Phenolyses of 1-Aryl-1-methylethyl *p*-Nitrobenzoates and Some Simple Alkyl Systems: Characteristic Features of Phenol as a Solvolytic Solvent

By **Kunio Okamoto,* Tomomi Kinoshita, Ken'ichi Takeuchi, Yutaka Shimizu, Kunihiko Takatsuki, Takaki Kamio, and Shin Matsui,** Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

In order to clarify the features of phenol as solvolytic solvent, phenolysis rates of the title compounds have been measured titrimetrically in pure phenol and in phenol–benzene as solvent at 50—125°. Specific rates in the presence of sodium phenoxide (apparent first-order rate constants) for the phenolysis of a series of α-methylated alkyl systems (RX; X = Br or OTs) change in the sequence R = Me > Et > $Pr^i \ll Bu^t$ in phenol–benzene (1 :1 w/w) at 125°. The first-order rate constants for the phenolysis of 1-aryl-1-methylethyl *p*-nitrobenzoates [$ArC(Me)_2$-OPNB; Ar = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Ph-, *m*-ClC_6H_4, and *p*-$NO_2C_6H_4$] obey a $\rho\sigma^+$ relationship with good precision (ρ −4.61 ; *r* 0.998 6) in pure phenol at 50°. The first-order phenolysis rates for a series of β-methylated primary alkyl tosylates (ROTs) increase in the order R = Me < Et $\simeq$ Pr^n < Bu^i $\simeq$ neo-C_5H_{11} in pure phenol at 100 and 125°, indicating the high ionizing power of phenol, which is also deduced from the high Grunwald–Winstein *Y* value (1.77). The first-order rate constants for solvolyses of neopentyl tosylate in several hydroxylic solvents, including pure phenol, obey an *mY* relationship with fairly good precision (*m* +0.633 ; *r* 0.977 0). These results along with examples previously reported, demonstrate that phenol possesses features common to solvolytic solvents.

We have reported[1] many examples of the retentive phenolyses of the substrates with no group imposing a rigid configuration. In addition to the ability of phenol to control the steric course of solvolyses, another important characteristic has been revealed by the phenolyses of some simple alkyl systems, indicating that phenol may be regarded as a solvolytic solvent.[2] However, examples of phenol as a solvolytic solvent are rare. Consequently, we have investigated the phenolysis of α-methylated alkyl bromides or tosylates, 1-aryl-1-methylethyl *p*-nitrobenzoates, and β-methylated primary alkyl tosylates. The three series of substrates have been selected as a basic series for the study of the dichotomy of the S_N mechanism, a model system for examination of $\rho\sigma^+$ relationship in phenol, and a simple series of primary alkyl systems for examination of the solvent ionizing power of phenol, respectively.

RESULTS AND DISCUSSION

Phenolysis Rates of Methyl, Ethyl, Isopropyl, and t-Butyl Systems.—In the early stages of their study of nucleophilic substitution, Hughes and Ingold[3] observed the reactivity sequence Me > Et > $Pr^i \ll Bu^t$ in the solvolysis of alkyl bromides in the presence of sodium hydroxide in 80% aqueous ethanol, and explained the sequence on the basis of the dichotomy of the S_N mechanism. Since this sequence may be considered as a tool for diagnosis of a solvolytic solvent, we decided to see whether this sequence, classical and fundamental, is observed in pure phenol or not.

Phenolysis rates of methyl and ethyl tosylates at 75° and of ethyl, isopropyl, and t-butyl bromides at 125° were measured titrimetrically in the presence of sodium phenoxide in phenol–benzene (1 : 1 w/w) as solvent.

The second-order rate constants k_2 for methyl and ethyl systems and the first-order rate constant k_1 for t-butyl bromide are in Table 1. In the case of isopropyl bromide, it was assumed that the phenolysis proceeded by concurrent S_N1 and S_N2 mechanisms; † the first- and second-order rate constants for the bromide were graphically estimated as follows. In the presence of various concentrations of added sodium phenoxide the initial specific rates $k_1°$ were determined (Table 5). Then, the values for $k_1°$ were plotted against the sodium phenoxide concentration to give a straight line. The first- and second-order rate constants were evaluated from the intercept and slope, respectively, of the $k_1°$ plot and are shown in Table 1.

TABLE 1

Solvolysis rates of α-methylated alkyl systems in phenol–benzene (1 : 1 w/w) at 125.0 ± 0.1°

	MeOTs [a]	EtOTs [a]	EtBr	Pr^iBr	Bu^tBr
10^5k_2/l mol^{-1} s^{-1}	400	27.0	573	39.5 [c]	
10^5k_1/s^{-1} [b]				2.75 [c]	3 250
10^5 Specific rate in 0.1N-NaOPh [d]	40.0	2.70	57.3	6.70	3 250

[a] At 75°. [b] Accurate to within ±2.5%. [c] Calculated graphically. [d] Calculated from k_2.

From the sequence of specific rate in 0.1N-sodium phenoxide (Table 1), it is clear that the phenolysis rate changes in the sequence Me > Et > $Pr^i \ll Bu^t$. This classical sequence, originally found in 80% aqueous ethanol,[3] provides an additional example in which phenol plays the role of a typical solvolytic solvent.

---

† Although the debate[4] on the concurrence of the mechanisms in a borderline case has not been settled, we tentatively treated the data on the basis of concurrent mechanisms.

[1] (*a*) K. Okamoto, T. Kinoshita, T. Oshida, T. Yamamoto, Y. Ito, and M. Dohi, *J.C.S. Perkin II*, 1976, 1617; (*b*) K. Okamoto, T. Kinoshita, Y. Takemura, and H. Yoneda, *ibid.*, 1975, 1426, and references therein.

[2] (*a*) H. Shingu and K. Okamoto, *Nippon Kagaku Zasshi*, 1960, **81**, 111 (*Chem. Abs.*, 1962, **36**, 380b); (*b*) K. Okamoto, K. Matsubara, and T. Kinoshita, *Bull. Chem. Soc. Japan*, 1972, **45**, 1191; (*c*) K. Okamoto and T. Kinoshita, *ibid.*, p. 2802; (*d*) K. Okamoto, T. Kinoshita, and Y. Ito, *ibid.*, 1973, **46**, 2905; (*e*) K. Okamoto and T. Kinoshita, *Chem. Letters*, 1974, 1037.

[3] (*a*) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1933, 1571; (*b*) J. L. Gleave, E. D. Hughes, and C. K. Ingold, *ibid.*, 1935, 236.

[4] For a recent example, see A. Queen and T. C. Matts, *Tetrahedron Letters*, 1975, 1503, and references therein.

Phenolysis Rates for 1-*Aryl*-1-*methylethyl* p-*Nitrobenzoates*.—Brown and Okamoto[5] selected 90% aqueous acetone as a standard solvent for their study of the $\rho\sigma^+$ relationship. To examine the solvolytic features of pure phenol, we tried to establish whether this basic linear free-energy relationship holds in the case of phenolysis. The solvolyses of various 1-aryl-1-methylethyl *p*-nitrobenzoates in pure phenol were carried out at 50°.* Among the *p*-nitrobenzoates, the *p*-methyl and *p*-methoxy-derivatives were so reactive at 50° that the rate constants were graphically estimated from data measured in phenol–benzene (Tables 6 and 7) by the use of the Grunwald–Winstein mY relationship.[6] The five first-order rate constants (Table 2), including two extrapolated values, obey a $\rho\sigma^+$ relationship (ρ −4.61; r 0.998 6; standard deviation along the log k_X/k_H ordinate 0.173). The ρ value closely resembles that (−3.74) for the hydrolysis of the *p*-nitrobenzoates in 70% aqueous acetone,[7] and that (−4.54) for the hydrolysis of the chlorides in 90% aqueous acetone.[5] These results also demonstrate that phenol possesses properties common to solvolytic solvents.†

TABLE 2

Phenolysis rates of substituted 1-aryl-1-methylethyl *p*-nitrobenzoates in pure phenol at 50.0°

Aryl substituent	Concentration (M)	[NaOPh]/ N	10^3k_1 [a]/ s^{-1}	$k_{1,rel}$
p-NO_2	0.097 9	0.110	0.000 482	0.000 380
m-Cl	0.097 0	0.108	0.033 5	0.026 4
H	0.095 7	0.107	1.27	1.00
p-Me	0.100	1.017	37.8 [b]	29.8
p-MeO	0.011 1	0.011 3	(10.2 ± 5.5) [c]	(8.0 ± 4.3)
	~0.018 1	~0.018 6	× 10^3	× 10^3

[a] Accurate to within ±2.0%, unless otherwise noted. [b,c] Extrapolated from the data in Tables 6 and 7, respectively, by use of the Grunwald–Winstein mY plot.[6]

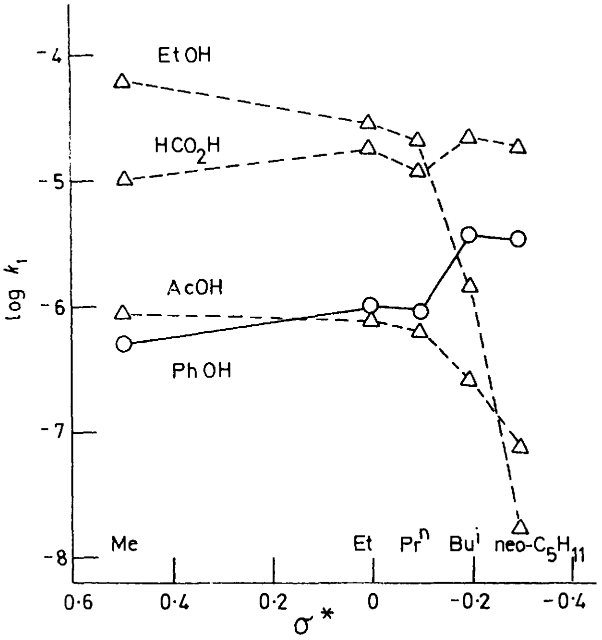
Phenolysis Rates of Methyl, Ethyl, n-Propyl, Isobutyl, and Neopentyl Tosylates.—Winstein and Marshall[9] have demonstrated that the solvolysis rates of a series of primary alkyl bromides increase in the order Me < Et ≃ Pr^n < Bu^i ≃ neo-C_5H_{11} in formic acid as solvent. When the same series of primary alkyl tosylates were subjected to phenolysis in pure phenol at 100 and 125°, a similar reactivity sequence was observed (Table 3). Following the treatment of Winstein and his collaborators[10] the log k_1 values extrapolated to 75° were plotted against Taft's σ^* values[11] (Figure), and compared with the reported plots for formolysis, acetolysis, and ethanolysis.[10] The similarity of phenol to formic acid in the reaction sequence and the shape of the plot can be clearly seen in the Figure.

TABLE 3

Solvolysis rates of some β-methylated primary alkyl tosylates in phenol

ROTs	$10^6k_1/s^{-1}$			$\Delta H^‡/$	$\Delta S^‡/$
R	125° [a]	100° [a]	75° [b,c]	J mol^{-1}	J K^{-1} mol^{-1}
Me	16.9	3.24	0.49	7.87 × 10^4	−142
Et	51.2	8.99	1.0	8.33 × 10^4	−121
Pr^n	41.4	6.88	0.88	8.58 × 10^4	−117
Bu^i	263	35.8	3.6	9.58 × 10^4	−75
neo-C_5H_{11}	291	36.1	3.3	10.0 × 10^4	−63

[a] Accurate to within ±1.0%. [b] Accurate to within ±3.5%. [c] Extrapolated from the data at 125 and 100°.



log k_1 *versus* σ^* plots for β-methylated primary alkyl tosylates in various solvents at 75°; ○ observed; △ reported by Diaz *et al.*[10]

In addition to the graphical comparison the large Y value (1.77) also indicates the high ionizing power of phenol, which is estimated by extrapolation of the reported Y values for phenol–benzene mixtures.[2b] Thus, in the sequence of Y values[6] for several solvents the value for phenol is between those for formic acid (2.05) and 80% aqueous ethanol (0.00). The value for phenol is almost equal to that of 50% aqueous ethanol (1.655) and substantially larger than that of acetic acid

---

* Because of the high reactivity of 1-aryl-1-methylethyl chlorides which were originally selected as a standard substrate,[5] the *p*-nitrobenzoates were subjected to phenolysis.

† The Yukawa–Tsuno treatment[8] [$\sigma^0 + r(\sigma^+ - \sigma^0)$] of the same data (Table 2) gives rise to a better correlation coefficient, 0.999 5, where ρ and r values are estimated to be −4.33 and 1.18, respectively. However, because of the uncertainty concerned with the distant extrapolation for the estimation of the k_1 for the *p*-methoxy-derivative (Table 7), it seems difficult to interpret unambiguously the refinement due to the Yukawa–Tsuno treatment.

[5] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979, and references therein.

[6] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

[7] H. Tanida and H. Matsumura, *J. Amer. Chem. Soc.*, 1973, **95**, 1586.

[8] Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Japan*, 1966, **39**, 2274.

[9] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1120.

[10] A. Diaz, I. L. Reich, and S. Winstein, *J. Amer. Chem. Soc.*, 1969, **91**, 5637.

[11] R. W. Taft, jun., in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

(−1.64) which has been widely used as a solvent for the study of solvolysis.

When the log k_1 values for neopentyl tosylate in ethanol,[10] acetic acid,[10] phenol, and formic acid [10] are plotted against the respective Y values, a linear relation (m 0.633; r 0.977 0; standard deviation along the log k_1 ordinate 0.368) was observed. Although the m value (0.633) is not as large as that (0.9—1.0) [12] found for typical S_N1 substrates, it is rather high compared with the m value for general primary alkyl systems,[12] suggesting the S_N1 character of neopentyl phenolysis. Stronger evidence for the S_N1 character of neopentyl phenolysis is obtained from the fact that all the phenolysis products (1,1-dimethylpropyl phenyl ether and 1,1-dimethylpropylphenol) from neopentyl tosylate have a rearranged structure.

In conclusion, these results clearly characterize phenol as a useful S_N1 solvolytic solvent.

EXPERIMENTAL

^{1}H N.m.r. spectra and i.r. spectra were taken with a Hitachi model R24 60 MHz instrument and with a Hitachi model 215 spectrophotometer, respectively. G.l.c. was performed with a Hitachi model 023-6003 instrument with an ionization detector. Microanalyses were performed by the Elemental Analysis Centre, Kyoto University.

Materials.—1-(p-Methoxyphenyl)-,[13] 1-(p-methylphenyl)-,[14] 1-phenyl-,[14] 1-(m-chlorophenyl)-,[13] and 1-(p-nitrophenyl)-1-methylethanol [15] were prepared by known methods. 1-(p-Methoxyphenyl)-,[7] 1-(p-methylphenyl)-,[7] 1-phenyl-,[16] 1-(m-chlorophenyl)-, and 1-(p-nitrophenyl)-1-methylethyl p-nitrobenzoates were synthesized by reactions of the respective alcohols with p-nitrobenzoyl chloride in pyridine; physical and spectral data are summarized for two new p-nitrobenzoates in Table 4.

TABLE 4

M.p.s, spectral data, and elemental compositions for 1-methyl-1-(m-chlorophenyl)ethyl (A) and 1-methyl-1-(p-nitrophenyl)ethyl p-nitrobenzoate (B)

		(A)	(B)
M.p. (°C) [a]		105.5—106.5	144.0—145.0
$\nu_{max.}$/cm^{-1}		2 990 [b]	2 980 [c]
		1 730 [b]	1 720 [c]
		1 530 [b]	1 520 [c]
		1 280 [b]	1 350 [c]
τ		1.85—2.77 (8 H, m) [b]	1.80—2.53 (8 H, m) [d]
		8.07 (6 H, s) [b]	8.07 (6 H, s) [d]
Found	C (%)	59.85	58.45
	H (%)	4.15	4.3
Required	C (%)	60.1	58.2
	H (%)	4.4	4.25

[a] Uncorrected. [b] In CCl_4. [c] In $CHCl_3$. [d] In $CDCl_3$.

n-Propyl,[17] isobutyl,[17] and neopentyl tosylates [17] were prepared from corresponding alcohols and toluene-p-sulphonyl chloride in pyridine.

Sodium phenoxide was prepared by refluxing a toluene solution of phenol with sodium metal and was purified by digesting with dry benzene six times; the purity was 99.7%, determined by titration.

Other organic reagents were of analytical grade and were fractionated prior to use. Karl Fischer titration indicated that the water content of phenol was $<10^{-3}$M.

Rate Measurements.—For solvolyses of 1-aryl-1-methylethyl p-nitrobenzoates and methyl, ethyl, n-propyl, isobutyl, and neopentyl tosylates in pure phenol, the usual aliquot technique [2] was employed. For solvolyses of methyl and ethyl tosylates and ethyl, isopropyl, and t-butyl bromides in phenol–benzene (1 : 1 w/w), the sealed ampoule (1 ml) technique [2] was employed. The reaction was followed by titration with standard 0.05N-hydrochloric acid with the use of Bromophenol Blue as indicator for 1-aryl-1-methylethyl p-nitrobenzoates and alkyl bromides and with standard 0.05N-perchloric acid in acetic acid with the use of Crystal Violet or Bromophenol Blue as indicator for primary alkyl tosylates. In each case the reaction was followed to at least 70% conversion. Infinity titres were determined after 10 half-lives except for the phenolyses of methyl and ethyl tosylates without an

TABLE 5

Initial specific rates for phenolysis of isopropyl bromide in phenol–benzene (1 : 1 w/w) in the presence of sodium phenoxide at 50.0°

[Pr^{i}Br]/M	[NaOPh]/N	$10^5k_1^{\circ}$ [a]/s^{-1}
0.050 9	0.052 0	4.81
0.049 8	0.103	6.81
0.050 3	0.147	8.49

[a] Initial specific rate within 20% completion; accurate to within ±2.0%.

TABLE 6

Phenolysis rates of 1-methyl-1-(p-methylphenyl)ethyl p-nitrobenzoate (ROPNB) in binary mixtures of phenol with benzene at 50.0°

wt% phenol	[ROPNB]	[NaOPh]/N	10^3k_1 [a]/s^{-1}
10	0.013 2	0.013 6	0.199
30	0.100	0.107	1.65
50	0.100	0.106	4.47
60	0.100	0.107	7.41
100	0.100	0.107	37.8 [b]

[a] Accurate to within ±3.5%. [b] Extrapolated from the above data by use of the Grunwald–Winstein mY plot.[6]

TABLE 7

Phenolysis rates of 1-methyl-1-(p-methoxyphenyl)ethyl p-nitrobenzoate (ROPNB) in binary mixtures of phenol with benzene at 50.0°

wt% phenol	[ROPNB]/N	[NaOPh]/N	k_1 [a]/s^{-1}
10	0.011 1	0.011 3	0.015 8
15	0.018 1	0.018 6	0.036 0
100	0.011 1	0.011 3	10.2 ± 5.5 [b]
	~0.018 1	~0.018 6	

[a] Accurate to within ±4.0%, unless otherwise noted. [b] Extrapolated from the above data by use of the Grunwald–Winstein mY plot.[6]

---

[12] See Table 29 in A. Streitwieser, jun., *Chem. Rev.*, 1956, **56**, 571.

[13] M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, 1962, **35**, 1552.

[14] H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897.

[15] H. Kwart and P. S. Francis, *J. Amer. Chem. Soc.*, 1955, **77**, 4907.

[16] L. B. Jones and J. P. Foster, *J. Org. Chem.*, 1970, **35**, 1780.

[17] C. S. Marvel and V. C. Sekera, *Org. Synth.*, 1955, Coll. Vol. III, 366.

added base, for which calculated values were adopted. All the rate data were treated graphically. For the phenolyses of methyl and ethyl tosylates with sodium phenoxide, smooth second-order relationships were obtained. For phenolysis of isopropyl bromide, the k_1 and k_2 values were determined as mentioned in the text (Tables 1 and 5). For the phenolyses of the other systems good first-order rate constants were observed. The rate data are summarized in Tables 1—3 and 5—7.

Product Analysis.—Phenolysis products for neopentyl tosylate were separated according to previously reported procedures.[1] The composition was assayed by g.l.c.

[6/1216 *Received*, 23*rd June*, 1976]