av. 0.98 ± 0.03) were measured spectrophotometrically by the excess acidity method. They were used to calculate the m^\ddagger -parameters (1.46 – 2.01). Comparisons were made with the hydrolyses of *exo*- and *endo*-2-norbornyl phenyl ethers and secondary alkyl methanesulfonates.

The excess acidity method was recently employed in the acid-catalyzed hydrolysis of *exo*- and *endo*-2-norbornyl phenyl ethers.¹ The reaction mechanism was concluded to be mainly the same, namely A-1 for both epimers (the character of the intermediate carbocation, R^+ , is probably different; Scheme 1) on the grounds of the *exo/endo* rate ratio (2570), activation entropies (14 – 17 J K⁻¹ mol⁻¹), solvent deuterium isotope effects ($k_H/k_D = 0.47$), excess acidity correlations and product analyses. However, the slope parameters of the excess acidity correlations [eqns. (1) and (2)],² in which X_0 is the excess acidity of the

$$\log k_\psi - \log c_{H^+} - \log [c_S / (c_S + c_{SH^+})] \quad (1)$$

$$= m^\ddagger m^* X_0 + \log (k_0 / K_{SH^+})$$

$$\log (c_{SH^+} / c_S) - \log c_{H^+} = m^* X_0 + pK_{SH^+} \quad (2)$$

solution],³ $m^* = 1.01$ and $m^\ddagger = 1.37$ and 1.55 , were somewhat exceptional in comparison with those proposed to be typical of the A-1 hydrolyses via initial protonation of an oxygen atom ($m^* = 0.4$ – 0.6 or 0.4 – 0.8 and $m^\ddagger > 1$ (or more probably 2–3), obtained from reactions where protonation occurs at a carbonyl oxygen).⁴

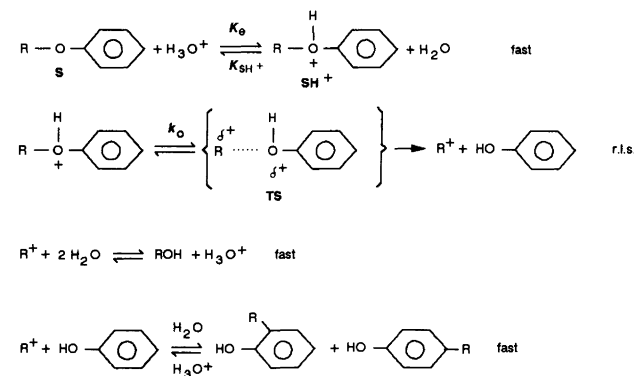
In this work the hydrolyses of isopropyl, cyclopentyl and cyclohexyl phenyl ethers in concentrated perchloric acid were studied to see what values of m^* and m^\ddagger are typical of the hydrolyses of secondary alkyl phenyl ethers. The reaction mechanism was certified by activation parameters, solvent deuterium isotope effects, excess acidity correlations, substituent effects and product analyses.

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Experimental

Syntheses. Isopropyl phenyl ether was prepared from 2-iodopropane and sodium phenoxide.⁵ The yield was 67% and the purity (by GLC) > 99%. Cyclopentyl and cyclohexyl phenyl ethers were synthesized from the corresponding sodium cycloalkoxides and iodobenzene.⁶ The yields were 42 and 60% and the purities 98.5 and 96.5%, respectively. The impurities were alicyclic compounds according to their gas-phase FTIR spectra, and thus they did not hamper the kinetic or basicity measurements by UV spectroscopy. The IR, ¹H NMR and ¹³C NMR spectra of the substrates were in accord with their expected structures.

Kinetic measurements. The disappearance of the substrates and formation of phenol were followed in aqueous perchloric acid solutions on a Cary 17 D spectrophotometer at 226 nm. The cell compartment was thermostatted to an accuracy of 0.1 K by circulating water. The first-order rate constants were calculated from the linear plots of



Scheme 1.

Table 1. Disappearance rate constants of isopropyl, cyclopentyl and cyclohexyl phenyl ethers in aqueous perchloric acid at different temperatures and acid concentrations, together with activation parameters at 298 K and solvent deuterium isotope effects.

$c(\text{HClO}_4) / \text{mol dm}^{-3}$ ^a	X_0 ^b	T/K	$k_p / 10^{-4} \text{ s}^{-1}$	Activation parameters ^e and deuterium isotope effects
Substrate: iPrOPh				
9.38		298.2	2.68(1)	$\Delta H^\ddagger = 95(2)$
9.38		298.2	2.80(16) ^c	$\Delta S^\ddagger = -11(7)$
9.35		308.2	10.26(16)	
9.31		318.2	35.3(8)	
9.26		328.2	98.4(13)	
7.29		338.2	6.30(3)	
7.23		338.2	11.43(9) ^d	$k_H/k_D = 0.49(1)$
7.92	3.15	308.2	0.414(9)	
8.47	3.51	308.2	1.715(14)	
8.95	3.88	308.2	5.79(4)	
9.35	4.18	308.2	10.26(16)	
9.81	4.56	308.2	36.6(6)	
10.35	5.00	308.2	148.9(16)	
10.79	5.40	308.2	446(5)	
Substrate: c-PentOPh				
8.04		279.2	0.126(5)	
8.03		288.2	0.729(8)	
8.01		298.2	3.18(1)	$\Delta H^\ddagger = 105(3)$
8.01		298.2	3.0(5) ^c	$\Delta S^\ddagger = 24(11)$
7.98		308.2	13.77(4)	
7.95		318.2	48.2(12)	
7.90		328.2	128(3)	
7.29		313.2	5.32(8)	
7.23		313.2	10.3(3) ^d	$k_H/k_D = 0.44(2)$
8.04	3.51	279.2	0.126(5)	
8.67	4.00	279.2	0.630(14)	
9.04	4.31	279.2	3.02(6)	
9.54	4.73	279.2	15.7(3)	
9.94	5.08	279.2	50(2)	
10.15	5.33	279.2	149(5)	
10.40	5.51	279.2	263(4)	
Substrate: c-HexOPh				
8.45		279.2	0.091(2)	
8.44		288.2	0.454(10)	
8.42		298.2	1.96(5)	$\Delta H^\ddagger = 107(1)$
8.42		298.2	1.97(15) ^c	$\Delta S^\ddagger = 25(5)$
8.39		308.2	8.80(6)	
8.35		318.2	32.7(7)	
8.30		328.2	101(4)	
7.29		323.2	4.47(8)	
7.23		323.2	7.5(2) ^d	$k_H/k_D = 0.50(4)$
8.45	3.82	279.2	0.091(2)	
9.04	4.31	279.2	0.437(12)	
9.54	4.73	279.2	1.749(4)	
9.89	5.04	279.2	3.82(8)	
10.19	5.31	279.2	14.6(5)	
10.40	5.50	279.2	19.3(5)	
10.78	5.87	279.2	103(4)	

^aCorrected according to the temperature. ^bExcess acidity of the solution³ corrected according to the temperature.² ^cCalculated from the activation parameters. ^dMeasured in $\text{DClO}_4(\text{D}_2\text{O})$. ^e ΔH^\ddagger in kJ mol^{-1} ; ΔS^\ddagger in $\text{J K}^{-1} \text{ mol}^{-1}$.

$\ln(A_t - A_\infty)$ vs. time (t) or, in the case of slow reactions, $\ln(A_t - A_{t+\Delta t})$ vs. time (the Guggenheim method).⁷ Parallel measurements were always made, and they gave rate constants equal within 4% (av. 2%). In all cases the absorbance reading slightly increased after 10 half-lives prob-

ably owing to the slow formation of 2- and 4-alkyl or -cycloalkyl phenols.

Product analyses. The hydrolysis products were analyzed by GLC using a Carbowax 20 M capillary column. Their

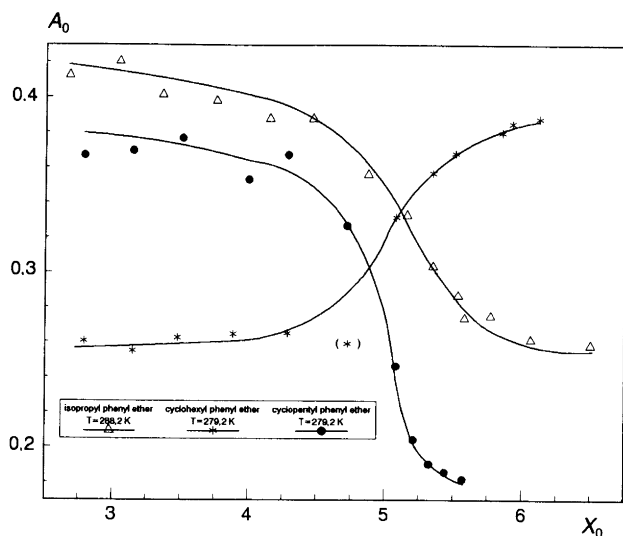


Fig. 1. Correlations of absorbances with excess acidities for isopropyl, cyclopentyl and cyclohexyl phenyl ethers in aqueous HClO_4 at 288.2 K (iPrOPh) or at 279.2 K (others).

retention times were compared with the following commercial products: phenol, 2-propanol, cyclopentanol, cyclohexanol, and 2-, 3- and 4-isopropyl phenols.

The pK_{SH^+} values of the protonated substrates. These were measured in concentrated aqueous perchloric acid solutions at 288.2 or 279.2 K by the UV spectrophotometric method described recently.¹ At high acid concentrations the hydrolysis of the substrates occurred significantly during the measurements. In these cases the maximum absorbance reading was followed to the end of the reaction, the first-order rate constant (k) was calculated and the absorbance was extrapolated to the initial time by a linear correlation between the left-hand side and the term $[1 - \exp(kt)]$ in eqn. (3).

$$A_{\text{exp}}(kt) = -A_{\infty}[1 - \exp(kt)] + A_0 \quad (3)$$

Results and discussion

Disappearance rate constants of isopropyl, cyclopentyl and cyclohexyl phenyl ethers were measured in aqueous perchloric acid at various temperatures and acid concentrations, and in deuterioperchloric acid. The results are listed in Table 1, together with activation parameters and solvent deuterium isotope effects. These kinetic parameters are of the same magnitude as those recently measured for 2-norbornyl phenyl ethers (see above), and are in agreement with the A-1 hydrolysis mechanism (Scheme 1).¹

According to the product analyses, alcohols corresponding to the alkyl groups of the substrates and phenol were formed as main products in the hydrolyses. In all cases 2- and 4-alkyl or -cycloalkyl phenols were also formed as minor products in an approximate ratio of 3:1. They were identified only in the case of isopropyl phenyl ether (see Experimental). Their generation in the reaction of 2-propa-

nol, cyclopentanol or cyclohexanol with phenol under the conditions used for the product analyses was separately observed, but the reaction was so slow that it cannot alone explain their amounts in the hydrolysis products of the alkyl phenyl ethers. Thus the formation of the 2- and 4-alkyl phenols accords with the A-1 mechanism via a carbocation (R^+ ; Scheme 1).

The pK_{SH^+} values of the alkyl phenyl ethers were measured from their UV spectra in 7.0–11.6 mol dm^{-3} perchloric acid.¹ The maximum absorbances at ca. 266 nm (the wavelength varied slightly with acid concentration) were plotted versus excess acidity X_0 (Fig. 1), and the K_{SH^+} and m^* values were evaluated from eqn. (4), which is a combination of eqns. (2) and (5).⁸ The parameters men-

$$A = (A_{\text{S}} - A_{\text{SH}^+})/[1 + (c_{\text{H}^+}/K_{\text{SH}^+})10^{m^*X_0}] + A_{\text{SH}^+} \quad (4)$$

$$c_{\text{SH}^+}/c_{\text{S}} = (A_{\text{S}} - A)/(A - A_{\text{SH}^+}) \quad (5)$$

tioned above, together with A_{S} (the absorbance of an unprotonated substrate) and A_{SH^+} (the absorbance of a totally protonated substrate), were computed by a nonlinear least-squares minimization from the experimental values of A , c_{H^+} (= perchloric acid concentration) and X_0 .¹ The results are given in Table 2.

Unfortunately, two rather reasonable minima were found close to each other, e.g. $pK_{\text{SH}^+} = -6.13$ or -5.82 and $m^* = 1.003$ or 0.956 , respectively, in the case of isopropyl phenyl ether. The existence of the two minima may cause at its worst an uncertainty of ca. 0.4 for the pK_{SH^+} values and of ca. 0.07 for the m^* values. The selection between them was made from plots of A vs. H_0 (H_0 values at 298.2 K),⁹ in which the approximate pK_{SH^+} values can be directly seen from the inflection points.⁸ The pK_{SH^+} value of -5.80 has been calculated earlier for isopropyl phenyl ether by Arnett and Wu⁸ from a plot of A vs. H_0 in aqueous sulfuric acid at 273 K (H_0 values at 298 K).¹⁰ The agreement with the present selected value (-6.13) is satisfactory.

In order to compare the measured pK_{SH^+} values mutually and with that of *endo*-2-norbornyl phenyl ether¹ it is better to correct them to the same temperature, e.g. 283 K. The values may depend significantly on temperature or may be practically independent of it.^{11,12} Let us use both approximations. In the former case, an assumption that the standard Gibbs energy ($\Delta G_{\text{m}}^\ominus$) for the deprotonation of the

Table 2. The values of pK_{SH^+} , m^* , A_{S} and A_{SH^+} for isopropyl, cyclopentyl and cyclohexyl phenyl ethers computed by eqn. (4) from absorbances, acid concentrations and excess acidities presented in Fig. 1.

Substrate	T/K	pK_{SH^+}	m^*	A_{S}	A_{SH^+}
iPrOPh	288.2	-6.13	1.003	0.417	0.256
c-PentOPh	279.2	-5.83	0.967	0.715	0.460
c-HexOPh	279.2	-5.76	0.956	0.355	0.502

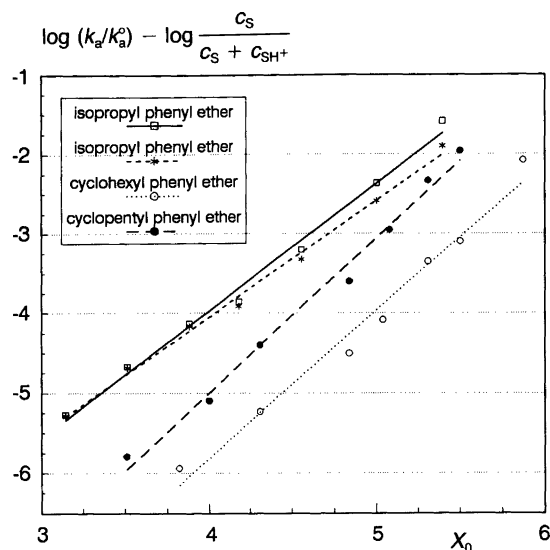


Fig. 2. Excess acidity plots [eqn. (1)] for the hydrolyses of isopropyl, cyclopentyl and cyclohexyl phenyl ethers in aqueous HClO_4 at 308.2 K [PriOPh (\square) for $\text{p}K_{\text{SH}^+} = -5.73$ and ($*$) for $\text{p}K_{\text{SH}^+} = -6.13$] or at 279.2 K (others).

protonated substrate is independent of temperature (i.e. $\Delta S_m^\circ = 0$) is sometimes made.¹¹ In this case the $\text{p}K_{\text{SH}^+}$ value at temperature T_2 can be calculated from its value at temperature T_1 from eqn. (6). In this way the following

$$\text{p}K_{\text{SH}^+}(T_2) = (T_1/T_2)\text{p}K_{\text{SH}^+}(T_1) \quad (6)$$

$\text{p}K_{\text{SH}^+}$ values at 283 K are obtained (the temperature-independent approximations are given in parentheses): isopropyl phenyl ether, -6.24 (-6.13), cyclopentyl phenyl ether, -5.75 (-5.83), cyclohexyl phenyl ether, -5.68 (-5.76), and *endo*-2-norbornyl phenyl ether, -5.66 (-5.56). The values become less negative as the alkyl group becomes bigger and the substrate more basic, which trend seems reasonable.⁸

The m^* values in Table 2 are similar to that (1.006) measured for *endo*-2-norbornyl phenyl ether at 288.2 K, but rather different from those (0.4–0.8) measured for protonation of carbonyl oxygens.⁴ Thus it seems evident that the value of m^* is ca. 1.0 (more accurately 0.98 ± 0.03)

for the protonation of the ether oxygen of alkyl phenyl ethers in aqueous perchloric acid.

The excess acidity method can be employed for studying the hydrolysis rates of the alkyl phenyl ethers by using eqn. (1). The correction term, $\log [c_s/(c_s + c_{\text{SH}^+})]$, can be estimated by eqn. (2) from the parameters in Table 2. In the case of isopropyl phenyl ether, the $\text{p}K_{\text{SH}^+}$ value and the rate constants were measured at different temperatures (288.2 and 308.2 K, respectively). The m^* parameter is evidently independent of temperature,¹³ but the $\text{p}K_{\text{SH}^+}$ value again may (eqn. 6)¹¹ or may not¹² depend on it. Thus both approximations are used: the temperature-independent value (-6.13) is obtained from Table 2 and the temperature-corrected value (-5.73) is obtained from eqn. (6) at 308.2 K. Now it is possible to employ eqn. (1) for the rate constants and excess acidities in Table 1. The plots (Fig. 2) are satisfactorily linear ($r = 0.992$ – 0.998) and allow the evaluation of the slope parameters, m^*m^\ddagger , and intercepts, $\log(k_0/K_{\text{SH}^+})$, wherefrom it is possible to calculate the values of m^\ddagger and of very rough medium-independent rate constants, k_0 , by using the m^* and $\text{p}K_{\text{SH}^+}$ values in Table 2. The results are collected in Table 3.

A comparison of the m^\ddagger parameters (1.46; 1.60) of isopropyl phenyl ether with those of *exo*- (1.37; 1.37)¹ and *endo*- (1.55; 1.65)¹ 2-norbornyl phenyl ethers (the latter values have been obtained from the temperature-corrected $\text{p}K_{\text{SH}^+}$ values) shows that they are rather similar. The measurements of the $\text{p}K_{\text{SH}^+}$ and m^* values were made at 288.2 K in all these cases, and the kinetic measurements were made at 308.2 K. However, the m^\ddagger parameters are close to 2 (2.01 and 1.93) in the cases of cyclopentyl and cyclohexyl phenyl ethers, whose $\text{p}K_{\text{SH}^+}$ and kinetic measurements were made at the same temperature (279.2 K). The latter values are more typical of the A-1 hydrolysis, although all the values fulfil the broader requirement ($m^\ddagger > 1$).⁴ The differences in the m^\ddagger values may be due to their dependences on temperature or to the approximate extrapolations of some $\text{p}K_{\text{SH}^+}$ values to the higher temperature.

The mutual comparison of the medium-independent rate constants (k_0 in Table 3) is not rational because of their poor accuracy and of their measurements at different tem-

Table 3. The parameters of eqn. (1) for the acid-catalyzed hydrolysis of some secondary alkyl phenyl ethers in aqueous perchloric acid.

R in ROph	T/K	m^*m^\ddagger	m^\ddagger	$\log(k_0/K_{\text{SH}^+})$	k_0/s^{-1}	r^a
Isopropyl ^b	308.2	1.46(5)	1.46(5)	-9.9(2)	2×10^{-4}	0.997
Isopropyl ^c	308.2	1.60(6)	1.60(6)	-10.4(3)	2×10^{-5}	0.996
Cyclopentyl	279.2	1.94(6)	2.01(6)	-12.8(3)	1×10^{-7}	0.998
Cyclohexyl	279.2	1.85(10)	1.93(11)	-13.2(5)	4×10^{-8}	0.992
<i>exo</i> -2-Norbornyl ^d	308.2	1.38(4)	1.37(4)	-6.27(7)	0.2	0.998
<i>exo</i> -2-Norbornyl ^e	308.2	1.38(4)	1.37(4)	-6.27(7)	9×10^{-2}	0.998
<i>endo</i> -2-Norbornyl ^d	308.2	1.56(3)	1.55(3)	-10.15(10)	3×10^{-5}	1.000
<i>endo</i> -2-Norbornyl ^e	308.2	1.65(4)	1.65(4)	-10.42(14)	6×10^{-6}	0.998

^a Correlation coefficients for linear plots of eqn. (1). ^b $\text{p}K_{\text{SH}^+} = -6.13$ (see Table 2). ^c $\text{p}K_{\text{SH}^+} = -5.73$ (temperature-corrected). ^d $\text{p}K_{\text{SH}^+} = -5.56$ and $m^* = 1.006$. ^e $\text{p}K_{\text{SH}^+} = -5.20$ (temperature-corrected).

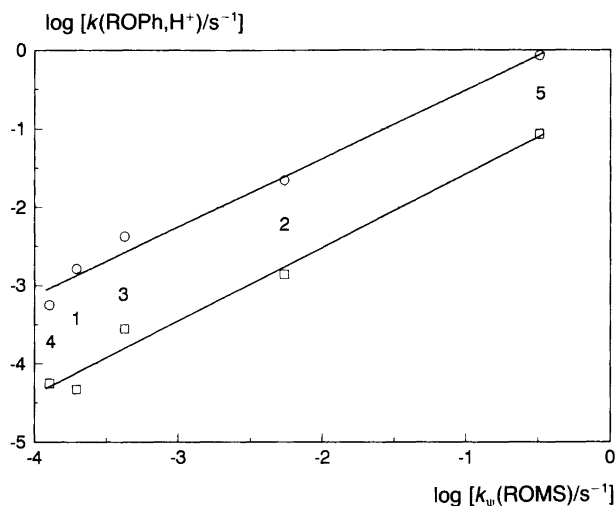


Fig. 3. Logarithms of rate constants of hydrolysis for some secondary alkyl phenyl ethers in $8.0 \text{ mol dm}^{-3} \text{ HClO}_4(\text{aq})$ at 308.2 K versus those for the corresponding alkyl methanesulfonates in water at 298.2 K (1 = isopropyl, 2 = cyclopentyl, 3 = cyclohexyl, 4 = *endo*-2-norbornyl and 5 = *exo*-2-norbornyl). In the upper plot $\log(k/\text{s}^{-1}) = \log(k_p/\text{s}^{-1}) - 1$ and in the lower plot $k = k_p$ for alkyl phenyl ethers.

peratures, but the experimental rate constants (Table 1) can be extrapolated to a proper state of comparison, e.g. 8.0 M HClO_4 at 308.2 K , and so they can be used. Their logarithms, together with those of *exo*- and *endo*-2-norbornyl phenyl,¹ are plotted against the logarithms of the rate constants of hydrolysis of the corresponding methanesulfonates (mesylates in water at 298 K)¹⁴ in Fig. 3. A fairly linear ($r = 0.991$) correlation is obtained, with a slope close to unity (0.94 ± 0.07). The corresponding plots against the logarithms of rate constants of solvolysis of the *p*-toluenesulfonates in different nonaqueous solvents¹⁵⁻¹⁸ show that the correlations are poorer ($r = 0.92-0.98$) and the slopes vary irregularly ($0.65-1.1$).

A more suitable correlation than that above should, however, prevail between the rate-limiting stage of the *A*-1 hydrolysis of the alkyl phenyl ethers (Scheme 1) and the stage of formation of a carbocation or an ion pair in the S_N1 solvolyses of the alkyl mesylates, because the characteristics of these stages are very similar. An internal return (from an ion pair to the substrate), which often troubles the studies of S_N1 solvolyses, is absent in the *A*-1 hydrolysis of the alkyl phenyl ethers, because the leaving group, phenol, has no charge.

The solvent-dependent rate constant (k_0) of the rate-limiting stage of the hydrolysis of the alkyl phenyl ethers (Scheme 1) can be calculated from the experimental rate constant, k_p , which is equal to $K_e k_0$. Thus $\log k_0 = \log k_p - \log K_e$, where $\log K_e = \log(c_{\text{SH}^+}/c_{\text{SC}_2\text{H}_5^+})$ and can be calculated by eqn. (2) from the parameters in Table 2. [pK_{SH^+} must be corrected to the temperature used, e.g. by eqn. (6).] The calculated k_0 values in $8.0 \text{ mol dm}^{-3} \text{ HClO}_4$ at 308.2 K are also correlated with the rate constants of hydrolysis of the corresponding alkyl mesylates¹⁴ in Fig. 3.

The logarithmic correlation is only somewhat better ($r = 0.992$, slope = 0.87 ± 0.07) than that between the uncorrected experimental rate constants (see above).

The fair correlation hints that either (a) the mechanisms of the hydrolyses of the alkyl phenyl ethers (e.g. *A*-1) and the alkyl mesylates (e.g. S_N1) do not change when the alkyl group varies, or (b) the changes of the mechanisms (e.g. from *A*-1 to *A*-2 and from S_{N1} or S_{Ni} to S_{N2} when the alkyl group becomes more electronegative) must be similar in quantity. The only weak evidence of existence of the *A*-2 mechanism is the slightly negative entropy of activation ($-11 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$) of isopropyl phenyl ether, and the solvent deuterium isotope effects being slightly closer to unity ($0.49-0.50$) for isopropyl and cyclohexyl phenyl ethers than those ($0.44-0.47$) for cyclopentyl and norbornyl phenyl ethers (Table 1 and Ref. 1; the values were measured at different temperatures or at varying acid concentrations). Thus if a change of mechanism takes place in the hydrolysis of the secondary alkyl mesylates when the alkyl group becomes more electronegative, it must be small, e.g. from S_{N1} or S_{Ni} to S_{N2} (intermediate), where a carbocation is generated in all cases from the alkyl group of the substrate. This is in accord with the results of Bentley *et al.*¹⁴⁻¹⁶

The value of -4.28 ± 0.05 ¹⁶ (or -4.03 ± 0.13)¹⁴ has been measured for the reaction constant (ρ^*) of hydrolysis of secondary alkyl mesylates. From that value it is possible to estimate the ρ^* value -4.0 ± 0.4 ($= -4.28 \times 0.94$) for the total disappearance and -3.7 ± 0.4 for the rate-limiting stage of the hydrolysis of the alkyl phenyl ethers. The values show that the generation of the positive charge is marked in the alkyl group of the transition state.

It is also possible to estimate the reaction constant in the hydrolysis of alkyl phenyl ethers when a substituent in the benzene ring is varied. The hydrolysis rate constants have been measured for *exo*-2-norbornyl phenyl ether with no substituent¹ and with the following substituents:¹⁹ *p*-COCH₃, *m*-CN and *p*-NO₂. By plotting their $\log k_p$ values vs. substituent constants σ , the reaction constant -0.76 ± 0.09 was obtained. Lambrechts and Cerfontain have measured the reaction constant -0.89 ± 0.10 from a correlation between pK_{SH^+} and σ for the protonation of the oxygen atom of methyl phenyl ethers by varying the substituent in the *para* position of the benzene ring.²⁰ From these values it is possible to estimate the value $+0.13 \pm 0.14$ for the rate-limiting stage of hydrolysis of alkyl phenyl ethers with a substituent in the benzene ring. It shows that there is a very little charge in the benzene ring at the transition state and that it is reduced rather than increased in the rate-limiting stage. This seems reasonable.

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