

Retentive Solvolysis. 15. Salt Effect on the Retentive Phenolyses of 1-(*p*-Substituted phenyl)ethyl *p*-Nitrobenzoates. The Pattern of Salt Effect and the Number of Ion-Pair Intermediates in the S_N1 Solvolysis

Tomomi KINOSHITA,* Koichi SHIBAYAMA, Keizo IKAI, and Kunio OKAMOTO†

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

(Received March 14, 1988)

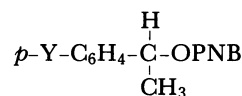
The salt effect of sodium phenoxide on the polarimetric (k_p) and titrimetric rate constants (k_t) has exhibited pattern B for the phenolysis of optically active 1-(*p*-methylphenyl)ethyl *p*-nitrobenzoate (ROPNB; (1)) in pure phenol. The other patterns A, C, and D were previously observed for the phenolyses of 1-phenylethyl *p*-nitrobenzoates with *p*-MeO- (2), *p*-H- (3), and *p*-NO₂-substituents (4), respectively. Thus, the k_p - k_t pattern changes in the order A → B → C → D as the stability of the intermediate decreases in the order of 2 > 1 > 3 > 4. All the k_p - k_t patterns can be correlated with the ion-pair stage for product formation, i.e., the pattern A with the second ion-pair intermediate and the patterns B, C, and D with the first one. The pattern of salt effect on the product distribution (% of ROPh, *o*- and *p*-RC₆H₄OH, and *p*-MeC₆H₄CH=CH₂) for 1 is also compatible with the k_p - k_t pattern B.

The structure of ion-pair intermediates in the S_N1 solvolysis²⁾ should be discussed after confirmation of the ion-pair stage of nucleophilic attack, e.g., the first ion-pair intermediate (Int-1) or the second one (Int-2). For such confirmation, the pattern of salt effect of an added salt on the polarimetric and titrimetric rate constants (k_p and k_t , respectively) can serve as a useful tool.^{2c,2i,3-8)} The possible k_p - k_t diagrams in the S_N1 solvolysis can be generally classified into four patterns, A, B, C, and D,^{8,9)} provided no normal salt effect¹⁰⁾ was observed (Fig. 1).

On the basis of a stability-selectivity relationship for solvolysis intermediate,¹¹⁾ it was anticipated that the k_p - k_t pattern should change in the order A → B → C → D with a decrease in the stability of ion-pair intermediate.⁹⁾ The retentive phenolyses of 1-(*p*-substituted phenyl)ethyl *p*-nitrobenzoates exhibited the patterns A, C, and D for the *p*-methoxy (2), *p*-H (3), and *p*-nitro derivatives (4), respectively, in the presence of sodium phenoxide.⁷⁾ However, the pattern B has not been known for any of 1-phenylethyl systems.

In this paper, we report that the k_p - k_t profile for the phenolysis of 1-(*p*-methylphenyl)ethyl *p*-nitrobenzoate (1) exhibited the pattern B, filling up the sequence and, as a consequence, we have confirmed a clear-cut correlation between the stability of phenolysis inter-

mediates (*p*-MeO > *p*-Me > H > *p*-NO₂) and the k_p - k_t pattern, A → B → C → D.



- 1: Y = CH₃
- 2: Y = CH₃O
- 3: Y = H
- 4: Y = NO₂

Results and Discussion

Phenolysis Rates and Stability of the Ion-Pair Intermediate. Racemic 1 was solvolyzed in pure phenol in the presence of NaOPh (0.106 M) (1M = 1 mol dm⁻³) at 125 °C. The phenolysis rate was determined by the titrimetric method. The k_t value is shown along with those for 2, 3, and 4, which had been previously reported,⁷⁾ in Table 1.

The k_t value decreases in the sequence 2 > 1 > 3 > 4 (relative rate 220 : 14.1 : 1.00 : 0.0430 at 125 °C). The k_p value ($k_p/k_t < 1.32$) also decreases in the sequence 3 > 4 (relative rate 1.00 : 0.034). Thus, each of the phenolysis intermediates should become less stable in the order of the rate sequence.

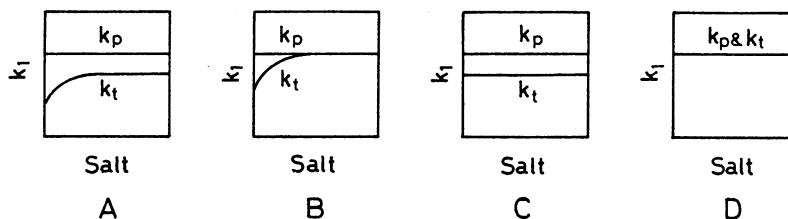


Fig. 1. Four patterns of salt effect on k_p and k_t in the S_N1 solvolysis (in the absence of normal salt effect; cited from Refs. 8 and 9).

† Current address: Meisei Chemical Works, Ltd., 1 Nakazawacho, Ukyo-ku, Kyoto 615.

Table 1. Phenolysis Rates of *p*-Substituted 1-Phenylethyl *p*-Nitrobenzoates **1**–**4** in the Presence of Sodium Phenoxide in Phenol at 125 °C

Substrate ^{a)}	[NaOPh] ₀ /M ^{b)}	<i>k_t</i> /s ⁻¹ ^{c)}	<i>k_{t,rel.}</i>	<i>k_p</i> /s ⁻¹ ^{c)}
2 ^{d)}	0.104	4.1 × 10 ⁻²	220	
1	0.107	2.61 × 10 ⁻³	14.1	
3 ^{d)}	0.103	1.85 × 10 ⁻⁴	1.00	
	0.105			2.45 × 10 ⁻⁴
4 ^{d)}	0.102	7.95 × 10 ⁻⁶	0.0430	
	0.115			(8.35 ± 0.37) × 10 ⁻⁶

a) [Substrate]₀ = 0.10–0.11 M. b) Determined by titration. c) Accurate to within ±1.0% for *k_t* and ±3.0% for *k_p*, unless otherwise noted. d) Cited from Ref. 7.

Table 2. Phenolysis Rates of 1-(*p*-Methylphenyl)ethyl *p*-Nitrobenzoate (ROPNB) in the Presence of Sodium Phenoxide in Phenol at 75 °C

[ROPNB] ₀	[NaOPh] ₀ /M ^{a)}	<i>k_t</i> /s ⁻¹ ^{b)}	<i>k_p</i> /s ⁻¹ ^{c)}
0.0511	0.000	1.03 × 10 ⁻⁴	
0.0999	0.000		1.25 × 10 ⁻⁴
0.0502	0.0178	1.17 × 10 ⁻⁴	
0.0496	0.0478	1.26 × 10 ⁻⁴	
0.0499	0.0445		1.27 × 10 ⁻⁴
0.0501	0.106	1.27 × 10 ⁻⁴	
0.100	0.101		1.28 × 10 ⁻⁴
0.0504	0.145	1.32 × 10 ⁻⁴	

a) Determined by titration. b) Accurate to within ±1.0%. c) Accurate to within ±3.0%.

Solvolysis rate constants for several aralkyl systems, including 1-phenylethyl acetates in aqueous ethanol,¹²⁾ are reported to be well correlated by the Brown-Okamoto equation.¹³⁾ In contrast, the σ^+ plot of log *k_t* shows definitely a curved line for the phenolyses of **1**–**4**, similarly to those of 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoates,⁸⁾ the hydrolyses of 1-phenylethyl chlorides,^{14,15)} and many other solvolyses.¹⁶⁾ However, a linear plot is given by the use of Yukawa-Tsuno equation,¹⁶⁾ $\log(k/k_0) = \rho[\sigma^0 + r(\sigma^+ - \sigma^0)]$ with $\rho = -1.78$ and $r = 1.88$ (correlation coefficient 0.9939) for the phenolyses of **1**–**4**. Such a *r* value is comparable with that (2.05)⁸⁾ for the phenolyses of 2,2-dimethyl-1-phenylpropyl system and is larger than those (1.25 and 0.28) for the hydrolyses of 1-phenylethyl chlorides^{14,15)} and those (0.542–1.350) for the other solvolysis systems,¹⁶⁾ which may be attributed to the larger resonance effect for the phenolysis system than those for the other systems. Although the *r* value might be a parameter characteristic of the structure of the possible transition state model as well as a parameter measuring the availability of the transition state resonance, it could hardly describe the number and the detailed structure of ion-pair intermediate.

The phenolyses of **1**–**4** exhibit a reactivity parallel with that of the corresponding chlorides in aqueous ethanol¹⁴⁾ and in aqueous acetone;¹⁵⁾ there is a linear free-energy relationship (correlation coefficient 0.991 and 0.988) between the phenolysis and the hydrolysis rates, reflecting approximately similar transition states to each other.

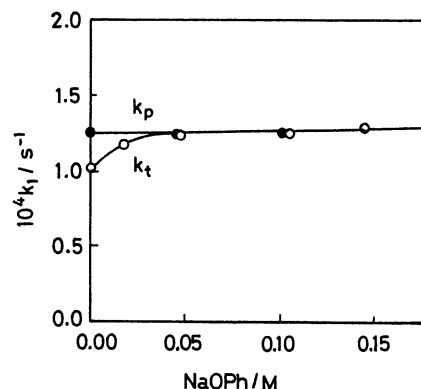


Fig. 2. Effect of added NaOPh concentration on the first-order rate constants (*k_p* and *k_t*) for the phenolysis of 1-(*p*-methylphenyl)ethyl *p*-nitrobenzoate in phenol at 75 °C.

Salt Effect on the Phenolysis Rates. The *k_p* and *k_t* for the optically active and racemic substrates **1** were measured in the presence of sodium phenoxide in phenol at 75 °C. Satisfactory first-order kinetic behavior, as expected for the S_N1 solvolysis, was observed at variable concentrations (0–0.145 M) of added sodium phenoxide. The *k_p* and *k_t* are summarized in Table 2, and are plotted against the salt concentrations (Fig. 2).

The salt effect of NaOPh on the *k_p*–*k_t* diagram for the phenolysis of **1** exhibits a pattern which belongs to the pattern B (Fig. 1) where the discrepancy between *k_p* and *k_t* virtually disappears, owing to the special salt effect^{3,4,17)} on *k_t*, at higher salt concentrations. We can characterize such salt effect using the parameters proposed by Winstein and his coworkers,^{17a)} i.e., $k_{t,ext}^0/k_t^0 = k_p^0/k_t^0 = 1.21$ and [salt]_{1/2} = 0.012 M and also using Winstein's equation^{17a)} $k_t = k_{t,ext}^0(1 + 0.0275 \cdot [\text{salt}])$, where *k_{t,ext}*⁰ is *k_t* value extrapolated at zero salt concentration from its linear part at higher salt concentrations, *k_t*⁰ and *k_p*⁰ are the *k_t* and *k_p* values at zero salt concentration, and [salt]_{1/2} is the salt concentration corresponding to 1/2 (*k_{t,ext}*⁰ + *k_t*⁰).

Such *k_p*–*k_t* pattern indicates that the phenoxide ion attacks the first ion-pair intermediate (Int-1), not the second one (Int-2), to produce all the products and to result in neither ion-pair return nor racemization of the intermediate itself at higher NaOPh concentrations.^{6,9)}

Table 3. The Relative Rates and the Features^{a)} of Four k_p - k_t Patterns for the Phenolyses of 1-(*p*-Substituted phenyl)ethyl *p*-Nitrobenzoates (RX) 1—4 in the Presence of Sodium Phenoxide in Phenol

RX	$k_{t,rel.}^{b)}$ (125 °C)	k_p - k_t pattern ^{c)}	No. of intermediate	Nucleophile ^{d)}	Ion-pair return	Ion-pair intermediate		
						Stability (Reactivity)	Life	Racemiza- tion
2	220	A	2	NaOPh	exists	higher (lower)	longer	more
1	14.1	B	1	NaOPh	exists ^{e)}	↑	↑	less ^{f)}
3	1.00	C	1	PhOH	exists	↓	↓	less
4	0.0430	D	1	PhOH	not exist	lower (higher)	shorter	no

a) Cited from Ref. 9. b) Cited from Table 1. c) See Fig. 1 for each profile. d) Reacting with ion-pair intermediate at higher salt concentrations. e) Does not exist at higher salt concentrations. f) No racemization at higher salt concentrations.

The other examples of this pattern have been observed for the phenolyses of 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoate,^{8,9)} 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl trifluoroacetate,⁸⁾ 1,5-dimethyl-1-ethylhexyl chloride⁸⁾ and *p*-nitrobenzoate,⁶⁾ and 1-methylheptyl tosylate,⁶⁾ the acetolysis of 2-(*p*-methoxyphenyl)propyl tosylate,^{††,4)} and the trifluoroacetolysis of 1-methylpropyl tosylate.¹⁸⁾

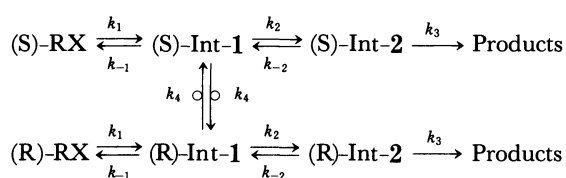
Features of the k_p - k_t profiles for 1—4 are summarized in Table 3. These results distinctly show that the k_p - k_t pattern does change in the sequence A → B → C → D as the stability of phenolysis intermediate decreases.

Thus, by means of each of the four k_p - k_t patterns, we can unambiguously determine (i) the number of ion-pair intermediate, in other words, the ion-pair stage of product formation, in addition, (ii) the species of nucleophile reacting with the ion-pair intermediate, and (iii) the existence or absence of ion-pair return.

The kinetic features of each k_p - k_t pattern (Table 3) can be expressed by the following reaction Schemes 1 and 2 for the patterns A and B-D, respectively.

According to such schemes, the total rate expressions for k_p and k_t can be derived as the following equations (Eqs. 1—4).

For the pattern A:



Scheme 1.

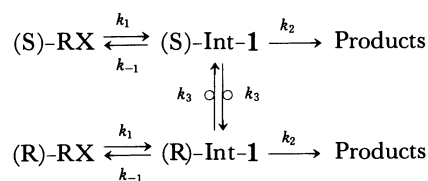
$$k_p = \frac{k_1}{1 + \frac{k_{-1}}{[k_2 k_3 / (k_3 + k_{-2})] + 2k_4}} \quad (1)$$

†† Although the pattern A was previously reported for this system,⁴⁾ reexamination of the pattern of salt effect has clarified that it does not follow pattern A, but B.⁹⁾

$$k_t = \frac{k_1}{1 + \frac{k_{-1}}{k_2 k_3 / (k_3 + k_{-2})}} \quad (2)$$

$$k_3 = k_3' + k_3'' [\text{PhOH}] + k_3''' [\text{NaOPh}]$$

For the patterns B, C, and D:



Scheme 2.

$$k_p = \frac{k_1}{1 + [k_{-1} / (k_2 + 2k_3)]} \quad (3)$$

$$k_t = \frac{k_1}{1 + k_{-1} / k_2} \quad (4)$$

$$k_2 = k_2' + k_2'' [\text{PhOH}] + k_2''' [\text{NaOPh}]$$

where $k_2''' = 0$ for the pattern C
 $k_2'' = 0$, and $k_3 = 0$ and/or $k_{-1} = 0$ for the pattern D

All solvolysis systems are summarized in Table 4, which have been unequivocally proved to proceed via multiple, e.g., two, and a single ion-pair intermediate on the basis of the k_p - k_t pattern. Table 4 suggests that, although S_N1 solvolysis has been generally recognized to proceed through multiple ion-pair intermediates,^{2a-h)} such a solvolysis system is rather exceptional and, in major ones, the first ion-pair intermediate (Int-1) is the product source.

Salt Effect on the Product Distribution. The product distribution was analyzed by the use of GLPC for the phenolysis of 1 (ROPNB) under identical conditions with those employed for the rate study. The

Table 4. S_N1 Solvolysis Systems Proved Experimentally to Proceed via Multiple (e.g., two) and a Single Ion-Pair Intermediate

Number of intermediate	k_p-k_t pattern ^{a)}	Substrate	Solvent	Added salt	Temp °C	Ref.
2	A	AnCH(Me)OPNB (2)	PhOH-benzene ^{b)}	NaOPh	25	c
		AnCH(<i>t</i> -Bu)OPNB	PhOH	NaOPh	75	d
					125	e
		AnCH(Me)CH(Me)X (X=OBs,OTs)	AcOH	LiClO ₄	25	f
1	B	TolCH(Me)OPNB (1)	PhOH	NaOPh	75	This work
		PhCH(<i>t</i> -Bu)OPNB	PhOH	NaOPh	75	d
		AnCH(<i>t</i> -Bu)OTFA	PhOH	NaOPh	75	e
		HexCH(Me)OTs	PhOH-benzene ^{b)}	Et ₃ N	75	g
		<i>i</i> -HexCMe(Et)Cl	PhOH-toluene ^{b)}	Et ₃ N	25	e
		<i>i</i> -HexCMe(Et)OPNB	PhOH-benzene ^{b)}	Et ₃ N	100	g
		AnCH(Me)CH ₂ OTs	AcOH	LiClO ₄	50	h
		EtCH(Me)OTs	CF ₃ COOH	NaOCOCF ₃	25	i
	C	PhCH(Me)OPNB (3)	PhOH	NaOPh	125	c
		PhCH(Me)Cl	PhOH-benzene ^{b)}	PhNH ₂	25	j
		PhCH(Et)OPNB	PhOH	NaOPh	125	e
		PhCH(<i>i</i> -Pr)OPNB	PhOH	NaOPh	125	e
		PhCH(<i>t</i> -Bu)OPNB	PhOH	Bu ₄ NClO ₄	75	d
		<i>p</i> -ClC ₆ H ₄ CH(Ph)OPNB	PhOH-benzene ^{b)}	NaOPh	100	e
		PhCMe(Et)OPNB	PhOH-benzene ^{b)}	Et ₃ N	50	e
		<i>exo</i> -2-NorbOBs	AcOH	KOAc	25	k
		PhCH(Me)Cl	60%aq.Dioxane	LiClO ₄	40	l
	D	<i>p</i> -O ₂ NC ₆ H ₄ CH(Me)OPNB (4)	PhOH	NaOPh	125	c
		<i>p</i> -O ₂ NC ₆ H ₄ CH(<i>t</i> -Bu)OPNB	PhOH	NaOPh	125	e
		<i>i</i> -HexCMe(Et)OTFA	PhOH-toluene ^{d)}	Et ₃ N	50	e
		<i>endo</i> -2-NorbOBs	AcOH	KOAc	75	k

a) The pattern of salt effect on k_p-k_t ; see Fig. 1, Table 3, and the text for each profile. b) A composition of 1:1 (w/w). c) Ref. 7. d) Ref. 9. e) Ref. 8. f) Ref. 3. g) Ref. 6. h) Ref. 4; see a footnote in the text. i) Ref. 18. j) Ref. 5. k) Estimated by us (Ref. 9) from the rate data at one or two concentrations of added KOAc (S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 and 1154 (1952)). l) P. B. D. de la Mare, D. M. Hall, and E. Mauger, *Rec. Trav. Chim. Pays-Bas*, **87**, 1394 (1968).

phenolysis produces a major amount of ROPh and small amounts of *o*- and *p*-RC₆H₄OH, and *p*-methylstyrene. Plots of the distribution (%) against the salt concentration exhibit patterns similar to the salt effect on k_t ; the yield (%) of aralkyl phenyl ether decreases and those of *o*- and *p*-aralkylphenol and *p*-methylstyrene increase (Fig. 3). Analogous patterns of the salt effect on product distributions were observed for the phenolyses of 1-aryl-2,2-dimethylpropyl systems.⁹⁾ The constancy of the product distribution at higher salt concentrations gives an indication that all the products come from the reaction of the ion-pair intermediate (Int-1) with added NaOPh, not with the solvent phenol molecule, at higher salt concentrations. The product distribution, which is extrapolated at zero base concentration from curves for respective products, suggests ROPh as the single product (Fig. 3). In contrast to such extrapolated product distribution, the phenolysis actually gave no ROPh but *o*- and *p*-RC₆H₄OH in the absence of NaOPh. This is most probably due to the slow rearrangement of ROPh to RC₆H₄OH by the liberated acid.¹⁹⁾

In conclusion, it has been clearly confirmed that we

can determine the number of ion-pair intermediate, namely, the ion-pair stage of nucleophilic attack by means of each of the four k_p-k_t patterns.

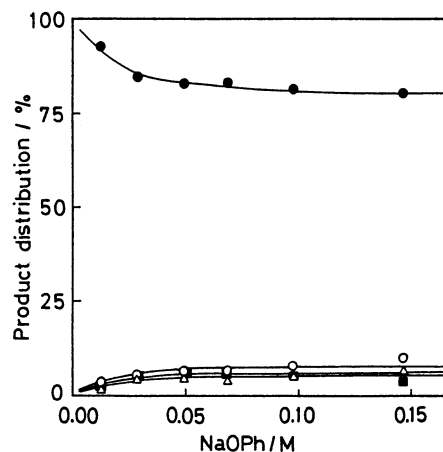


Fig. 3. Effect of added NaOPh concentration on the product distribution for the phenolysis of 1-(*p*-methylphenyl)ethyl *p*-nitrobenzoate in phenol at 75°C. ●: ROPh, ○: *o*-RC₆H₄OH, △: *p*-RC₆H₄OH, ■: *p*-MeC₆H₄CH=CH₂.

Table 5. Physical Constants, Spectral Data, and Elemental Compositions for 1-(*p*-Methylphenyl)ethyl Derivatives (RX) Relevant to the Phenolysis

RX	Mp(°C) (bp(°C/Pa))	Spectral data					Elemental composition/%			
		IR ^{a)} cm ⁻¹	¹ H NMR (δ) ^{b)}				Found		Required	
			CH ₃	-CH-	Ar	OH	C	H	C	H
ROPNB	69.8—70.5	1710(C=O) ^{c)}	1.69 (d) 2.33 (s)	6.13 (q)	7.10 —7.40 (m) 8.21 (s)		67.29	5.12	67.36 ^{d)}	5.30 ^{d)}
ROPh	(140—142/370)	1240(C—O—C)	1.57 (d) 2.24 (s)	5.22 (q)	6.79 —7.27 (m)		84.89	7.51	84.87 ^{c)}	7.60 ^{e)}
RC ₆ H ₄ OH (<i>o</i> -)	(162—163/270)	3540(OH) 3610(OH)	1.54 (d) 2.23 (s)	4.30 (q)	6.52 —7.23 (m)	5.08 (s,broad)	85.16	7.69	84.87 ^{c)}	7.60 ^{e)}
RC ₆ H ₄ OH (<i>p</i> -)	(175—176/270)	3400(OH) 3610(OH)	1.52 (d) 2.24 (s)	3.98 (q)	6.60 —7.29 (m)	6.14 (s,broad)	84.74	7.62	84.87 ^{c)}	7.60 ^{e)}

a) In CCl₄, unless otherwise noted. b) In CDCl₃. c) KBr disk. d) For C₁₆H₁₅NO₄. e) For C₁₅H₁₆O.

The structure of ion-pair intermediate will be discussed in the following paper on the basis of the stereochemical outcomes for *O*- and *C*-alkylations in the phenolysis of **1**.

Experimental

¹³C and ¹H NMR spectra were taken with a JEOL model JNM FX-90Q 22.5 MHz (FT) and a Hitachi R-24 60 MHz instruments, respectively. IR spectra were recorded with a Hitachi model 215 spectrophotometer. Optical rotations were measured with a JASCO model DIP-SL polarimeter. GLPC was performed with Hitachi model 163 and model 023-6003 instruments. MPLC was done with a chromatograph system composed of a FMI model RP-SY-2 pump and a Merck silica gel 60 column. Melting points were measured on a Yamato model MP-21 apparatus. Microanalyses were performed by the Elemental Analytical Center, Kyoto University.

Materials. Sodium phenoxide was synthesized in the usual way.⁷⁾ Racemic¹⁴⁾ and optically active ROH's²⁰⁾ were synthesized by the literature method. Other organic reagents were of analytical grade, dried, and fractionated prior to use.

Synthesis of 1-(*p*-Methylphenyl)ethyl *p*-Nitrobenzoate. According to the usual method,⁷⁾ optically active ROPNB was synthesized. A solution of (*R*)-(+)-ROH (10.017 g, 0.0735 mol, [α]_D^{26.0} +20.5±0.03° (*c* 10.90, ethanol)) and *p*-nitrobenzoyl chloride (15.66 g, 0.08440 mol) in pyridine (40 ml) was stirred at room temperature for 3 h. After usual work-up,²¹⁾ (*R*)-(-)-ROPNB (12.29 g, 58.60% yield; mp 69.8—70.5°C (uncorr.); [α]_D^{23.4} -8.27±0.05° (*c* 3.784, benzene) was obtained. Racemic ROPNB was obtained in a similar manner. The physical constants and spectral data for ROPNB are shown along with those for the phenolysis products in Tables 5 and 6.

Rate Measurements. The usual aliquot technique was employed for measurements of *k_p* and *k_t* as previously described.²¹⁾ In each run, the reaction was followed to at least

Table 6. ¹³C NMR Spectral Data for 1-(*p*-Methylphenyl)ethyl Derivatives (RX) Relevant to the Phenolysis^{a)}

RX	CH ₃	-CH-	Ar
ROPNB	21.01 (q) 21.95 (q)	73.97 (d)	123.29 (d) 135.79 (s) 125.99 (d) 137.85 (s) 129.16 (d) 150.29 (s) 130.51 (d) 163.68 (s)
ROPh	21.03 (q) 24.45 (q)	75.63 (d)	115.86 (d) 136.85 (s) 120.47 (d) 140.21 (s) 125.42 (d) 157.99 (s) 129.19 (d) ^{b)}
<i>o</i> -RC ₆ H ₄ OH	20.83 (q) 20.93 (q)	38.02 (d)	115.81 (d) 132.19 (s) 120.69 (d) 135.65 (s) 127.22 (d) 142.24 (s) 127.29 (d) 153.06 (s) 127.75 (d) 129.19 (d)
<i>p</i> -RC ₆ H ₄ OH	20.83 (q) 22.00 (q)	43.41 (d)	115.15 (d) 135.24 (s) 127.29 (d) 138.87 (s) 128.56 (d) 143.68 (s) 128.93 (d) 153.21 (s)

a) δ; in CDCl₃. b) Corresponding to four carbon atoms.

80% conversion; smooth first-order linear relationships were obtained (the correlation coefficients ≥ 0.999). The rate data against the added NaOPh concentration are shown in Tables 1 and 2 and Fig. 1.

Product Distribution Analysis. Each phenolysis of racemic **1** was carried out in the presence of diphenyl ether as an internal standard under the conditions identical with those adopted for the rate study. After usual work-up²²⁾ with ether, each ethereal solution was concentrated by a distillation using a short column. Then product distributions were analyzed by GLPC in a manner similar to those reported earlier.²²⁾ They are plotted against the added NaOPh concentration in Fig. 3.

Isolation of the Phenolysis Products. Residues of the reaction solutions used for the rate measurements were combined. After the usual work-up as described previously,²¹⁾ products were separated by MPLC, distilled in vacuo, and identified on the basis of their IR, ¹³C and ¹H NMR spectral data, chromatographic data, and the elemental compositions. They are summarized along with those for ROPNB in Tables 5 and 6.

The authors thank the Ministry of Education, Science and Culture for a Grant-in-Aid for Scientific Research.

References

- 1) Part 14, T. Kinoshita, K. Komatsu, K. Ikai, T. Kashimura, S. Tanikawa, A. Hatanaka, and K. Okamoto, *J. Chem. Soc., Perkin Trans. 2*, in press.
- 2) For recent reviews, a) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Pub.*, **19**, 109 (1965) and their many earlier papers cited therein; b) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972); c) F. G. Bordwell, *ibid.*, **5**, 374 (1972); d) R. A. Snee, *ibid.*, **6**, 46 (1973); e) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, "Ions and Ion Pairs in Organic Reactions," ed. by M. Szwarc, John Wiley & Sons, New York, N. Y. (1974), Chap. 3; f) J. M. Harris, *Progr. Phys. Org. Chem.*, Vol. 11, pp. 88—174 (1974); g) T. W. Bently and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, Vol. 14, pp. 1—67 (1977); h) D. Bethell, "Reactive Intermediates," Vol. 1, ed. by M. Jones, Jr., and R. A. Moss, John Wiley & Sons, New York, N. Y. (1978), Chap. 4; i) K. Okamoto, *Pure Appl. Chem.*, **56**, 1797 (1984).
- 3) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).
- 4) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **80**, 459 (1958).
- 5) K. Okamoto, K. Takeuchi, and H. Shingu, *Bull. Chem. Soc. Jpn.*, **35**, 525 (1962); detailed reexamination for the salt effect on k_p – k_t will be described in a following paper (Part 16; T. Kinoshita, T. Ueno, K. Ikai, M. Fujiwara, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, in press).
- 6) K. Okamoto and T. Kinoshita, *Bull. Chem. Soc. Jpn.*, **45**, 2802 (1972).
- 7) K. Okamoto, T. Kinoshita, Y. Takemura, and H. Yoneda, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1426.
- 8) K. Okamoto, T. Kinoshita, T. Oshida, T. Yamamoto, Y. Ito, and M. Dohi, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 1617.
- 9) T. Kinoshita, K. Ikai, T. Kashimura, M. Fujiwara, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **59**, 2843 (1986).
- 10) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2743 (1956).
- 11) K. Okamoto and T. Kinoshita, *Chem. Lett.*, **1974**, 1037 and references cited therein.
- 12) E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Manion, *J. Am. Chem. Soc.*, **91**, 7381 (1969).
- 13) a) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957); b) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).
- 14) V. J. Shiner, Jr., W. E. Buddenbaum, P. L. Murr, and G. Lamaty, *J. Am. Chem. Soc.*, **90**, 418 (1968).
- 15) G. T. Bruce, A. R. Cooksey, and K. J. Morgan, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 551.
- 16) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **32**, 965 and 971 (1959).
- 17) a) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954); b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956); c) A. H. Fainberg, G. C. Robinson, and S. Winstein, *ibid.*, **78**, 2777 (1956); d) S. Winstein and E. Clippinger, *ibid.*, **78**, 2784 (1956); e) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).
- 18) A. D. Allen, I. C. Ambidge, and T. T. Tidwell, *J. Org. Chem.*, **48**, 4527 (1983).
- 19) K. Okamoto, T. Kinoshita, O. Makino, and H. Shingu, *Bull. Chem. Soc. Jpn.*, **47**, 1770 (1974).
- 20) O. Červinka and J. Fusek, *Z. Chem.*, **8**, 145 (1968).
- 21) K. Okamoto, T. Kinoshita, and Y. Osada, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 253.
- 22) K. Okamoto, K. Matsubara, T. Kinoshita, and H. Shingu, *Bull. Chem. Soc. Jpn.*, **45**, 1191 (1972).