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Short Communication

Application of the Excess Acidity Method to the Acid-Catalyzed Hydrolysis of Isopropyl Phenyl Ether at Different Temperatures

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The excess acidity method[1] is an advanced tool to study acid-catalyzed reactions in concentrated aqueous acids. Both the basicity of the substrates and the dependence of the rate constants upon the acidity of medium can be determined, parameters which give important information about the mechanism of a reaction. The method seems to be sufficiently reliable for investigation of the position of the transition state in slow proton-transfer reactions (Ad_E2 or $A\text{-}S_E2$ mechanism).[2,3] When rate measurements of the disappearance of norbornenes were made at different temperatures and acid concentrations, the position of the transition state, as measured by the slope parameter $m^{\neq}$ of the excess acidity plot ('the excess acidity α', comparable to the Brönsted α), seemed to move slightly toward the initial state with increasing temperature.[2] An exceptionally large decrease of $m^{\neq}$ was also observed in the A-1 hydrolysis of secondary and tertiary alkyl phenyl ethers.[4] Unfortunately, the measurements were made with different substrates at different temperatures. It was therefore necessary to perform the excess acidity measurements with one substrate at several temperatures. Isopropyl phenyl ether was selected as substrate, because its rate of hydrolysis (Scheme 1; R = isopropyl) in concentrated aqueous perchloric acid solutions was found to be suitable.[5]

The rate constants for the disappearance of isopropyl phenyl ether were measured by the GC method[2] using an FFAP capillary column, norcamphor as internal standard and dichloromethane as the extracting solvent. The measurements were performed in concentrated aqueous perchloric acid at different temperatures and acid concentrations. The results are listed in Table 1. The observed rate constants are in satisfactory agreement with the ones recently determined spectrophotometrically.[5] The experimental scatter appears to be smaller by the present GC method than by the spectrophotometric method. The present data seem therefore to be more reliable.

The excess acidity method[1] was employed for the observed pseudo-unimolecular rate constants, k_ψ in the form of eqn. (1)[4]

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

which is a combination of the original eqns. (2) and (3) in the case of the unimolecular mechanism of acid-catalyzed hydrolysis (A-1; Scheme 1).[1]

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

$$\log k_\psi - \log c_{H^+} - \log[c_S/(c_S + c_{SH^+})] = m^{\neq} m^* X_0 + \log(k_0/K_{SH^+}) \quad (3)$$

In the equations, X_0 represents the excess acidity of the perchloric acid solution of acid concentration c_{H^+},[6] while $m^{\neq}$ and m^* are slope parameters, the former being indicative of the transition state (TS) and the latter of the site of proton attack. K_{SH^+} stands for the thermodynamic dissociation constant of the protonated substrate, c_S and c_{SH^+} are the concentrations of the unprotonated and protonated substrate, while k_0 is the medium-independent rate constant of the rate-limiting stage (r.l.s.) of the reaction. The parameters in eqn. (1), i.e. $m^{\neq}$, m^*, K_{SH^+} and $\log(k_0/K_{SH^+})$, can be evaluated by the method of a nonlinear least-squares minimization by fitting the experimental values of $\log k_a$ vs. c_{H^+} and X_0 ($k_a = k_\psi/c_{H^+}$; c_{H^+} and X_0 have been corrected for the temperature).[1] The curves of $\log k_a$ vs. X_0 are presented

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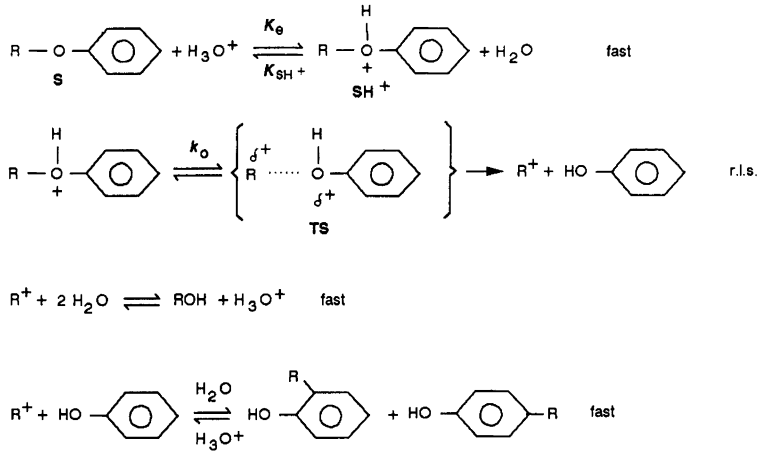

Scheme 1.

Table 1. Rate constants for the disappearance of isopropyl phenyl ether in aqueous perchloric acid at different temperatures and acid concentrations.

$c(HClO_4)$/[a] mol dm^{-3}	X_0[a]	$k_\psi/10^{-5}$ s^{-1}				
		278.2 K	288.2 K	298.2 K	308.2 K	318.2 K
6.85	2.52					1.52(1)
7.37	2.87				0.98(1)	4.44(4)
7.95	3.25			0.779(6)	3.7(1)	15.7(1)
8.26	3.51			1.64(1)	7.5(1)	32.2(4)
8.58	3.73	0.152(3)	0.774(6)	3.66(5)	15.9(1)	66.0(7)
8.89	3.95	0.358(3)	1.90(2)	8.54(9)	35.8(8)	148(3)
9.32	4.28	1.006(7)	5.13(7)	23.1(3)	93.5(7)	360(5)
9.62	4.51	2.70(2)	13.5(3)	55.8(7)	212(3)	752(16)
10.07	4.90	10.4(2)	50.0(8)	194(3)	679(16)	
10.55	5.31	36.6(9)	156(7)	580(8)		
11.00	5.74	146(3)	636(7)			
11.58	6.29	708(26)	2520(60)			

[a] Acid concentration and excess acidity at 298.2 K.[6]

in Fig. 1, and the values of the parameters are given in Table 2.

The negligible increase in the slope parameter m^* with increasing temperature, ca. 2 %/40 K, suggests that this change is within experimental error. The mean value of m^*, 0.99 ± 0.01, is typical of protonation of an ether oxygen in aqueous perchloric acid.[4,5] The slope parameter $m^{\neq}$ decreases slightly with rising temperature, as was recently also observed in the protonation of norbornenes,[2] but the change, ca. 5 %/40 K, is of the order of experimental uncertainity. The present values of m^* and $m^{\neq}$ do not clearly disagree with the conclusion made by Cox and Yates[7,8] that the parameters m^* and $m^{\neq}$ are independent of temperature. Thus, the large variation of $m^{\neq}$ recently observed with different substrates at different temperatures[4] does not seem to be due to the change in temperature (at least not alone).

Table 2. The parameters of the excess acidity equation [eqn. (1)] at different temperatures for the hydrolysis of isopropyl phenyl ether in $HClO_4$(aq).

T/K	m^*	pK_{SH^+}	$m^{\neq}$	$\log(k_0/K_{SH^+})$
278.2	0.980(11)	−7.6(2)	1.432(22)	−12.35(16)
288.2	0.990(13)	−7.4(1)	1.426(22)	−11.48(8)
298.2	0.988(16)	−7.0(2)	1.389(23)	−10.44(8)
308.2	1.001(3)	−7.2(1)	1.368(10)	−9.65(4)
318.2	1.001(2)	−6.8(1)	1.368(3)	−8.87(1)

The pK_{SH^+} values (Table 2), which indicate the basicity of isopropyl phenyl ether in aqueous perchloric acid, increase with rising temperature approximately according to eqn (4).[7,8]

$$pK_{SH^+,T(2)} = [T(1)/T(2)]pK_{SH^+,T(1)} \quad (4)$$

The values, however, are more negative than the previous ones determined spectrophotometrically: −5.80 at 273 K,[9] −6.13 at 288 K,[5] and −6.33 at 308 K,[4] values which in addition suggest a decrease with increasing temperature. A possible cause for the discrepancy, which seems real as viewed by the estimated experimental errors in the two methods, may be due to the use of UV light in the spectrophotometric method.[5,9] Light may induce excitation of the substrate and/or of its protonated form

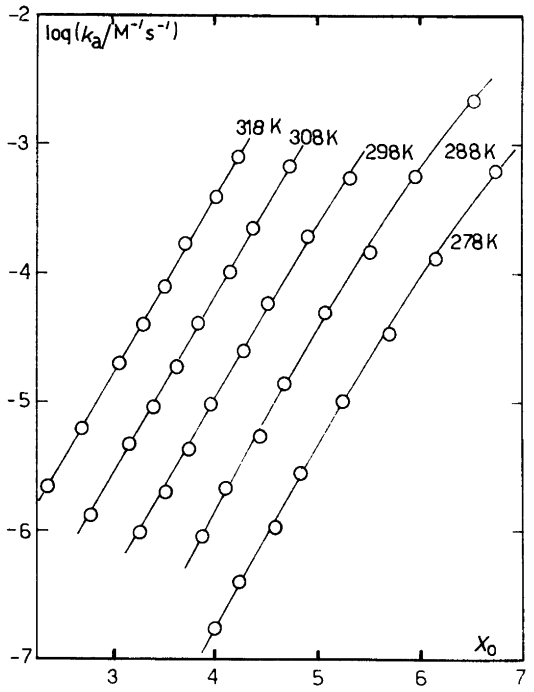

Fig. 1. Excess acidity plots for the hydrolysis of isopropyl phenyl ether in $HClO_4$(aq) at different temperatures. $k_a = k_\psi/c(HClO_4)$. The curves have been calculated by using eqn. (1) and the parameters listed in Table 2.

in an acidic medium and thus cause a change in the pK_{SH^+} values.[10]

References

1. Cox, R. A. *Acc. Chem. Res. 20* (1987) 27.
2. Lajunen, M. Virta, M. and Kylliäinen, O. *Acta Chem. Scand. 48* (1994) 122.
3. Lajunen, M. *Acta Chem. Scand. 45* (1991) 377.
4. Lajunen, M. and Tanskanen-Lehti, K. *Acta Chem. Scand. 48* (1994) 861.
5. Lajunen, M. and Kähkönen, M. *Acta Chem. Scand. 46* (1992) 726.
6. Cox, R. A. and Yates, K. *Can. J. Chem. 59* (1981) 2116.
7. Cox, R. A., Goldman, M. F. and Yates, K. *Can. J. Chem. 57* (1979) 2960.
8. Cox, R. A. and Yates, K. *Can. J. Chem. 62* (1984) 2155.
9. Arnett, E. M. and Wu, C. Y. *J Am. Chem. Soc. 82* (1960) 5660
10. Stewart, R. *The Proton: Application to Organic Chemistry*, Academic Press, New York, 1985, pp. 231–237.

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