AROMATIC REACTIVITY
XLV*. THE EFFECT OF SOLVENT COMPOSITION ON THE RATE OF ACID CLEAVAGE OF ARYLTRIMETHYLSTANNANES IN AQUEOUS ETHANOL

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SUMMARY

The rates of cleavage of $XC_6H_4SnMe_3$ compounds by aqueous ethanolic perchloric acid decrease with increase in the water content from 0.6 to about 6 M and then increase on addition of more water up to 17 M. The value of the ρ constant for the reaction also decreases in the range 0.6 to 6 M water, but then subsequently remains effectively constant. The variation in the rates and values of ρ are discussed in terms of counteracting solvating effects of water on the proton and on the transition state.

The influence of the p-F and p-Me relative to that of the m-Cl substituent varies somewhat with the water content of the medium, but that of the p-SMe group does not.

INTRODUCTION

Acid cleavages of (XC_6H_4)–MR_3 bonds (M = Si, Ge, Sn, Pb) in protic media are electrophilic substitutions in which the proton transfer to carbon from the solvent is rate-determining[2,3]. The effects of substituents can be correlated in terms of the Yukawa–Tsuno equation $\log k_{rel} = \rho \cdot [\sigma + r \cdot (\sigma^+ - \sigma)]$, where k_{rel} is the rate of reaction of the substituted compound, $XC_6H_4MR_3$, relative to that of the parent compound $C_6H_5MR_3$[3]. We describe below a study of the variation of both the rates of cleavage and the values of ρ for some $XC_6H_4SnMe_3$ compounds with the water content of a water–ethanol mixture.

RESULTS AND DISCUSSION

Table 1 lists for cleavage by 0.188 M perchloric acid in 0.67–17.4 M water in ethanol, the values of the observed first order rate constant k, values of k_{rel}, and the

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* For part XLIV, see ref. 1.

TABLE 1

CLEAVAGE OF $XC_6H_4SnMe_3$ COMPOUNDS BY 0.188 M AQUEOUS-ETHANOLIC PERCHLORIC ACID AT 50.0°

$[H_2O]$ (M)	$10^3 k_1$ (min^{-1})				k_{rel}			$-\rho$		r
	H	m-Cl	m-Br	p-F	m-Cl	m-Br	p-F	m-Cl	m-Br	p-F
0.67	337	48.1	48.3	310	0.143	0.143	0.920	2.12	2.08	0.33
1.78	213	36.5	36.4	207	0.171	0.171	0.972	1.92	1.90	0.41
2.89	187	33.8	33.2	181	0.181	0.178	0.968	1.86	1.85	0.41
4.00	170	31.7	32.5	169	0.186	0.191	0.994	1.83	1.77	0.45
5.56	163	32.3	31.8	168	0.198	0.195	1.03	1.76	1.76	0.51
7.34	166	33.1	33.0	171	0.199	0.199	1.03	1.76	1.73	0.50
11.8	187	37.5	36.9	194	0.201	0.197	1.04	1.75	1.74	0.52
17.4	242	47.0	47.8	263	0.195	0.198	1.09	1.78	1.74	0.61

values of ρ derived from the k_{rel} values for the compounds with X = m-Cl and m-Br*. Table 2 gives similar data for cleavage of a slightly wider range of compounds by 0.047 M perchloric acid in a comparable solvent range.

TABLE 2

CLEAVAGE OF $XC_6H_4SnMe_3$ COMPOUNDS BY 0.047 M AQUEOUS ETHANOLIC PERCHLORIC ACID AT 50.0°

$[H_2O]$ (M)	$10^3 k_1$ (min^{-1})					k_{rel}				$-\rho$	r		
	H	m-Cl	p-F	p-Me	p-SMe	m-Cl	p-F	p-Me	p-SMe	m-Cl	p-F	p-Me	p-SMe
1.00	55.9	9.06	46.2	209	285	0.162	0.826	3.74	5.10	1.98	0.15	0.85	0.59
2.11	40.0	7.65	36.8	151	194	0.191	0.920	3.78	4.85	1.80	0.31	1.06	0.63
7.66	34.2	7.27	32.9	122	147	0.213	0.962	3.57	4.30	1.69	0.39	1.12	0.62
17.7	50.0	10.5	52.1	185	227	0.210	1.04	3.70	4.54	1.70	0.52	1.17	0.64

It will be seen from Table 1 and Fig. 1 that as water is added to ethanol the rate constants go through a minimum at about 6 M water content. The degree of protonation of a neutral nitrogen base by 0.1 M aqueous-ethanolic hydrochloric acid, given by $[BH^+]/[B]$, shows a generally similar variation with water content in the region concerned, but with a flat minimum at 30–40 mole %**,[4,5], and it is reasonable to assume that the factors which govern the ratio $[BH^+]/[B]$ also mainly govern

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*. Values of ρ for the m-Cl and m-Br compounds have been derived by use of σ^+-constants in the equation $\log k_{rel} = \rho \cdot \sigma^+$. This is partly justified by the fact that the average value of r in the Yukawa–Tsuno equation is probably > 0.5, but has mainly been done for simplicity, since the σ^+-constants are effectively equal for the two substituents and so lead to similar ρ values for the two halogeno compounds, whereas use of σ-constants, which differ somewhat for the two meta-halogens, would give two somewhat different sets of ρ values. Slightly higher ρ values would result if σ-constants were used, but the conclusions would be wholly unaffected.

** We have avoided at this point use of the term "acidity function", since there is doubt about the applicability of the acidity function concept in aqueous organic media[5]; the indicator ratio $[BH^+]/[B]$ is an experimentally obtained quantity.

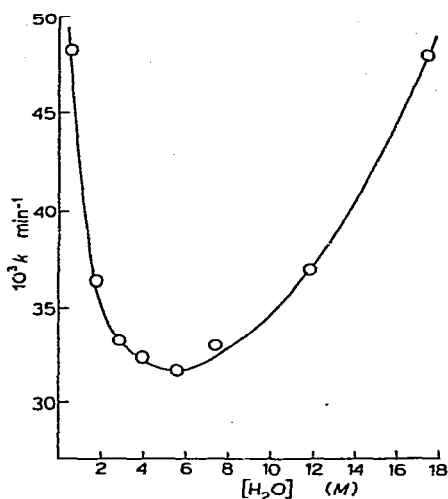Fig. 1..Plot of the rate constant for cleavage of m-BrC$_6$H$_4$SnMe$_3$ against the concentration of water in 0.188 M aqueous ethanol at 50°.

the notional ratio $[SH^+]^‡/[S]$ ($[SH^+]^‡$ refers to the pseudoequilibrium "concentration" of the transition state involving an oxonium ion and the aromatic substrate S). For a more complete analysis of these factors, discussions of the acidity function variations should be consulted[4,5]. The main considerations, however, are that as water is added to the ethanolic acid, ethoxonium ions are first gradually replaced by the less acidic hydroxonium ions, but as more water is added and the proton availability falls, the quasi-crystalline structure of the water becomes more complete and the medium becomes less effective at stabilizing the hydroxonium ions by specific solvation, so that the proton availability rises again. The effectiveness of solvation of the charged anilinium ions is also of considerable importance in determining the indicator ratio, and analogously the solvation of the diffuse charged transition state is important in determining the rate of the cleavage reaction, such general solvation being likely to increase progressively with the water content of the medium. It would not be expected that the position of the minima would necessarily be the same for the indicator ratio and the rate of cleavage. (The rate of the acid-catalysed rearrangement of 1-phenyl-2-buten-1-ol is known to go through a minimum at ca. 30 mole% water in 1.0 M aqueous ethanolic hydrochloric acid, whereas the minimum for the indicator ratio is at ca. 50 mole% water at this acid concentration)[6].

It will also be seen from Table 1 that the value of ρ falls as the water content is increased from 0.67 M to about 5–6 M, and then remains effectively constant. (The overall change in k_{rel} for the m-halogeno compounds over the range 0.67 to about 5.6 M is outside experimental error, but the subsequent variations are not.) If there were no other influence at work, at the low water concentrations the value of ρ might be expected to rise with increasing water content as the protons become less available since the transition state should become closer to the Wheland Intermediate, and thus involve a greater charge on the aromatic ring, as the electrophile becomes less reactive. At the same time, however, for a given degree of charge transfer to the ring, the interaction of the substituents with the charge will be smaller the more effective the

dispersal of the charge by solvation, and on this account ρ will tend to fall as the water content is increased. It seems that in this case, as distinct from the variation in the rate, the latter effect predominates in the low water range, and that subsequently the two influences effectively cancel.

Comparison of Tables 1 and 2 show that the ρ values appear to be slightly higher (*i.e.* the values of k_{rel} for the *m*-chloro compound lower) with 0.188 M than with 0.047 M perchloric acid for a given water content. The maximum differences are only about 10%, however, so that if one set of k_{rel} values were systematically 5% high and the other 5% low the apparent difference would be accounted for, and such margins of error cannot be ruled out.

There are small but definite variations in the influence of *p*-F and *p*-Me groups relative to that of *meta*-halogens as the water content is varied. This is most obvious for the *p*-F group, which deactivates at the lowest and activates at the highest water concentrations used (Tables 1 and 2). For convenience in considering the magnitude of the variation, values of r derived from the Yukawa–Tsuno equation are shown in Tables 1 and 2. The derived values of r for the *p*-F and *p*-Me groups are rather sensitive to errors in k_{rel}, and a 5% error in k_{rel} for the *p*-F compound would give rise to an error of 0.08 in the value of r. The variations in r are too large to be ascribed to such errors, however, and it seems that there is a significant increase in the contribution from the electron-releasing resonance component of the substituent effect in the case of *p*-F and *p*-Me groups. There is, however, no significant change in the value of r for the *p*-SMe group, which would be expected to be markedly more sensitive to any real change in the electron demand in the system, since the value of $(\sigma^+ - \sigma)$, which is a measure of the variability of response to different types of electron demand, is larger for this group (*viz.* 0.60) than any other yet studied. While more data would be needed for certainty, it seems that the variable influences of the *p*-F and *p*-Me substituents may involve effects specific to those substituents rather than reflect any substantial general change in the nature of the electron demand in the reacting system as the water content is varied. The variations in r for the *p*-F and *p*-Me groups serve to emphasize once again that overall r values for a reaction averaged over several substituents can be markedly dependent on the choice of substituents involved, and thus great care must be exercised in considering the variation in r from one reaction to another (*cf.* ref. 7).

EXPERIMENTAL

Materials

The preparation of the $XC_6H_4SnMe_3$ compounds have been previously described[8].

In the preparation of the 0.188 M perchloric acid solutions, 5 ml of 9.40 M aqueous perchloric acid were diluted with an appropriate quantity of water and ethanol was added to give a total value of 250 ml. The 0.047 M solutions were prepared analogously.

Rate Measurements

These were carried out spectrophotometrically at $50.05 \pm 0.05°$, as previously described[9], natural infinity values of the optical density being used. The wave-lengths

used were as follows: (X=) H, 259; m-Cl, m-Br, 276; p-F, 270 and 274; p-Me, 272 and 273; p-SMe, 266 and 271 nm.

REFERENCES

1 C. EABORN, A. R. THOMPSON AND D. R. M. WALTON, *J. Chem. Soc. B*, (1970) 357.
2 C. EABORN, *Pure Appl. Chem.*, 19 (1969) 375; C. EABORN AND R. W. BOTT, in A. G. MACDIARMID (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Part 1, New York, 1968, pp. 407–414, and references therein.
3 R. O. C. NORMAN AND R. TAYLOR, *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, 1965, pp. 234–245.
4 E. A. BRAUDE AND E. S. STERN, *J. Chem. Soc.*, (1948) 1976.
5 F. A. LONG AND M. A. PAUL, *Chem. Rev.*, 57 (1957) 935; C. H. ROCHESTER, *Acidity Functions*, Academic Press, London, 1970, Chapter 6.
6 E. A. BRAUDE AND E. S. STERN, *J. Chem. Soc.*, (1948) 1982.
7 R. W. BOTT AND C. EABORN, *J. Chem. Soc.*, (1963) 2139.
8 C. EABORN AND J. A. WATERS, *J. Chem. Soc.*, (1962) 1131; C. EABORN, H. L. HORNFELD AND D. R. M. WALTON, *J. Organometal. Chem.*, 10 (1967) 529.
9 C. EABORN AND J. A. WATERS, *J. Chem. Soc.*, (1961) 542.