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A STABILITY-SELECTIVITY RELATIONSHIP FOR PHENOLYSES OF ALKYL CHLORIDES AND p-NITROBENZOATES

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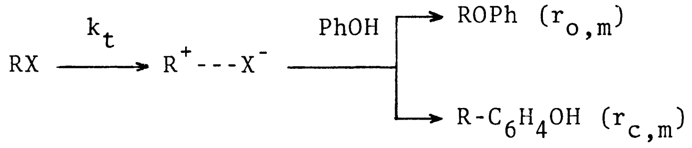
The existence of a linear free-energy relationship between the phenolic reactivity and the selectivity for attack of the phenol molecule on carbonium ion intermediates has been established for the titled substrates. The examples are the first ones for the reaction between the carbonium ions and an ambident molecule.

A linear free-energy relationship between hydrolysis rates of alkyl chlorides reacting via carbonium ions and the selectivity for attack on the nucleophiles (by azide ion and water) was first observed by Sneen, Carter, and Kay.[1)] This treatment was extended to include a number of less reactive chlorides,[2,3)] and 2-adamanty p-substituted-benzenesulfonates,[4)] using azide[2)] or ethanol[3,4)] as a competing nucleophile.

In view of the existence of such stability-selectivity relationship with regard to two competitive nucleophiles,[2-4)] it seemed of interest to verify whether the Sneen-Carter-Kay treatment[1)] is successful when the S_N1 solvolysis is conducted in a phenolic solvent which acts as an ambident nucleophile to afford an alkyl phenyl ether (with proportion $r_{o,m}$[5a)]) and alkylated phenols (with proportion $r_{c,m}$[5a)]).



Scheme

From inspection of Figure it is obvious that such a stability-selectivity

Table 1. Rates and products ratios for the reaction of phenol molecule with the ion pair intermediates in the phenolyses of alkyl chlorides in a 50 wt% phenol-benzene solvent at 50°a)

RCl R-	k_t sec^{-1}	$r_{o,m}$ b) %	$r_{c,m}$ b) %
Tetrahydrolinalyl (1)	9.90 x 10^{-3}	99.84	0.16
Ethylisobutylmethylcarbinyl (2)	6.20 x 10^{-3}	99.5	0.5
1-Phenylethyl (3)	1.42 x 10^{-3}	98.5	1.5
tert-Amyl (4)	7.17 x 10^{-4}	99.1	0.9
tert-Butyl (5)	2.67 x 10^{-4}	99.0	1.0
exo-2-Norbornyl (6)	1.43 x 10^{-4}	96.8	3.2
Phenyl-tert-butylcarbinyl (7)	7.96 x 10^{-6}c)	94.3	5.7
1-Adamantyl (8)d)	5.75 x 10^{-6}c)	91.5e)	8.5e)
Isopropyl (9)	1.72 x 10^{-8}c)	89.1	10.9
sec-Butyl (10)	1.70 x 10^{-8}c)	88.0	12.0
2-Octyl (11)	1.78 x 10^{-9}c)	73.2	26.8

a) Satisfactory analytical data have been obtained on all new compounds.
b) Determined by glc. c) Extrapolated value from data at 75°, 100°, and 125°.
d) Cited from Ref. 5a. e) The value at 100°.

Table 2. Rates and products ratios for the reaction of phenol molecule with the ion pair intermediates in the phenolyses of aralkyl p-nitrobenzoates in phenol at 125°a)

$ROOCC_6H_4NO_2$(p-) R-	k_t sec^{-1}	$r_{o,m}$ b) %	$r_{c,m}$ b) %
$\text{An-}\underset{\text{Me}}{\text{CH}}\text{-}$ (12)	2.00c)	99.5	0.5
$\text{Ph-}\underset{\text{Et}}{\text{CMe}}\text{-}$ (13)	6.43 x 10^{-2}	99	1
$\text{i-Hex-}\underset{\text{Et}}{\text{CMe}}\text{-}$ (14)	5.69 x 10^{-2}	98.5	1.5
$\text{p-Cl-C}_6\text{H}_4\text{-}\underset{\text{Ph}}{\text{CH}}\text{-}$ (15)	2.86 x 10^{-3}c)	94	6
$\text{Ph-}\underset{\text{Me}}{\text{CH}}\text{-}$ (16)	1.71 x 10^{-4}	89.5	10.5
$\text{Ph-}\underset{\text{Et}}{\text{CH}}\text{-}$ (17)	4.03 x 10^{-5}	82.8	17.2
$\text{Ph-}\underset{\text{i-Pr}}{\text{CH}}\text{-}$ (18)	2.05 x 10^{-5}	84.4	15.6
$\text{Ph-}\underset{\text{t-Bu}}{\text{CH}}\text{-}$ (19)	8.50 x 10^{-6}	75.6	24.4
$\text{p-O}_2\text{N-C}_6\text{H}_4\text{-}\underset{\text{Me}}{\text{CH}}\text{-}$ (20)	3.18 x 10^{-6}	69.3	30.7

a) Satisfactory analytical data have been obtained on all new compounds.
b) Determined by glc. c) The calculated value from data in a 50 wt% phenol-benzene solvent (assuming m = 1.00).

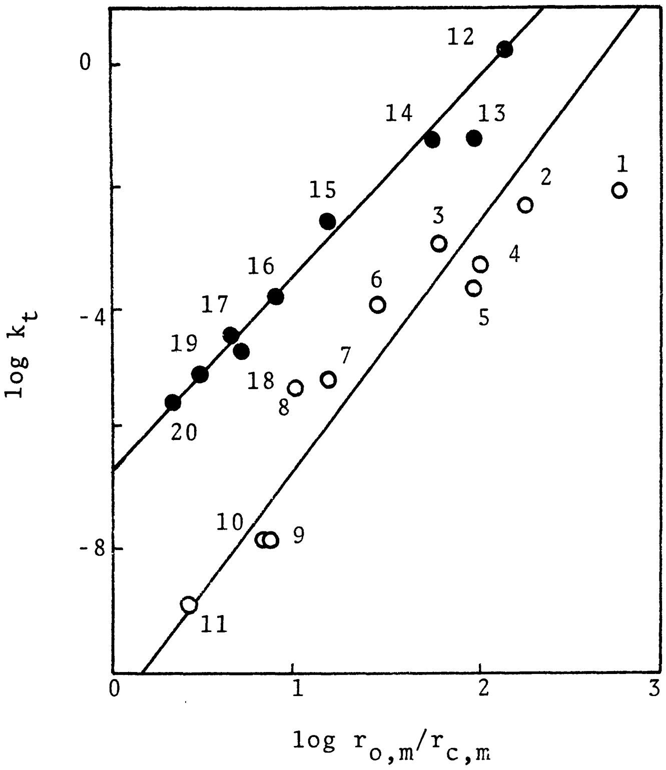


Figure. A plot of log k_t against log $r_{o,m}/r_{c,m}$ for the phenolyses of alkyl chlorides (o) in 50 wt% phenol-benzene at 50° and of aralkyl p-nitrobenzoates (●) in phenol at 125°.

relation does exist between log k_t (titrimetric rate constant over a range varying 6 - 7 powers of ten) for phenolyses of eleven alkyl chlorides (Table 1) and of nine aralkyl p-nitrobenzoates (Table 2) and log $r_{o,m}/r_{c,m}$ (a measure of selectivity of a carbonium ion towards O- and C-alkylations of the phenol molecule). The k_t's, in the absence of the added base, were obtained by the graphic extrapolation method[5] from the titrimetric rate constants observed in the presence of variable concentrations of a base. The $r_{c,m}$'s were calculated for the sum of the yields of o- and p-alkylphenols. The linearity for the correlation is reasonably good for the chlorides and benzoates; the correlation coefficients for the least square lines are 0.93 and 0.99; the standard deviations in log k_t are 1.08 and 0.37, respectively.

Even if the solvolysis rate reflects only the stability of the intermediate, the k_t may not afford an entirely accurate estimate of the relative stability of carbonium ions, because the intrinsic ionization rate may be greater than the k_t. Furthermore, similarly to the hydrolysis case which was discussed by Schleyer and his collaborators,[2] more than two intermediates may be involved for a phenolysis of a single substrate.6) In addition, the devided treatment of $r_{c,m}$ into two $r_{c,m}$'s respectively for the ortho- and para-alkylphenols was unsuccessful for this linear free-energy relationship. These make the physical meaning of the selectivity of the carbonium ion a little ambiguous.

Although these deficiencies, in addition to those which were criticized by Schleyer2) for the stability-selectivity relationship, should not be underestimated, the good straight lines for the stability-selectivity relationship, observed in these phenolyses, provide a supporting evidence for a typical S_N1 nature of solvolyses of these secondary and tertiary systems in the phenolic solvent.

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