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Retentive Solvolysis. 13.[1] The Number and the Stability of Carbocation Intermediate in the S_N1 Phenolysis. Salt Effect on Retentive Phenolyses of Optically Active 2,2-Dimethyl-1-(*p*-substituted phenyl)propyl *p*-Nitrobenzoates†

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The salt effect of $(n\text{-Bu})_4NClO_4$ and NaOPh on the polarimetric and titrimetric rate constants (k_p and k_t, respectively) has been examined for the S_N1 solvolyses of optically active 2,2-dimethyl-1-(*p*-methoxyphenyl)-propyl (**1**) and 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoates (**2**) in pure phenol solvent. Four patterns, A, B, C, and D of the k_p—k_t profile against the added salt concentration have been observed for the phenolyses of **1**, **2**, and 2,2-dimethyl-1-(*p*-nitrophenyl)propyl *p*-nitrobenzoate (**3**). The patterns can specify the number of the sequential ion-pair intermediates (i.e., one or two), the product-forming stage (i.e., the 1st or the 2nd intermediate), and the species of reactant at the product-forming step (i.e., solvent phenol molecule, the phenoxide, or the perchlorate). The feature of the pattern of the k_p—k_t profile is predominantly controlled by two factors, (i) the stability of the carbocation intermediate derived from the substrates **1**—**3** and (ii) the nucleophilicity of the added salt. The patterns of salt effect on the product distribution (% of ROPh, *o*- and *p*-RC_6H_4OH) are also compatible with such rationalization of the four patterns.

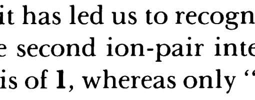
In view of the recent recognition of multiple intermediates in S_N1 solvolysis,[2] we need to know how many ion-pair intermediates exist in each solvolysis, before we consider about the structure of the ion pair as the intermediate. However, the example which actually presents experimental evidence for the presence of multiple intermediates has not so often been reported except by Winstein's[3,4] and our groups.[5—8]

As a result of such dearth of examples in the literature, there has been seen diversity of suggested structures on the ion-pair intermediates, especially for the second stage.[9] By the same token, there has been little direct proof[10] to a view that, as the reactivity of substrate is varied, the relative proportions of simultaneous nucleophilic attack at the different intermediate stages will change.[10,11]

It was previously reported that retentive phenolyses of optically active aralkyl systems can apparently be classified into two groups in which the products derived from either the first or the second ion-pair intermediate, on the basis of four patterns of the salt effect of sodium phenoxide on k_p (polarimetric rate constant) and k_t (titrimetric rate constant) profile.[5,6] However, the examples were so insufficient to correlate explicitly the ion-pair stage (the first or the second) of the product formation with the ion-pair stability (or the reactivity).

Recently, we have further investigated on the salt effect of two salts with different nucleophilicity (i.e., sodium phenoxide and tetrabutylammonium perchlorate) on the k_p and k_t and also on the product distribution (% of ROPh, *o*-, and *p*-RC_6H_4OH) for the phenolyses of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl (**1**) and 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoates (**2**). Thus, it has led us to recognize that products come from "the second ion-pair intermediate" alone in the phenolysis of **1**, whereas only "the first ion-pair intermediate" is the source of the products in that of **2**, reflecting the stability sequence of the carbocation intermediate derived from **1** and **2**.

In addition, it has been disclosed in the phenolysis of **2** that the added salts, i.e., sodium phenoxide and tetrabutylammonium perchlorate, can change the k_p—k_t pattern from the pattern B to the pattern C depending on their nucleophilicity, and hence the virtual reactant toward the ion-pair intermediate can be specified as the phenoxide in the presence of sodium phenoxide and as the phenol molecule in the presence of tetrabutylammonium perchlorate.



$$p\text{-Y-}C_6H_4\text{-}\underset{\displaystyle R}{\underset{|}{CH}}\text{-OPNB}$$

(1) R=*t*-Bu, Y=MeO
(2) R=*t*-Bu, Y=H
(3) R=*t*-Bu, Y=NO_2

Results and Discussion

Phenolysis Rates and Stability of the Ion-Pair Intermediates. The titrimetric rate constants for the phenolyses in phenol at 125 °C in the presence of sodium phenoxide (0.1 M (1 M=1 mol dm^{-3})) have previously been reported for **1**—**3**.[6] The $k_{t,rel.}$ and the k_p values, which were not cited in the previous paper,[6]

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Table 1. Phenolysis Rates of *p*-Substituted 2,2-Dimethyl-1-phenylpropyl *p*-Nitrobenzoates **1**—**3** in the Presence of Sodium Phenoxide at 125 °C

Substrate[a)]	$[\mathrm{NaOPh}]_0$/M	k_t/s^{-1} [b,c)]	$k_{t,\mathrm{rel.}}$	k_p/s^{-1} [d)]
1	0.111	4.13×10^{-3}	1.78×10^{5}	
	0.142			6.36×10^{-3}
2	0.104	1.50×10^{-6}	6.49×10	
	0.114			1.78×10^{-6}
3	0.117	2.31×10^{-8}	1.00	

a) $[\mathrm{Substrate}]_0=0.10$—0.11 M. b) Cited from Ref. 6. c) Accurate to within ±1.0%. d) Accurate to within ±3.0%.

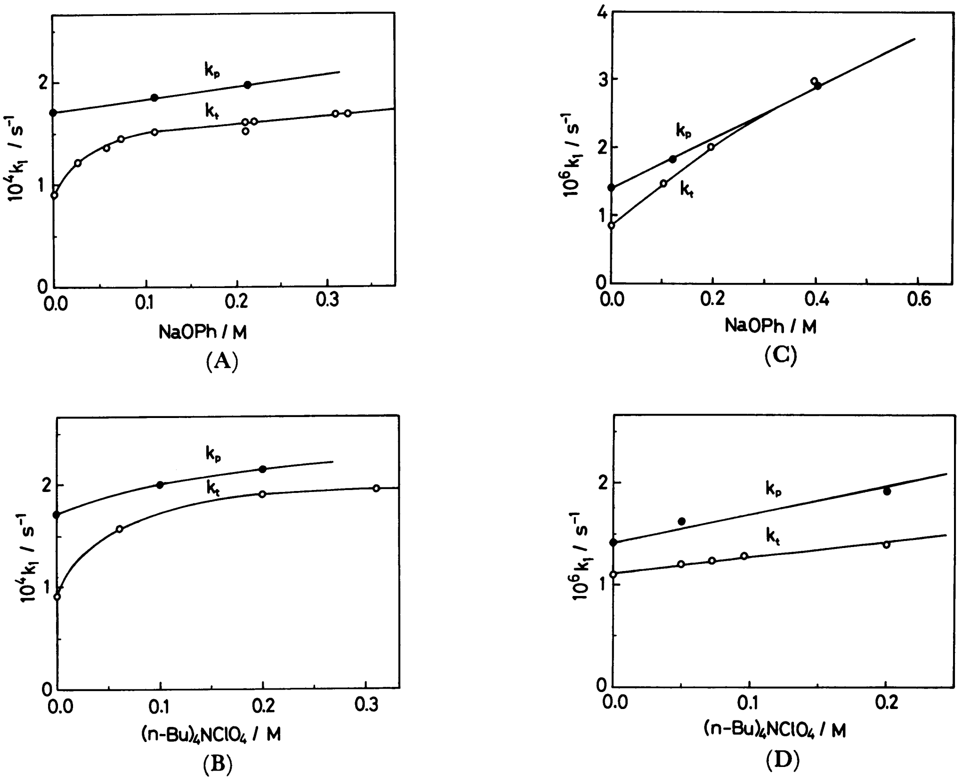

Fig. 1. Effect of added salt concentration on the first-order rate constants (k_p and k_t) in the phenolyses.
(A): (1) in the presence of NaOPh at 75 °C.
(B): (1) in the presence of $(n\text{-Bu})_4\mathrm{NClO}_4$ at 75 °C.
(C): (2) in the presence of NaOPh at 125 °C.
(D): (2) in the presence of $(n\text{-Bu})_4\mathrm{NClO}_4$ at 125 °C.

are shown along with the k_t values in Table 1.

The k_t decreases in the sequence **1**>**2**>**3** (relative rate; 178000:64.9:1.00). The k_p ($k_p/k_t<1.4$) decreases in the same sequence **1**>**2**. Thus, each of the phenolysis intermediate should become less stable in the order of rate sequence.

Salt Effect on Phenolysis Rates. The measurement of k_p and k_t values were carried out at variable concentrations of added sodium phenoxide or tetrabutylammonium perchlorate for the optically active substrates **1** at 75 °C and **2** at 125 °C. Subsequently, the k_p and k_t were plotted against the salt concentration (Fig. 1).

Such k_p—k_t diagrams can in general be classified into four patterns, A–D (Fig. 2), provided that there is no normal salt effect.[6)]

A common feature of patterns A and B is seen in "the special salt effect" on k_t, which has first been recognized in acetolyses of many substrates by Winstein and his coworkers.[3,4,9,15)] The special salt effect indicates that the added salt reacts with an ion-pair intermediate making the rate of ion-pair return negligibly low as compared with the rate of the product formation.

Table 2. Salt Effect on k_p-k_t for the Phenolyses of 2,2-Dimethyl-1-(*p*-substituted phenyl)propyl *p*-Nitrobenzoates **1**—**3** in Phenol

Substrate[a]	Salt	Temp / °C	k_t° [b,c] / s^{-1}	$k^\circ_{t,ext}$[b] / k°_t	$[Salt]_{1/2}$[b] / M	b_t[b]	k_p° [a,c] / s^{-1}	b_p[b]	k_p-k_t pattern[d]
1	NaOPh	125[e]	2.93×10^{-3}	1.74	0.10	0.50	5.90×10^{-3}	0.52	A
		75	9.31×10^{-5}	1.58	0.025	0.40	1.71×10^{-4}	0.61	A
	TBAP[f]	75	9.31×10^{-5}	1.58	0.01	1.6	1.71×10^{-4}	1.7	A
2	NaOPh[e]	125	8.50×10^{-7}	1.67	0.041	2.54	1.42×10^{-6}	2.54	B
	TBAP[f,g]	125	8.50×10^{-7}	1.00	—	4.00	1.42×10^{-6}	2.32	C
3[e]	NaOPh	125	1.75×10^{-8}	1.00	—	2.71	—	—	D[h]

a) $[Substrate]_0=0.10$—0.12 M. b) See the text. c) Accurate to within ±2% for k_t° and within ±3% for k_p° unless otherwise noted. d) The pattern of salt effect on k_p-k_t (see Fig. 2). e) Cited from Ref. 6. f) Tetrabutylammonium perchlorate. g) In the presence of 2,6-di-*t*-butyl-4-methylpyridine (0.1 M). h) Concluded from the k_t diagram against the added NaOPh concentration and from no racemization of the reclaimed substrate at 50% conversion.

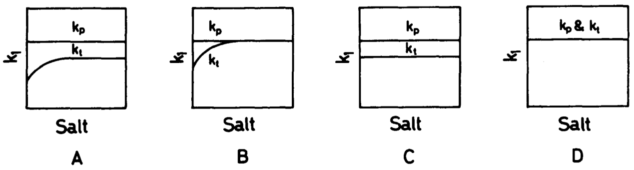

Fig. 2. Four patterns of salt effect on k_p and k_t in S_N1 solvolysis (in the absence of normal salt effect; cited from Ref. 6).

In pattern A, the k_p exceeds the k_t over the whole range of the added salt concentration and the k_p/k_t ratio is constant at higher concentrations of the salt. This indicates the existence of two kinetically-distinguishable intermediates in the solvolysis system as pointed out by Winstein and his coworkers.[3,4]

By contrast, in pattern B the discrepancy between k_p and k_t virtually disappears with increase in the salt concentration. The coincidence in the k_p and k_t values at higher salt concentrations suggests that the consumption rate of the ion-pair intermediate becomes far greater than the return rate and consequently that the solvolysis proceeds via a single ion-pair intermediate alone.

The k_t values in patterns C and D are invariant despite of increase in concentration of the added salt. Thus, the patterns C and D indicate that not the salt but a solvent molecule alone participates in the formation of the product. They clearly indicate that the intermediate is so reactive as to react with the solvent molecule before it does with the added salt. Consequently, we can see from the patterns C and D the existence of a single ion-pair intermediate alone in the reaction system.

In the pattern C, in addition, the intermediate partially returns to the substrate, partially reacts with the solvent molecule, and partially racemizes in itself. In the pattern D, however, all of the intermediate is scavenged by the solvent molecule alone.*

We can characterize such salt effect on k_p and k_t, using the parameters proposed by Winstein and his coworkers,[13] i.e., $k^\circ_{t,ext}/k^\circ_t$ ($k^\circ_{t,ext}$: k_t value extrapolated at [salt]=0 from its linear part at higher salt concentrations, k°_t: k_t value at [salt]=0) and $[salt]_{1/2}$ (salt concentration corresponding to $0.5(k^\circ_{t,ext}+k^\circ_t)$) for special salt effect, and also using Winstein's equations[13] $k_p=k^\circ_p(1+b_p[salt])$ (k°_p: k_p value at [salt]=0) and $k_t=k^\circ_{t,ext}(1+k_t[salt])$ for normal salt effect on k_p and k_t, respectively. Such parameters for phenolyses of **1**—**3**, which include some previously-reported,[6] are tabulated in Table 2.

The phenolysis of **1** in the presence of NaOPh or $(n\text{-Bu})_4NClO_4$, follows pattern A (Fig. 1 and Table 2; $k^\circ_{t,ext}/k^\circ_t>1$, $[salt]_{1/2}>0$, and $k_p/k_t>1$) which suggests that both NaOPh and $(n\text{-Bu})_4NClO_4$ attack the second intermediate (I_2).

The other examples of pattern A have been observed in the phenolysis of 1-(*p*-methoxyphenyl)ethyl *p*-nitrobenzoate in the presence of NaOPh[5] and also in the acetolyses of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl brosylate and tosylate in the presence of $LiClO_4$.[3]

The k_p-k_t profile for **2** against the added NaOPh concentration, which belongs to pattern B (Fig. 1 and Table 2; $k^\circ_{t,ext}/k^\circ_t>1$, $[salt]_{1/2}>0$, and $k_p/k_t=1$), indicates that the phenoxide ion attacks the first ion-pair intermediate to result in neither ion-pair return nor racemization of the intermediate itself at higher NaOPh concentrations. The other examples of pattern B have been found in the phenolyses of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl trifluoroacetate,[6] 1-ethyl-1,5-dimethylhexyl chloride and *p*-nitrobenzoate,[7] and 1-methylheptyl tosylate,[7] the acetolysis of

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* The intermediate may return without racemization and also without isotope scrambling of two oxygen atoms in the *p*-nitrobenzoyloxy group of leaving one.

2-(*p*-methoxyphenyl)propyl tosylate,4) and the trifluoroacetolysis of 1-methylpropyl tosylate.14)

In this context, it deserves to mention that Winstein and his coworkers measured the sum ("k_1"$=k_t+k_r$) of the k_t for 2-(*p*-methoxyphenyl)propyl tosylate and the rearrangement rate (k_r) to 1-(*p*-methoxyphenyl)-1-methylethyl tosylate as the ionization rate constant instead of the k_p and they regarded the "k_1"$-k_t$ (instead of k_p-k_t) profile for the acetolysis of 2-(*p*-methoxyphenyl)propyl tosylate as pattern A in the presence of $\mathrm{LiClO_4}$.4) However, the ratios of "k_1"$/k_t$ for this system are calculated to be 1.24, 1.14, and 1.03 at $\mathrm{LiClO_4}$ concentrations 0.0300, 0.0600, and 0.100 M, respectively, by the use of their rate data.4) Thus, it certainly decreases to 1.00 at higher $\mathrm{LiClO_4}$ concentrations. In other words, the "k_1" and k_t lines must coincide with each other at the higher salt concentration than 0.1 M. Consequently, the profile should not belong to pattern A, but to pattern B, and hence the nucleophile should attack the first, not the second, ion-pair intermediate in the acetolysis.

The phenolysis of **2** in the presence of $(n\text{-Bu})_4\mathrm{NClO_4}$[†] exhibits pattern C (Fig. 1 and Table 2; $k^\circ_{t,\mathrm{ext}}/k^\circ_t=1$, $[\mathrm{salt}]_{1/2}=0$, and $k_p/k_t>1$) instead of B. The added perchlorate is less nucleophilic than NaOPh and the intermediate is scavenged by the solvent phenol instead of the perchlorate. Thus, this is reflected in the changeover of the pattern from B to C (Table 2).

The same pattern C has been observed in the other phenolyses of 1-phenylethyl,5) 1-phenylpropyl,6) 2-methyl-1-phenylpropyl,6) 1-methyl-1-phenylpropyl,6) *p*-chlorobenzhydryl *p*-nitrobenzoates6) in the presence of NaOPh), and 1-phenylethyl chloride (in the presence of $\mathrm{PhNH_2}$[††]). The same pattern C has been also found in the acetolysis of *exo*-2-norbornyl brosylate in the presence of KOAc.[†††],16)

The *p*-nitrobenzoate (**3**) should give a relatively less stable and short-lived ion-pair intermediate, and the racemization was not observed in the reclaimed substrate at a half life. Hence, although the k_p was not measured for **3**, it is most probable that **3** follows pattern D (Table 2; $k^\circ_{t,\mathrm{ext}}/k^\circ_t=1$, $[\mathrm{salt}]_{1/2}=0$, and $k_p/k_t=1$). The phenolyses of 1-(*p*-nitrophenyl)ethyl *p*-nitrobenzoate5) and 1-ethyl-1,5-dimethylhexyl trifluoroacetate in the presence of NaOPh6) and the acetolysis of *endo*-2-norbornyl brosylate in the presence of KOAc[†††],16) offer the other examples of pattern D.

Among the phenolyses of the three substrates **1**—**3**, the reaction temperature (75 °C) for **1** in the presence of $(n\text{-Bu})_4\mathrm{NClO_4}$ is lower than those for the others (see Table 2). However, the pattern A for **1** has been observed in the presence of NaOPh at both 1256) and 75 °C (Table 2). Therefore, the k_p-k_t pattern for $(n\text{-Bu})_4\mathrm{NClO_4}$ would most probably follow pattern A even at 125 °C.

Accordingly, under the exactly identical conditions the k_p-k_t profiles for phenolyses of **1**—**3** should exhibit pattern A for **1**, B in the presence of NaOPh for **2**, C in the presence of $(n\text{-Bu})_4\mathrm{NClO_4}$ for **2**, and D for **3**.

The similar feature of the k_p-k_t profile has been observed for the phenolysis of 1-phenylethyl system, A for *p*-$\mathrm{CH_3O}$, C for unsubstituted, and D for *p*-$\mathrm{NO_2}$.5)

These results, in turn, show that the k_p-k_t pattern should change in the order A→B→C→D as the stability of phenolysis intermediate decreases and also as the nucleophilicity of added salt decreases. For **1** which gives the most stable carbocation among the homologue, the second ion-pair intermediate ($\mathrm{I_2}$) is attacked by both NaOPh and $(n\text{-Bu})_4\mathrm{NClO_4}$. For **2** which generates relatively less stable carbocation, the phenoxide ion and a solvent molecule (in a solvation shell) attack the first ion-pair intermediate ($\mathrm{I_1}$), but $(n\text{-Bu})_4\mathrm{NClO_4}$ can not have the chance to react with $\mathrm{I_1}$. For **3** which produces the most reactive carbocation among the homologue, $\mathrm{I_1}$ reacts instantly with the solvent phenol molecule alone as it forms.

A similar tendency is seen in the comparison of acetolyses of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl and 2-(*p*-methoxyphenyl)propyl tosylates; their rates (k°_p) decrease in the sequence the former ($2.70\times10^{-5}\,\mathrm{s^{-1}}$ at 25 °C3)) > the latter ($1.79\times10^{-5}\,\mathrm{s^{-1}}$ at 50 °C4)) and follow the k_p-k_t patterns A and B, respectively (vide supra).

It has been claimed that in the S_N1 solvolysis the product may be produced via some or all of possible intermediates.2) In addition, a view10,11) has been presented that as the stability of the intermediates varies, the relative portions of nucleophilic attack stages will change. However, little direct evidence10) has been given to the view. Our result shows that, conservatively speaking of the phenolysis, all of the products are substantially derived from a single ion-pair intermediate, either $\mathrm{I_1}$ or $\mathrm{I_2}$.

Thus, from the k_p-k_t patterns, we can determine the number of ion-pair intermediate, in the other words, the product-forming stage and the species of reactant (the solvent molecule or the added salt). Hence, the intermediate stage of nucleophilic attack is fundamen-

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[†] 2,6-Di-*t*-butyl-4-methylpyridine was added to the phenolysis of **2** in the presence of $(n\text{-Bu})_4\mathrm{NClO_4}$ in order to neutralize the liberated acid which might cause the rearrangement of the phenyl ether to the alkylphenols.15)

[††] Although the pattern A was previously reported for the phenolysis of 1-phenylethyl chloride in the presence of aniline,8) reexamination of the salt effect for the system in our laboratory has now disclosed that it does not follow pattern A, but C.

[†††] For the acetolyses of *exo*-16) and *endo*-2-norbornyl brosylates,17) the rates were measured only at one or two concentrations of added KOAc. The k_p-k_t patterns, however, can be estimated to be C for the exo-isomer and D for the endo-isomer.

Table 3. Features of Four Patterns of the k_p-k_t Diagram against Concentration of Added salt in the Phenolyses of 2,2-Dimethyl-1-(*p*-substituted phenyl)propyl *p*-Nitrobenzoates **1**—**3**

X[a)]	Pattern[b)]	No. of intermediate	Added salt	Nucleophile[c)]	Ion-pair return	Ion-pair intermediate		
						Life	Stability (Reactivity)	Racemization
CH_3O **1**	A	2	NaOPh TBAP[d)]	NaOPh TBAP[d)]	Exists	Longer	Higher (Lower)	More
H **2**	B	1	NaOPh	NaOPh	Exists[e)]	Shorter	Lower (Higher)	Less[f)]
H **2**	C	1	TBAP[d)]	PhOH	Exists	Shorter	Lower (Higher)	Less
NO_2 **3**	D	1	NaOPh	PhOH	Not exist	Much shorter	Much lower (Much higher)	No

a) *p*-Substituent. b) See the text for each profile. c) Reacting with ion-pair intermediate. d) Tetrabutylammonium perchlorate. e) Not exist at higher salt concentration. f) No racemization at higher salt concentrations.

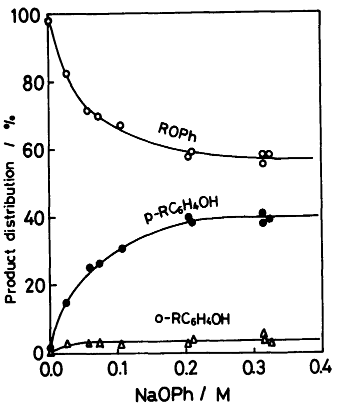

Fig. 3. Product distribution in the phenolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nirtobenzoate (**1**) in the presence of added sodium phenoxide in phenol at 75 °C.

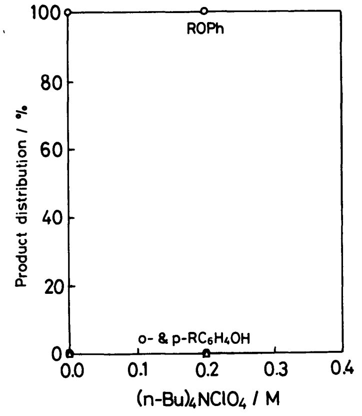

Fig. 4. Product distribution in the phenolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (**1**) in the presence of added tetrabutylammonium perchlorate in phenol at 75 °C (at 0% reaction extrapolated from product distributions at 5—70% reaction).

tally dependent on the stability (the reactivity or the life span) of SN1 ion-pair intermediate and the nucleophilicity of the added salt or the solvent molecule. These are summarized in Table 3.

Salt Effect on Product Distribution. The product distribution (% of ROPh, *o*-, and *p*-RC_6H_4OH) was examined by the use of GLPC for the phenolyses of **1** with variable concentrations (0—0.3 M) of added NaOPh or $(n\text{-Bu})_4NClO_4$ at 75 °C under conditions identical with those employed in rate measurements. When the distribution was plotted against the concentration of added salt, patterns similar to the salt effect on k_t were observed in the diagrams; the results are shown in Figs. 3—5, along with that for **2** which was reported in the previous paper.

For **1** and **2** in the presence of NaOPh, the yield of *p*-alkylphenol increases and that of alkyl phenyl ether decreases in a pattern similar to the special salt effect on k_t (Figs. 2 and 4). The yield of *o*-alkylphenol is

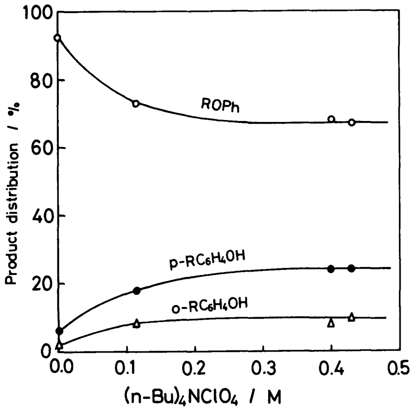

Fig. 5. Product distribution in the phenolysis of 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoate (**2**) in the presence of added sodium phenoxide in phenol at 125 °C (cited from Ref. 6).

almost invariable. From constancy of the product distribution at higher salt concentrations, it is concluded that almost all of the products at higher salt concentrations are derived from the reaction of the phenolysis intermediate with the added salt, not with the solvent phenol molecule.

For **1** in the presence of $(n\text{-Bu})_4NClO_4$, the product distribution is almost invariable inspite of increase in the added salt concentration and predominantly the phenyl ether alone (extrapolated at 0% reaction from product distribution curves at 5—70% reaction¶; Fig. 3).

Thus, the special salt effect by NaOPh appears on both the k_t value and the product distribution, whereas the special salt effect by $(n\text{-Bu})_4NClO_4$ does not appear on the product distribution but on the k_t value alone.

The perchlorate certainly reacts with the intermediate to give another intermediate, which is rapidly consumed by the solvent phenol molecule alone. On the role of $(n\text{-Bu})_4NClO_4$ at the product formation stage, further examination is in progress.

In conclusion, only after confirmation of the ion-pair stage of nucleophilic attack, we can deduce the detailed structure of the ion-pair intermediates from the stereochemical outcomes for both O- and C-alkylations in phenolyses. The ion-pair structure will be discussed in the following paper.

Experimental

^{13}C and ^{1}H NMR spectra were taken with a JEOL model JNM FX-100 25 MHz and a Hitachi model R-24 60 MHz instruments, respectively; IR spectra with a Hitachi model 215 spectrophotometer, and GLPC was performed with Hitachi model 163 and model 023-6003 instruments. Optical rotations were measured with a JASCO DIP-SL polarimeter.

Materials. Optically active **1** and **2** were synthesized in the previously-reported manner.[6] Sodium phenoxide was prepared by refluxing a toluene solution of phenol with sodium metal. Tetrabutylammonium perchlorate, an analytical reagent grade, was recrystallized from ethanol and dried in vacuo. 2,6-Di-*t*-butyl-4-methylpyridine was prepared by a known method.[18]

Titrimetric Rate Constants (k_t). The usual aliquot technique[5,6] was employed for measurement of k_t. The diminution in base concentration in the presence of NaOPh was followed by titration in acetone with standard hydrochloric acid; the increase in acid concentration in the presence of $(n\text{-Bu})_4NClO_4$ or in the absence of added salt was followed by titration with aqueous sodium hydroxide solution. Methyl Red was used as an indicator. The k_t values are tabulated in Table 2.

Polarimetric Rate Constants (k_p). The previously-reported procedure[5,6] was followed. The rate data against the added salt concentration are summarized in Table 2.

Product Distribution Analysis. Product distributions of phenolyses were analyzed by GLPC in a manner similar to that reported earlier.[19]

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