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Phenolyses of 1-Adamantyl Chloride, Bromide, and *p*-Toluenesulfonate in Binary Mixtures of Phenol with Benzene. The Rates and the Product Distribution

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Adamantyl derivatives, the bridgehead substrates, have been chosen as the reference compounds in the assessment of the ionizing power of phenolic solvents in the S_N1-type solvolysis. The S_N1-phenolyses of 1-adamantyl chloride, bromide, and *p*-toluenesulfonate have been studied at several temperatures in binary mixtures of phenol with benzene; the enthalpies and entropies of activation have been calculated. Phenolysis has also been made on *t*-butyl chloride in order to estimate the Grunwald-Winstein Y values for the phenol-benzene solvents. The solvolysis rates of 1-adamantyl compounds, including the literature values, have been correlated with the Y values and also with the dielectric constants $((D-1)/(2D+1))$. A significant deviation is found for the phenolic solvents in both correlations; this deviation is discussed in terms of the electrophilic assistance by hydrogen-bonding of the phenolic solvents to the leaving group. The isolated phenolysis products have been characterized as 1-adamantyl phenyl ether, *o*-, and *p*-1-adamantylphenols. The product compositions for the reactions of the ion-pair intermediate with the phenol molecule and with the phenoxide ion have been estimated on the basis of the variation in the overall product compositions, caused by the increase in the concentrations of the added phenoxide or amine.

In previous studies of the phenolysis rates for *t*-butyl halides,[1] benzyl chloride,[1] 1-phenylethyl derivatives,[2] and benzhydryl bromide,[1] it has been demonstrated that phenol is a typical solvolytic solvent and that it is prominent[3] in giving hydrogen-bonding electrophilic assistance to the ionization of these substrates. However, little study has been made of the quantitative assessment of its solvolytic ionizing power.

Because the adamantyl system has no possibilities for elimination or for rear-side solvent attack, and because, consequently, its solvolysis rate exactly reflects the rate of the ionization process, Schleyer and his collaborators[4] recently suggested the use of 1-adamantyl bromide as a reference compound for the assessment of the ionizing power of a solvolytic solvent.

In the present paper we will report on the results of the assessment of the ionizing power of the phenolic

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[1] H. Shingu and K. Okamoto, *Nippon Kagaku Zasshi*, **81**, 111 (1960).

[2] K. Okamoto, T. Kinoshita, and H. Shingu, This Bulletin, **43**, 1545 (1970), and the references cited therein.

[3] K. Okamoto and H. Shingu, *ibid.*, **34**, 1131 (1961).

[4] D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5977 (1970).

solvent by the use of this new reference system, including 1-adamantyl chloride, bromide, and *p*-toluenesulfonate; we will also report on the distribution of 1-adamantyl phenyl ether, *o*-, and *p*-1-adamantylphenols in the phenolysis products.

Results

Phenolysis Rate in Binary Mixtures of Phenol with Benzene. The rates of phenolysis for 1-adamantyl chloride, bromide, and *p*-toluenesulfonate (0.05 M for each) were determined titrimetrically in the presence of 0.05 M triethylamine at several temperatures between 25 and 100°C for binary mixtures of 10, 20, 30, 50, and 70 wt% phenol with benzene. A good first-order behavior was observed for each run. The results are tabulated in Table 1.

Table 1. First-order rate constants for phenolyses of 1-adamantyl derivatives in the presence of 0.05 M Et_3N in phenol-benzene solvents

Temp. (°C)	$k_1 \times 10^6$ (sec^{-1}) PhOH wt% 70	50	30	20	10
	1-Adamantyl *p*-toluenesulfonate				
25.0			39000	13000	1360
	1-Adamantyl bromide				
100.0		1830	200		
75.0	1790	397	51.3		
50.0	299	59.7	8.18		
25.0	29.4	8.18	1.19[a)]		
	1-Adamantyl chloride				
100.0	201	151			
75.0	20	38.9			
50.0		5.75			
25.0		0.832[a)]			

a) Extrapolated from data at the other temperatures.

Table 2. First-order rate constants for phenolyses of *t*-butyl chloride in the presence of 0.05 M Et_3N in phenol - benzene solvents

Temp. (°C)	$k_1 \times 10^6$ (sec^{-1}) PhOH wt% 90	70	50	30	20	10
100.0					418	47.0
86.0						20.5
75.0					110	9.60
60.0			633			3.12
50.0			288		12.8	1.30
45.0	1740					
40.0	1100					
35.0	675					
25.0	248[a)]	117	24.6	6.16	1.74[a)]	0.153[a)]
Y[b)]	+1.427	+1.101	+0.425	−0.192	−0.711	−1.791

a) Extrapolated from data at the other temperatures.

b) k_1 (80% aq. EtOH, 25.0°C)$=9.26\times10^{-6}$ (sec^{-1}) (A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956)).

For the evaluation of the Grunwald-Winstein Y values[5)] for these phenolic solvents, the phenolysis rates of *t*-butyl chloride in various phenol - benzene mixtures were also determined in the presence of triethylamine at several temperatures between 25 and 100°C; the results are presented in Table 2, along with the Y values.

The activation parameters for the adamantyl system, calculated from the data of Table 1, are presented in Table 3. The $\Delta H^{\ddagger}$ values for the phenolic solvents are smaller than those (19—27 kcal/mol) observed for such other hydroxylic solvents[4,6)] as aqueous ethanol, aqueous methanol, aqueous dioxane, aqueous tetrahydrofuran, aqueous dimethyl sulfoxide, acetic acid, and formic acid; the $\Delta S^{\ddagger}$ values are more negative than the $\Delta S^{\ddagger}$ values (−2——18 eu) for the other hydroxylic solvents.[4,6)] The activation parameters for *t*-butyl chloride are also presented in Table 3.

In order to examine the effect of the triethylamine concentration upon the first-order rate constant, the phenolysis rate for 1-adamantyl bromide was determined in a 50 wt% phenol - benzene solvent with variable triethylamine concentrations between 0.00 and 0.10 M at 50.0°C. The results are presented in Table 4. The rate constants are almost invariant in the concentration range employed.

Table 3. Enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation for phenolyses of 1-adamantyl chloride, 1-adamantyl bromide, and *t*-butyl chloride in binaryl mixtures of phenol with benzene

Solvent	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu, 25°C)
	1-Adamantyl chloride	
50 wt% PhOH	15.2	−35.4
	1-Adamantyl bromide	
30 wt% PhOH	15.1	−35.1
50 wt% PhOH	15.5	−29.9
70 wt% PhOH	16.3	−24.4
	t-Butyl chloride	
10 wt% PhOH	16.7	−33.9
20 wt% PhOH	16.1	−31.0
50 wt% PhOH	17.7	−20.2
90 wt% PhOH	17.6	−16.0

Table 4. Effect of added triethylamine upon the phenolysis rate for 1-adamantyl bromide in 50 wt% phenol - benzene solvent at 50.0°C

Et_3N (M)	RBr (M)	$k_1 \times 10^5$ (sec^{-1})
0.000	0.052	3.51
0.0040	0.0040	5.72
0.011	0.0080	5.77
0.020	0.016	5.71
0.050	0.040	5.92
0.100	0.080	5.94

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5) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

6) D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *ibid.*, **92**, 7300 (1970).

The Product Distribution for the Phenolysis. The reaction mixture from the phenolysis of 1-adamantyl bromide in 50 wt% phenol - benzene at 50°C was chromatographed over silica gel after a usual work-up. The structures of the isolated products (1-adamantyl phenyl ether, *o*-, and *p*-1-adamantylphenols) were assigned on the basis of the elemental compositions and the NMR and IR spectra. The details of the physical constants for these products are described in Table 8 (see Experimental section).

The runs for the product distribution analysis were carried out in a base concentration about ten times greater than the substrate concentration; the composition was assayed by gas chromatography. The effects of added triethylamine and sodium phenoxide upon the product compositions are tabulated in Tables 5 and 6.

Table 5. Effect of added triethylamine upon the product distribution for the phenolysis of 1-adamantyl compounds

Et_3N (M)	RX (M)	Product distribution %[a] ROPh	*o*-RPhOH	*p*-RPhOH
1-Adamantyl chloride (50 wt% PhOH-Benzene, 100.0°C)				
0.00625	0.005	91.5	7.9	0.8
0.0125	0.010	91.5	7.9	0.8
0.025	0.020	91.5	7.9	0.8
0.028	0.025	90.7	8.5	0.8
0.050	0.005	91.7	7.6	0.7
0.100	0.010	89.3	9.6	1.1
0.200	0.050	89.1	9.6	1.3
0.300	0.030	88.9	10.0	1.1
1-Adamantyl bromide (50 wt% PhOH-Benzene, 50.0°C)				
0.0000	0.052	0.0[b]	39.0	61.0
0.00625	0.005	89.4	9.1	1.5
0.0125	0.010	89.3	9.7	1.0
0.025	0.020	90.8	8.0	1.2
0.050	0.040	90.3	8.3	1.4
1-Adamantyl *p*-toluenesulfonate (30 wt% PhOH(-Benzene), 25.0°C)				
0.010	0.0010	89.4	9.0	1.6
0.030	0.0030	88.0	10.3	1.7
0.200	0.002	86.3	11.0	2.7

a) (ROPh+*o*-RPhOH+*p*-RPhOH) %=100%
b) In the absence of triethylamine, the phenyl ether was undergone the rapid rearrangement to afford *o*- and *p*-1-adamantylphenols, owing to liberation of hydrogen bromide in the course of the phenolysis.

Table 6. Effect of added sodium phenoxide upon the product distribution for the phenolysis of 1-adamantyl chloride in 50 wt% phenol-benzene solvent at 100.0°C

NaOPh (N)	RCl (M)	Product distribution %[a] ROPh	*o*-RPhOH	*p*-RPhOH
0.005	0.0005	89.3	9.7	1.0
0.010	0.0010	86.8	11.4	1.8
0.020	0.0020	84.9	13.1	2.0
0.030	0.0030	83.0	14.2	2.8
0.050	0.0050	80.1	16.4	3.5
0.100	0.010	75.9	19.3	4.8
0.150	0.015	72.3	21.9	5.8

a) (ROPh+*o*-RPhOH+*p*-RPhOH) %=100%

Rearrangement of 1-Adamantyl Phenyl Ether. It has been known that the *sec*- or *tert*-alkyl phenyl ether readily undergoes rearrangement to give *o*- and *p*-alkylphenols under an acidic catalyst.[7] In fact, in the absence of triethylamine, no phenyl ether was found in the phenolysis products of 1-adamantyl bromide, because of the rapid rearrangement of the phenyl ether to the *o*- and *p*-1-adamantylphenols, a rearrangement caused by the liberated HBr under the phenolysis conditions (Table 5). Therefore, the possibility of the rearrangement for 1-adamantyl phenyl ether could not be eliminated even with the acidity of the solvent phenol. However, we observed no rearrangement of the phenyl ether in the 50 wt% phenol - benzene solvent at 100°C in a 20-hr reaction.

Discussion

The S_N-1 Character of the Phenolysis of 1-Adamantyl Derivatives. The effect of added triethylamine upon the titrimetric first-order rate constants for 1-adamantyl bromide are illustrated in Fig. 1 (see also Table 4). The rate constants are almost independent of the concentrations of triethylamine except in the concentration range lower than 0.0050 M. This constancy obviously indicates the S_N1 character of this phenolysis. However, a definite decrease in the rate constant in the absence of an added base indicates that there exists a small amount of "return" in the course of the ionization,[6] one of the simplest reaction schemes to account for the return process may be described as follows:

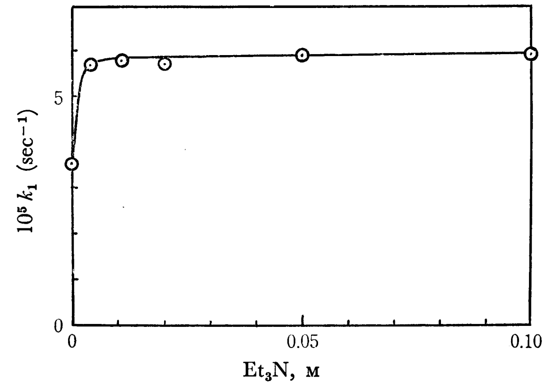

Fig. 1. The effect of added triethylamine upon the titrimetric first-order rate constants for 1-adamantyl bromide in the 1 : 1 (by wt.) Phenol-benzene solvent at 50.0°C.

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\text{Ion-pair Intermediate}] \xrightarrow{k_2[PhOH]+k_{2'}[PhO^{\ominus}]} \text{Products}$$

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[7] *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed., Cornell University Press, Ithaca and London (1969), pp. 904—906.

According to this scheme, we can express the total rate constant, $k_{\mathrm{obs.}}$, by Eq. (1);

$$k_{\mathrm{obs.}} = \frac{k_1(k_2[\mathrm{PhOH}]+k_{2'}[\mathrm{PhO}^{\ominus}])}{k_{-1}+k_2[\mathrm{PhOH}]+k_{2'}[\mathrm{PhO}^{\ominus}]} \tag{1}$$

When the magnitude of $(k_2[\mathrm{PhOH}]+k_2'[\mathrm{PhO}^{\ominus}])$ in Eq. (1) becomes much greater than that of k_{-1} at higher concentrations of $\mathrm{PhO}^{\ominus}$, $k_{\mathrm{obs.}}$ will virtually agree with k_1 (an ionization rate constant); on the contrary, in the absence of the phenoxide ion ($[\mathrm{PhO}^{\ominus}]=0.00$), $k_{\mathrm{obs.}}$ is expressed by Eq. (2);

$$k_{\mathrm{obs.}} = \frac{k_1k_2[\mathrm{PhOH}]}{k_{-1}+k_2[\mathrm{PhOH}]} \tag{2}$$

Thus, if these equations apply to this phenolysis, we can calculate the rate ratio k_{-1}/k_2 to be 3.43 for the phenolysis of 1-adamantyl bromide in the 50 wt% phenol-benzene solvent at 50°C, assuming that $k_{\mathrm{obs.}}$ at the 0.10 M triethylamine concentration is practically equal to k_1 (see Fig. 1).

In the phenolysis of 1-phenylethyl chloride, we observed a similar decrease in the titrimetric rate constant, k_t, at the lower concentrations of the added base.[8] In this case, the polarimetric rate constant, k_α, was found to be greater than the k_t value are the whole range of base concentrations; furthermore, the gap between k_α and k_t actually widened as the base concentration increased. From this fact we suggested the existence of two successive S_N1 intermediates in the phenolysis of 1-phenylethyl chloride.

In view of the observation for the 1-phenylethyl system, we can not exclusively rule out the possibility of the existence of two successive intermediates for the 1-adamantyl phenolysis, although we have tentatively treated the 1-adamantyl case as a phenolysis with a single ion-pair intermediate in the above reaction scheme. In order to work out a final solution for this problem, we would have to measure directly an intrinsic ionization rate constant, k_1, which may be afforded by the assessment of the oxygen-18 scrambling rate in the phenolysis, using the substrate containing the oxygen-18 atom in the carboxylic-leaving group; this remains a topic for future study.

Ionizing Power for the Phenol-Benzene Solvent. A plot of the logarithms of the rate constants (25°C) for 1-adamantyl bromide and *p*-toluenesulfonate *vs.* the Grunwald-Winstein *Y* values[5] is shown in Fig. 2. The open circles represent the values for the phenol-benzene solvents; the closed circles for 1-adamantyl bromide and *p*-toluenesulfonate designate, respectively the values cited by Schleyer *et al.*[4] and by Kevill *et al.*[6]

It is immediately obvious that the points for phenol-benzene solvents show significant deviations for both bromide and tosylate. Among the reported values, the points for aqueous trifluoroethanol[4] (1-adamantyl bromide) and for acetic acid (1-adamantyl tosylate) also deviate significantly. These anomalies may be ascribed to the results of the specific-substrate and leaving-group interaction.[4] If the extent of the ion-pair return for these phenolysis conditions is not significantly high, the high deviation of the phenolic solvent may be attributed to its high ability of hydrogen-bonding to the leaving group. This feature of the phenolic solvent has been suggested on the basis of the fact[3] that the substantial rate acceleration by *p*-nitrophenol in the acetolysis of *t*-butyl bromide is completely lost in the case of *o*-nitrophenol, the *intermolecular* hydrogen-bonding power of which is reduced or prevented by its *intramolecular* hydrogen-bonding.

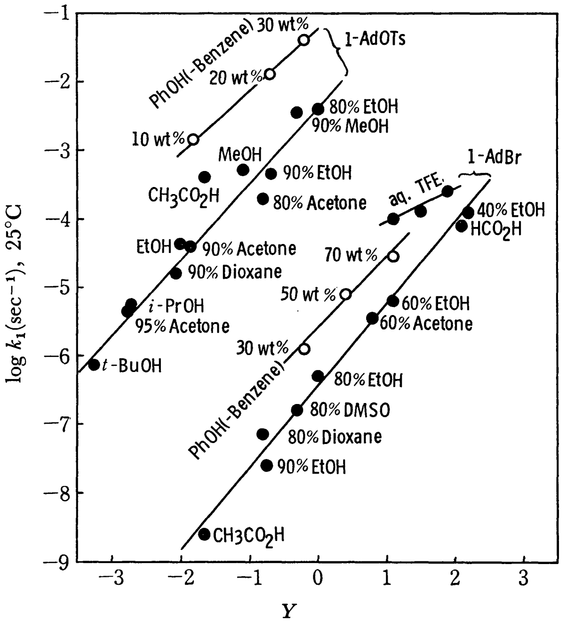

Fig. 2. Correlations of the 1-adamantyl solvolysis rates with Grunwald-Winstein *Y* values.

Since the role of the solvolytic solvent is generally ascribed to the electrostatic stabilization of the transition state,[4,9] it is of interest to express this general solvent effect on the solvolysis rates for 1-adamantyl and *t*-butyl systems by the use of a measure for the electrostatic solvation energy.

When we assume the transition state for the solvolysis to be a polarized molecule with a strong dipole moment, it is convenient to use a dielectric constant as a measure of the electrostatic solvation energy and to use the Eyring-Laidler treatment[10] in the assessment of the general solvent effect.

When we denote, following their treatment, the free-energies for the electrostatic solvation process for the molecule (RX) in the initial state and the molecule (RX*) in the transition state by the expression proposed by Kirkwood,[11] the rate constants of the S_N1 solvolysis can be expressed as follows:[9]

$$\ln k_{\mathrm{obs.}} + C = \left(\frac{N}{\boldsymbol{RT}}\right)\left(\frac{D-1}{2D+1}\right)\left(\frac{\mu^2_{\mathrm{RX}}}{r^3_{\mathrm{RX}}} - \frac{\mu^2_{\mathrm{RX}^*}}{r^3_{\mathrm{RX}^*}}\right) + \frac{\Phi_{\mathrm{RX}}-\Phi_{\mathrm{RX}^*}}{\boldsymbol{RT}} \tag{3}$$

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[8] K. Okamoto, K. Takeuchi, and H. Shingu, This Bulletin, **35**, 525 (1962).

[9] H. Shingu and K. Okamoto, *Nippon Kagaku Zasshi*, **78**, 558 (1958).

[10] K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

[11] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

where N is the Avogadro number, μ and r are the dipole moment (Debye unit) and the molecular radius (Å), respectively, D is the dielectric constant of the solvent, and the Φ's are non-electrostatic terms for the solvation process of RX and RX*.

Provided that the non-electrostatic terms are negligibly small or independent of the nature of the solvents, a plot of $\ln k_{\text{obs.}}$ (or $\log k_{\text{obs.}}$) *vs.* $(D-1)/(2D+1)$ should give a straight line. The plots of the $\log k_{\text{obs.}}$'s for 1-adamantyl derivatives and for *t*-butyl chloride *vs.* $(D-1)/(2D+1)$ for various solvents are shown in Figs. 3, 4, and 5. Among a variety of solvents, the phenol - benzene solvent and also the acetic acid solvent deviate far from the points expected for the linear relation between $\log k$ for the other hydroxylic solvents *vs.* $(D-1)/(2D+1)$, indicating that the non-electrostatic terms for these solvents are quite different in nature from the other solvents; thus, the gap from the straight line would mostly be a reflexion of the electrophilic acceleration by hydrogen-bonding, the existence of which has been suggested from the dispersion of the phenolic solvent and the acetic acid solvent in the $\log k$ *vs.* Y correlation (Fig. 2).

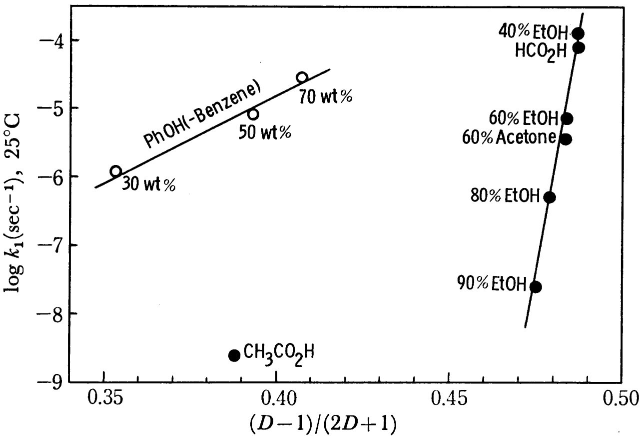


Fig. 3. The correlation of 1-adamantyl bromide solvolysis rates with $(D-1)/(2D+1)$.

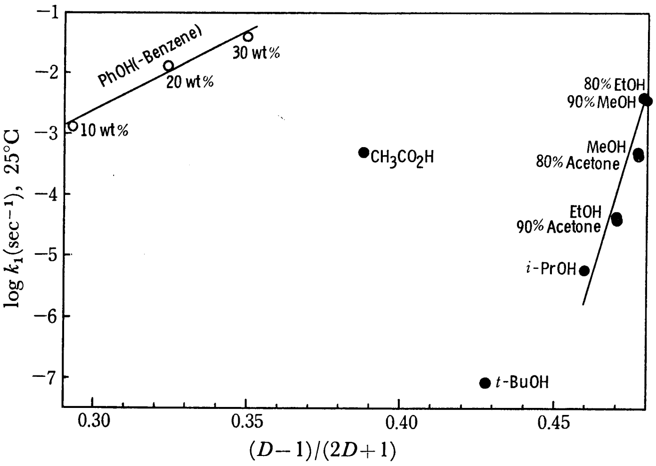


Fig. 4. The correlation of 1-adamantyl tosylate solvolysis rates with $(D-1)/(2D+1)$.

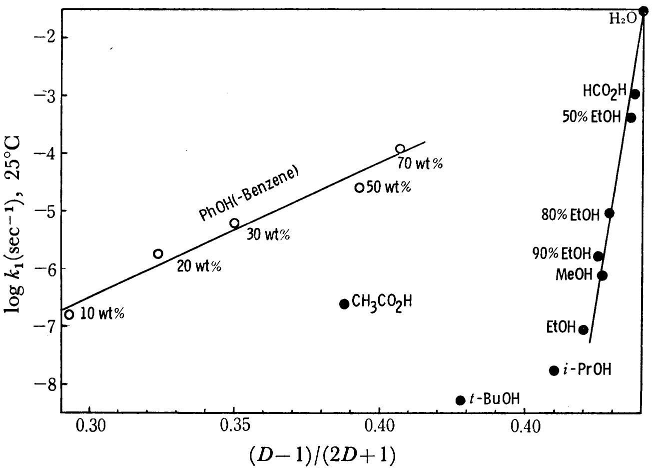


Fig. 5. The correlation of *t*-butyl chloride solvolysis rates with $(D-1)/(2D+1)$.

The Product Distribution for the Phenol and the Phenoxide Reactions. As is presented in the above reaction scheme, in the reaction media which contain sodium phenoxide (or triethylamine), there probably exist two kinds of nucleophiles, the phenol molecule and the phenoxide ion (or its ion-pair); it is of interest to estimate the distribution of the products with regard to each nucleophile.

The distribution for the products which stem from the reaction of the phenol molecule with the S_N1 intermediate can be graphically estimated by plotting the product compositions (r_{ether}, r_{ortho}, and r_{para}) *vs.* the concentrations of the added sodium phenoxide or triethylamine, and subsequently by extrapolating the r values (%) to a zero concentration of the added nucleophile. This is illustrated in Fig. 6 for the phenolysis of 1-adamantyl chloride in the 50 wt% phenol-benzene solvent at 100°C.

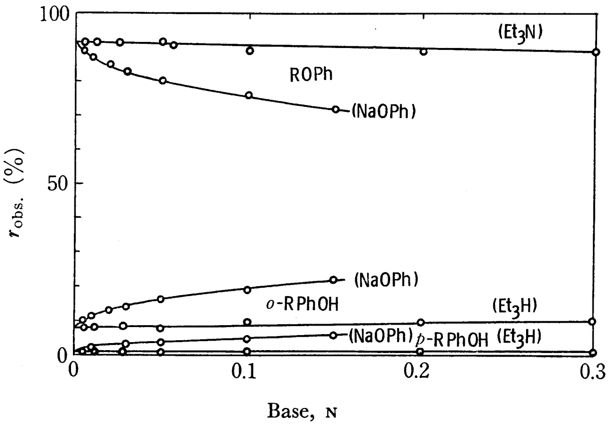


Fig. 6. The product distribution for 1-adamantyl chloride phenolysis in the presence of sodium phenoxide or triethylamine at 100.0°C.

The results of such estimations for chloride, bromide, and tosylate are tabulated in Table 7. The product distributions for the three substrates are in fair agreement with each other, irrespective of the nature of the leaving group and the reaction temperature; this may indicate the structural resemblance of the ion-pair intermediate for each substrate.

For the phenolysis with triethylamine, the product composition is less affected by the increase in the amine

TABLE 7. PRODUCT DISTRIBUTIONS FOR THE REACTIONS OF THE PHENOL MOLECULE AND TME PHENOXIDE ION

Substrate	Temp. (°C)	Product distribution %		
		ROPh	*o*-RPhOH	*p*-RPhOH
	The reaction of the phenol molecule			
RCl	100.0	91.5	8	0.5
RBr	50.0	90	9	1.0
ROTs	25.0	90	9	1.0
	The reaction of the phenoxide ion			
RCl[a]	100.0	70	23	9.0

a) The (k_2'/k_2) values for ROPh, *o*-RPhOH, and *p*-RPhOH are respectively 128, 134, and 56.

concentration compared with case of sodium phenoxide (Fig. 6). This can probably to be attributed to the lower dissociation degree of the phenol-triethylamine adduct into the free phenoxide ion.

The distribution of the products derived from the reaction of the phenoxide ion with the intermediate can be estimated by the following procedure. Provided that the phenoxide-ion concentrations are virtually constant at high ratios (>10) of the phenoxide concentration and the substrate concentration, we can derive the following equations (Eqs. (4), (5), and (6)) which express the relationships between the observed overall distributions of the products ($r_{\text{obs., ether}}$, $r_{\text{obs., }ortho}$ and $r_{\text{obs., }para}$) and the estimated proportions of the products for the phenoxide reaction ($r_{\text{i, ether}}$, $r_{\text{i, }ortho}$ and $r_{\text{i, }para}$) and for the phenol reaction ($r_{\text{m, ether}}$, $r_{\text{m, }ortho}$ and $r_{\text{m, }para}$). The inferior letters, i, m, ether, *ortho*, and *para*, denote the phenoxide ion, the phenol molecule, 1-adamantyl phenyl ether, *o*-1-adamantylphenol, and *p*-1-adamantylphenol, respectively.

$$\text{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\text{Ion-pair intermediate}] \text{ — }\begin{cases} \xrightarrow{k_2[\text{PhOH}]} \underset{r_{\text{m, ether}}}{\text{ROPh}} + \underset{r_{\text{m, }ortho}}{o\text{-RPhOH}} + \underset{r_{\text{m, }para}}{p\text{-RPhOH}} \\ \xrightarrow{k_{2'}[\text{PhO}^\ominus]} \underset{r_{\text{i, ether}}}{\text{ROPh}} + \underset{r_{\text{i, }ortho}}{o\text{-RPhOH}} + \underset{r_{\text{i, }para}}{p\text{-RPhOH}} \end{cases}$$

$$r_{\text{obs., ether}} = \frac{[\text{ROPh}]_\infty}{[\text{ROPh}]_\infty+[o\text{-RPhOH}]_\infty+[p\text{-RPhOH}]_\infty} = \frac{k_2[\text{PhOH}]\times r_{\text{m, ether}}+k_{2'}[\text{PhO}^\ominus]\times r_{\text{i, ether}}}{k_2[\text{PhOH}]+k_{2'}[\text{PhO}^\ominus]} \qquad (4)$$

$$r_{\text{obs., }ortho} = \frac{[o\text{-RPhOH}]_\infty}{[\text{ROPh}]_\infty+[o\text{-RPhOH}]_\infty+[p\text{-RPhOH}]_\infty} = \frac{k_2[\text{PhOH}]\times r_{\text{m, }ortho}+k_{2'}[\text{PhO}^\ominus]\times r_{\text{i, }ortho}}{k_2[\text{PhOH}]+k_{2'}[\text{PhO}^\ominus]} \qquad (5)$$

$$r_{\text{obs., }para} = \frac{[p\text{-RPhOH}]_\infty}{[\text{ROPh}]_\infty+[o\text{-RPhOH}]_\infty+[p\text{-RPhOH}]_\infty} = \frac{k_2[\text{PhOH}]\times r_{\text{m. }para}+k_{2'}[\text{PhO}^\ominus]\times r_{\text{i, }para}}{k_2[\text{PhOH}]+k_{2'}[\text{PhO}^\ominus]} \qquad (6)$$

Eqs. (4), (5), and (6) are transformed into Eq. (7), in which x denotes ether, *ortho*, or *para*.

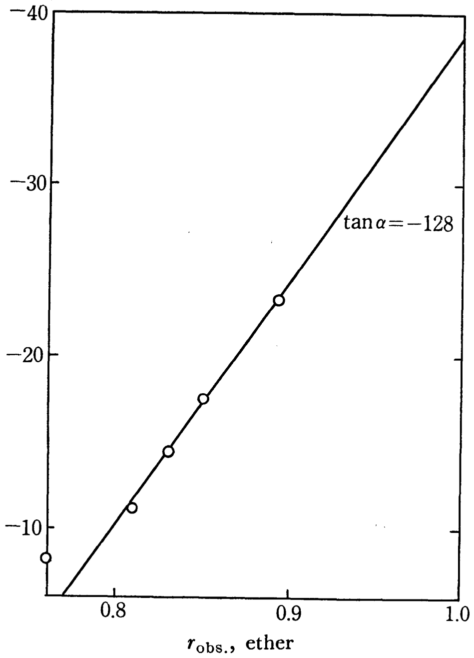


Fig. 7. Examination of the correlation shown in Fig. (6) for the distribution of 1-adamantyl phenyl ether in the 1-adamantyl chloride phenolysis products.

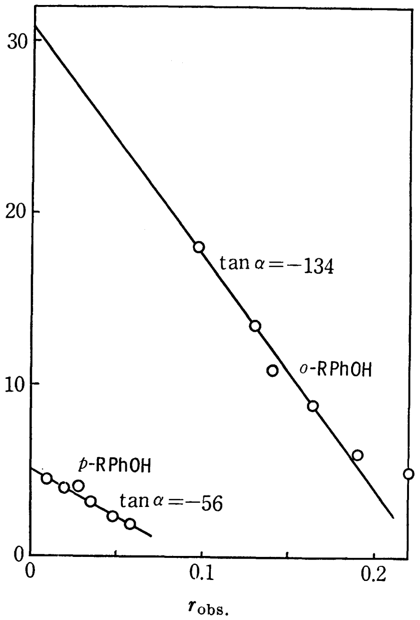


Fig. 8. Examination of the correlation shown in Eq. (6) for the distribution of *o*- and *p*-adamantylphenols in the 1-adamantyl chloride phenolysis products.

$$\frac{(r_{\text{obs., x}}-r_{\text{m, x}})}{([\text{PhO}^\ominus]/[\text{PhOH}])} = \left(\frac{k_{2'}}{k_2}\right) r_{\text{obs., x}} + \left(\frac{k_{2'}}{k_2}\right) r_{\text{i, x}} \qquad (7)$$

In the reaction medium, the phenoxide ion may be dissolved as an ion-pair or as an aggregate at somewhat higher concentrations. However, in the lower concentrations we may consider that the phenoxide ion almost completely dissociates and that the ion concentration may be approximately equal to that of the added sodium phenoxide. Thus, using Eq. (7), we can evaluate the values for $r_{\text{i, x}}$ and for (k_2'/k_2) from the observed values for $r_{\text{obs., x}}$, $r_{\text{m, x}}$ and ([PhO$^\ominus$]/

[PhOH]); a graphical procedure for the estimation of $r_{1,x}$'s is illustrated in Figs. (7) and (8) by plotting the amounts of the left side of Eq. (7) against $r_{obs\cdot,x}$ (see Table 6) for 1-adamantyl chloride. The results thus obtained for $r_{i,x}$ values are presented in Table 7. As is shown in Table 7, the sum of the $r_{i,x}$ values amounts to 102%. Therefore, the expected error limits for this estimation may be about 2% or less. The larger amount of carbon alkylation observed in the phenoxide reaction is in marked contrast to the results for the phenol reactions.

Experimental[12]

Materials. 1-Adamantyl chloride mp 165.0—166.0°C (lit,[13] 165°C), 1-adamantyl bromide mp 118.5—119.0°C (lit,[14] 119—120°C), and 1-adamantyl *p*-toluenesulfonate mp 76—79°C (lit,[6] 72—79°C) were prepared by the reported methods.[6,13] Phenol, benzene, and triethylamine were fractionated just prior to use. Titration with a Karl Fischer reagent indicated the water content of phenol to be less than 10^{-2} M. The sodium phenoxide was prepared by refluxing the toluene solution of phenol with sodium metal.

Rate Measurement. Most of the measurements were carried out by a sealed ampoule technique; for the reactions which were rapid at lower temperatures, an aliquot method was employed. For the more rapid reactions of 1-adamantyl tosylate, a single sample for a specified reaction time was prepared as follows. A benzene solution of the tosylate and a triethylamine solution in 45 wt% phenol(-benzene) were each temperature-equilibrated at 25°C, then they were mixed in a glass-stoppered reaction vessel at 25°C to make 30 wt% phenol (-benzene) solution; after a specified length of time, the reaction was interrupted by the addition of a large quantity of acetone, which had been cooled in Dry Ice-methanol, to the reaction vessel. For the phenolysis of 1-adamantyl bromide, carried out in the absence of a base, the free-space in the ampoule was filled with the HBr liberated in th course of the phenolysis. In that case, the ampoule had been cooled in liquid-nitrogen before it was opened in a large quantity of acetone which contained a small amount of aqueous NaOH.

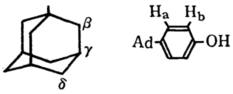
The titrating solutions were, for the titration in acetic acid used as a stop-solvent, 0.05 N perchloric acid in acetic acid and, for the titration in an acetone solution, 0.01 N aqueous HCl. The indicators used were respectively crystal violet (in acetic acid) and lacmoid (in EtOH). All the rate data were treated graphically, and in each case the reaction was followed to at least 70% reaction and a smooth linear first-order relationship was obtained.

1-Adamantyl Bromide Phenolysis Products. 1-Adamantyl bromide (1.505 g, 7.00 mmol) was dissolved in 68 m*l* of a 1 : 1 (by wt.) mixture of phenol and benzene, containing triethylamine (1 m*l*, 7.17 mmol). After 28 hr (about 10 half-lives) at 50°C, the solution was diluted with 200 m*l* of ether, washed with 10% aqueous NaOH (25 m*l*×5) and 20% aqueous NaCl (100 m*l*×2), and dried ($MgSO_4$); most of solvent was then removed by distillation. A part (1/22 by wt.) of the residual liquid was examined by gas chromatography. The remainder was evaporated and separated by chromatography on silica gel (50 g) to give 0.866 g of 1-adamantyl phenyl ether (the eluent, 2 : 1 (by vol.) hexane-benzene), a 1 : 1 mixture (0.691 g) of 1-adamantyl phenyl, ether and *o*-1-adamantylphenol (1 : 2 hexane-benzene), and 0.048 g of *p*-1-adamantylphenol (20 : 1 benzene-ether). A mixture of the phenyl ether and the *ortho*-phenol was rechromatographed on alumina to give pure *o*-1-adamantylphenol (the eluent, 1 : 1 ether-ethanol). The structures of these products were assigned on the basis of the following spectral data and elemental compositions (Table 8). The gas-chromatographical analysis of a part of the reaction mixture, which had been taken out before the column chro-

TABLE 8. MELTING POINTS, SPECTRAL DATA, AND ELEMENTAL COMPOSITIONS FOR THE PHENOLYSIS PRODUCTS

	1-Ad-OPh	*o*-1-Ad-PhOH	*p*-1-Ad-PhOH
mp °C (corr.)	113.5—114.0[a]	146.9—147.5[b]	182.4—182.8[a]
IR (cm^{-1})[c]			
ν_{C-H}	2940 2870	2920 2880	2920 2880
$\nu_{arom.\ ring}$	1597	1597 1580 1500	1615 1595 1510
ν_{O-H}		3580	3240
NMR (τ, J Hz)[d]			
ring proton	2.35—3.02 (m, 5H)	2.44—3.27 (m, 4H)	2.68 (d, $2H_a$, 8.7) 3.14 (d, $2H_b$, 8.7)
β-H	8.09 (6H)	7.82 (9H)	8.12 (6H)
γ-H	7.77 (3H)		7.90 (3H)
δ-H	8.32 (6H)	8.17 (6H)	8.21 (6H)
OH		5.15 (s, 1H)	6.45 (s, 1H)
Elemental composition[e]			
Found C%	84.41	83.92	84.22
Found H%	8.96	8.92	9.10

a) Recrystallized from methanol.
b) Recrystallized from *n*-hexane.
c) In CCl_4.
d)



e) Calcd: C, 84.16; H, 8.83% (for each compound).

TABLE 9. THE DIELECTRIC CONSTANTS OF PHENOL - BENZENE MIXTURES

Phenol wt%	D (25.0°C)
70.0	7.60
50.0	6.51
30.0	4.52
20.0	3.76
10.0	3.13
0.0	2.27[a]

a) A. S. Brown, P. M. Levin, and E. W. Abrahamson, *J. Chem. Phys.*, **19**, 1226 (1951).

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[12] A. Shimadzu Model GC-2B gas chromatographic instrument, equipped with a thermal conductivity detector, a Hitachi Model 023—6003 gas chromatographic instrument, with a flame ionization detector, a Shimadzu Model IR-27 spectrophotometer, and a Japan Electronic Optics 60 MHz NMR instrument were used for the analytical work. Microanalyses were performed by the Elemental Analysis Center, Kyoto University.

[13] H. Stetter, M. Schwarz, and A. Hirshhorn, *Chem. Ber.*, **92**, 1629 (1959).

[14] St. Landa, S. Kriebel, and E. Knobloch, *Chem. Listy*, **48**, 61 (1954).

matography, revealed the presence of 1-adamantyl phenyl ether, *o*-, and *p*-1-adamantylphenols in the ratio of 88.9 : 8.2 : 2.9 (see below).

Product Distribution Analysis by Gas Chromatography. To several mg of an adamantyl compound, placed in a 2-m*l* ampoule, we added 1 m*l* of a phenol - benzene (1 : 1 by wt.) mixture which also contained a specified amount of triethylamine or sodium phenoxide. The sealed ampoule was kept at a reaction temperature for 10 half-lives. The reaction mixture was diluted with 30 m*l* of benzene, washed with 10% aq. NaOH (3 m*l*) and 10% aq. NaCl (10 m*l*), dried ($MgSO_4$), and distilled to leave 0.3—0.5 m*l* of the residual liquid, which was analyzed by gas chromatography using a 2-m Apiezon Grease column at 200°C.

Measurement of the Dielectric Constant. A resonance method was used; the frequency of the oscillator was 1 MHz, and the calibration of the test condenser, equipped with two circular platinum plates, was carried out using water, acetic acid, and acetic anhydride as the standard liquids. The results are presented in Table 9.