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Reactivity Patterns in Phenolysis Reactions. Evidence for the Importance of π Complexing

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Summary Changing reactivity patterns in solvolysis of a series of alkyl and arylalkyl chlorides in six mixed phenolic solvents provide evidence for the importance of π-complexing in phenolysis reactions.

Earlier studies[1] have demonstrated that the solvolytic reactivity of the strong π-acceptor substrate, 2,4,7-trinitro-9-fluorenyl toluene-*p*-sulphonate, can be increased by a factor of 10^3 or more by complexation with aromatic π-donors. In such systems, designed to maximize the chemical effects of complexing, strong charge-transfer interaction between the ground state ester and donor is enhanced in the solvolysis transition state. Since a variety of carbonium ions are strong π-acceptors[2] it seemed possible that π-complexing could have an important influence on the rates of solvolysis of arylalkyl halides and related compounds in π-donor solvents, even where there is no appreciable donor–acceptor interaction between the ground state reactants. We report here the results of an examination of reactivity patterns in phenolysis reactions, which indicates that effects due to π complexing can indeed be important.

Table. First order rate constants (10^5 k/s^{-1}) for phenolysis.[a]

Phenol[b]	Substrate Bu^{t}Cl[c]	(Ia)	(Ib)	(Ic)	(Id)	(IIa)[d]	(IIb)[e]
p-Chlorophenol ..	0·027	475	270	4·9	0·019	6·6	0·067
Phenol	0·025	293	139	2·7	0·021	2·9	0·067
m-Cresol	0·012	144	56	1·1	0·017	2·2	0·063
p-Cresol	0·010	128	55	1·1	0·019	1·8	0·060
2-Naphthol	0·021	245	89	1·8	0·020	3·3	0·068
1-Naphthol	0·014	151	67	1·6	0·11	12·1	1·51

[a] At 25 °C unless otherwise indicated. [b] 50:50 (v/v, 60 °C) phenol–dioxan containing 0·05 M sodium phenolate or 2,6-lutidine. [c] Extrapolated from rate constants at 55 and 75 °C. [d] 75 °C. [e] 100 °C.

The substrates studied were t-butyl chloride, the phenylmethylethyl chlorides (Ia—d), and the fluorenyl chlorides (IIa and b). First order rate constants, measured titrimetrically in a series of 50:50 (v/v, 60 °C) phenol–dioxan mixtures containing 0·05 M of the corresponding sodium phenolate or 2,6-lutidine (slight molar excess over substrate), are listed in the Table. Under these conditions the theoretical amount of HCl was liberated and the kinetics were strictly first order in substrate. The rate constants were independent of base concentration, and were identical with 2,6-lutidine and phenolate base. No spectral evidence for charge-transfer complexation could be detected in any of the reaction mixtures. Selected product analyses indicate that the tertiary halides lead entirely to the expected aryl ether plus olefin, while (IIa) leads to aryl fluorenyl ethers and 9-fluorenylphenols.

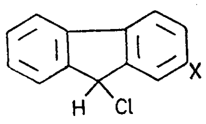
t-Butyl chloride was chosen to define a 'standard' reactivity pattern in the absence of π-complexing effects.

This pattern is complex but can be understood qualitatively at least on the basis of the order of acidities[3] (*p*-chlorophenol > 2-naphthol > 1-naphthol > phenol > *m*-cresol > *p*-cresol) and the molar volumes (*i.e.*, molarity of OH groups) of the phenols. This pattern of reactivity, with minor variations, is maintained with chlorides (Ia), (Ib), and (Ic), suggesting that π-complexing is of negligible importance in the stabilization of the respective phenolysis transition states. The importance of solvent π-donor strengths (1-naphthol > 2-naphthol > *p*-cresol > *m*-cresol > phenol > *p*-chlorophenol) is clearly reflected in the reactivity patterns for (Id), (IIa), and (IIb). The clearest indication of the increased importance of π-complexing with electron-withdrawing substituents and with the larger planar fluorenyl ring system is the ratio of the 1-naphthol: 2-naphthol rates. This ratio changes over a factor of 36 as follows: t-butyl chloride 0·67, (Ia) 0·62, (Ib) 0·75, (Ic) 0·89, (IIa) 3·7, (Id) 5·5, and (IIb) 22.

$XC_6H_4CMe_2Cl$

(I)

a; X = *p*-F
b; X = H
c; X = *m*-Cl
d; X = *p*-NO_2



(II)

a; X = H
b; X = NO_2

A mechanism in which electron transfer precedes bond fission[4] seems to be ruled out by the independence of the rates on the concentration and identity of the base, by the normal effects of substitution on the rates in all six solvents, and by the results of a more complete study of 1-(*p*-nitrophenyl)ethyl *p*-nitrobenzoate.[5]

Evidence for stabilization of the tri-*p*-anisylmethyl cation by π-complexation with phenols has recently been reported by Bunton and Huang.[6] The possibility of π-complexing in phenolysis is relevant also to the mechanism for the retention of configuration in the phenolysis of 1-phenylethyl chloride[7] and related compounds.[6]

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