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Number and Structure of Solvolysis Intermediates. Part 2.[1]
A Novel Example of the Common Ion Rate Depression Arising at the Stage of the Second Ion Pair Intermediate in the S_N1 Solvolysis

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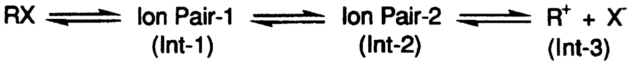
The solvolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate in phenol provides a novel example of the common ion salt effect (*rate depression*) which arises at the stage of the second ion pair intermediate (Int-2; the rear-side shielded ion pair intermediate), not the dissociated (free) carbocation intermediate as generally supposed so far. This example demonstrates that "the common ion rate depression" could not give evidence for the intermediacy of the dissociated carbocation intermediate in the S_N1 solvolysis, but an indicator for the stability of solvolysis intermediates including the ion pair intermediate.

It has been accepted by most researchers in the field that the Winstein ion pair mechanism for sequential ionization (Scheme 1),[2,3] involving two kinds of ion pair intermediate (Int-1 and Int-2)[4] and a dissociated (free) carbocation intermediate, provides a reasonable general framework for discussion of solvolysis reactions.[3] However, we cannot find an example of the solvolysis system which has been ascertained to contain all the three kinds of intermediate in the medium. The mechanism of S_N1 solvolysis should be, in general, discussed after confirmation of the number of solvolysis intermediate stages, via which the solvolysis proceeds. The pattern analysis for the salt effect on the k_p–k_t diagram (k_p: polarimetric rate constant, k_t: titrimetric rate constant), which was partly proposed by Winstein and his coworkers[2,3,8] and established by us,[9] can serve as a practically-useful tool for the determination of the number of solvolysis intermediate stages; i.e., *a single stage* or *multiple stages.* The k_p–k_t pattern method, however, can provide no information which can serve to distinguish the intermediation of the dissociated carbocation intermediate in the S_N1 solvolysis system.[9]

For the intermediacy of *the dissociated carbocation* in the S_N1 solvolysis reaction, the observation of "*the common ion rate depression* (*mass law effect*)" has been considered to give strong evidence.[10,11] It was explained in the classical solvolysis theory, assuming *a single carbocation intermediate*, that the rate depression might be caused by the acceleration of recombination of the dissociated carbocation with the counter anion.[3,5] After the finding of the intervention of the ion pair intermediates (Scheme 1),[2,3,12] the common ion effect has been explained by an enhancement of "*external ion return.*"[3,11] On the other hand, the common ion rate depression in the solvolysis of *t*-butyl chloride in phenol was supposed to be caused at the stage of an ion pair intermediate.[13] However, none of many examples of common ion rate depression[10,11] have given experimental evidence for the solvolysis intermediate stage (i.e., truly *the dissociated carbocation intermediate stage* or/and *an ion pair intermediate stage* ?), at which the added common ion salt attacks to generate the common ion effect.[2,3,8] Thus, we intended to examine the common ion salt effect on a solvolysis system which has been ascertained to proceed via multiple solvolysis intermediate stages. Many examples of solvolysis are confirmed to proceed via a single ion pair intermediate stage,[9] whereas a few examples of solvolysis provide experimental evidence for the existence of multiple solvolysis intermediate stages;[9] such a few examples are only the phenolyses of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl[5a,5b,9] and 1-(*p*-methoxyphenyl)ethyl system[9,14] and the acetolysis of the 2-(*p*-methoxyphenyl)-1-methylpropyl system.[8,9,15] On the two former phenolysis systems, the common ion salt effect has not been studied. For the latter acetolysis system, no common ion rate depression was reported.[8,16] As a target system for the investigation, we have chosen the phenolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl system in which *no dissociated carbocation intermediate participates* (vide infra).[1]



Scheme 1.[4]

In this paper, we wish to report a novel example of the common ion rate depression arising at the stage of the second ion pair intermediate (Int-2; the rear-side shielded ion pair intermediate[5]) in the solvolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate in phenol.

Results and Discussion

Solvolysis Rates in the Presence of Tetrabutylammonium *p*-Nitrobenzoate. Optically active and racemic 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoates (ROPNB) were solvolyzed in phenol in the presence of a common ion salt, tetrabutylammonium *p*-nitrobenzoate ($(n\text{-Bu})_4N^+OPNB^-$), at 75 °C under the conditions identical with those employed in the previous work[5] except the addition of the salt. The solvolysis rates were measured by both the polarimetric and the titrimetric methods. Satisfactory first-order kinetic behavior, as expected for the S_N1 solvolysis, was observed at variable concentrations (0.000—0.399 M) (1 M=1 mol dm^{-3}) of the added common ion salt (correlation coefficients $\geq$0.9990 for k_t and $\geq$0.9980 for k_p). The k_p and k_t values are summarized in Table 1 and are plotted against the salt concentration in Fig. 1.

The effect of the added common ion salt appears as a rate depression, i.e., "common ion rate depression,"[10,11] on the k_t values at the 0.05—0.15 M region of the added salt concentration (Fig. 1). Extrapolation of the plots at 0.10—0.15 M region in Fig. 1 to zero salt concentration furnishes estimation of fully depressed solvolysis rate constant, k_t^d, correlated for normal salt effects.[11a] The ratio, k_t^0/k_t^d, characterizing the common ion rate depression is 1.3 (±0.1) in this case. This ratio is comparable to those in the acetolyses of cholesteryl brosylate and tosylate and 2-(2,4-dimethoxyphenyl)ethyl brosylate, for which the values are 1.1_3, 1.2_0, and 1.5_7, respectively.[11a] Such a rate depression is not observed in the k_p values (vide infra). If this rate depression was eliminated, the k_t values would show a similar simple increase (normal salt effect[18]) to that for the k_p values with an increase in the added salt concentration in the region lower than 0.15 M (Fig. 1). The rate decrease in both the k_t and k_p values at the higher concentrations than 0.15 M is most probably due to the decrease in the concentration of solvent phenol.[19] Since the common ion rate depression arises at about one tenth concentration of the added common ion salt in the solvolyses in the other solvents than phenol,[10,11] no rate measurement was carried out at such the range of higher concentrations as that in phenol, where the rate decrease owing to the decrease in the solvent concentration might be observed.

Table 1. The Solvolysis Rates of 2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl *p*-Nitrobenzoate (ROPNB) in the Presence of Tetra-*n*-butylammonium *p*-Nitrobenzoate ($(n\text{-Bu})_4N^+OPNB^-$) in Phenol at 75 °C[a)]

$(n\text{-Bu})_4N^+OPNB^-$/M	k_t/s^{-1} b)	k_p/s^{-1} c)
0.000 d)	1.02×10^{-4}	1.71×10^{-4}
0.050	9.56×10^{-5}	1.92×10^{-4}
0.100 d)	9.51×10^{-5}	
0.101		1.96×10^{-4}
0.150	1.05×10^{-4}	
0.197	1.04×10^{-4}	
0.231		1.96×10^{-4}
0.301	9.06×10^{-5}	
0.399	7.95×10^{-5}	

a) $[\text{ROPNB}]_0$ 0.0995—0.100 M. b) Titrimetric rate constant; accurate to within ±2%. c) Polarimetric rate constant; accurate to within ±3%. d) An average value for duplicate measurements.

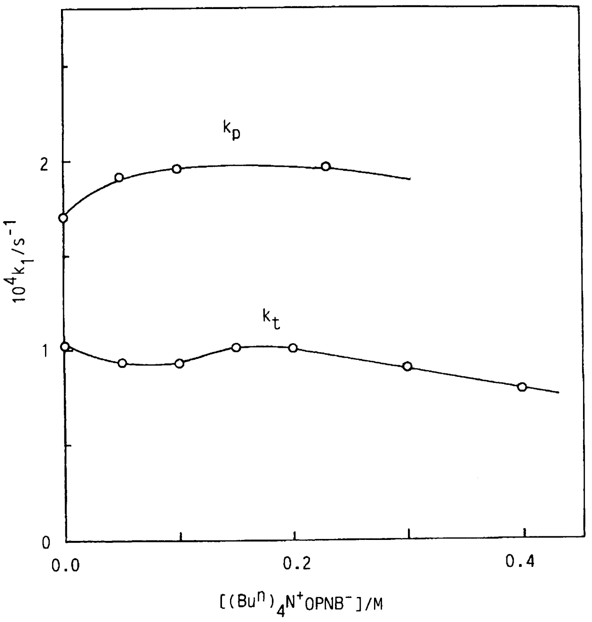


Fig. 1. Effect of added $(n\text{-Bu})_4N^+OPNB^-$ on the polarimetric and titrimetric rate constants (k_p and k_t) for the solvolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate in phenol at 75 °C.

Product Distribution. The product distribution was analyzed by the use of G.L.P.C. for the solvolysis of ROPNB in the presence of $(n\text{-Bu})_4N^+OPNB^-$ under the conditions identical with those employed for the rate study (Table 2). The solvolysis produced a major amount of ROPh and small amounts of *o*- and *p*-RC_6H_4OH similar to those in the absence of the added common ion salt.[5] The product distribution is invariable within experimental errors over the whole range of added salt concentrations, which suggests that the product-forming solvolysis intermediate in the presence of the added common ion salt may have the same structure (rear-side shielded ion pair) as that in the absence of the added common ion salt.[5]

Stereochemical Courses. Optically active ROPNB was subjected to the solvolysis in the presence of $(n\text{-Bu})_4N^+OPNB^-$ (0.100 M) under the identi-

Table 2. The Product Distribution for the Solvolysis of 2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl *p*-Nitrobenzoate (ROPNB) in the Presence of Tetra-*n*-butylammonium *p*-Nitrobenzoate ($(n\text{-Bu})_4N^+OPNB^-$) in Phenol at 75 °C[a)]

$(n\text{-Bu})_4N^+OPNB^-$	Product distribution/% b)		
M	ROPh	*o*-RC_6H_4OH	*p*-RC_6H_4OH
0.000	96.6	1.1	2.3
0.052	97.6	0.2	2.2
0.099	97.1	0.4	2.5
0.199	98.7	0.4	0.9
0.300	96.9	1.2	1.9
0.400	98.4	0.4	1.2

a) $[\text{ROPNB}]_0$=0.100—0.102 M. b) Determined by G.L.P.C.; (ROPh+*o*-RC_6H_4OH+*p*-RC_6H_4OH) % =100 %.

cal conditions with those mentioned above. The solvolysis produced partially retained ROPh, *o*-RC_6H_4OH, and *p*-RC_6H_4OH with predominant racemization, respectively (Table 3). The products were not completely racemized under the reaction conditions. The racemization % for each product is somewhat larger than those in the absence of the common ion salt. These stereochemical facts indicate the increase in the external return rate in the presence of the common ion salt.

Table 3. The Stereochemical Courses for the Products of the Solvolyses of 2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl *p*-Nitrobenzoate (ROPNB) in the Presence of Tetra-*n*-butylammonium *p*-Nitrobenzoate ($(n\text{-Bu})_4N^+OPNB^-$) in Phenol at 75 °C

Added salt	Concentration	ROPNB/M	Net stereochemical course/α%,[b] $\{[\alpha]_D(°)\}$[a]		
	M	$\{[\alpha]_D(°)\}$[a]	ROPh	*o*-RC_6H_4OH	*p*-RC_6H_4OH
$(n\text{-Bu})_4N^+OPNB^-$ [d]	0.100	0.100 {+77.04 (±0.12)}[c]	0.85(±0.09) ret. {+0.187(±0.019)}	7.56(±1.89) ret. {−2.36(±0.59)}	2.26(±0.65) ret. {+0.661(±0.190)}
None[d,e]	0.000	0.0973	1.09(±0.13) ret.	20.4(±5.1) ret.	3.57(±0.29) ret.
NaOPh[e]	0.102	0.0956	3.83(±0.13) ret.	6.31(±0.81) ret.	5.02(±0.76) ret.

a) In benzene, c 0.81—7.05. b) Calculated from the optical purity of the product on the basis of that of the starting ROH, from which ROPNB was synthesized; the maximum specific rotations are taken to be −44.83°, +161.4°, +45.0°, −64.5°, and +60.4° for ROH, ROPNB, ROPh, *o*-RC_6H_4OH, and *p*-RC_6H_4OH with *S*-configuration, respectively (cited from Ref. 5). c) Synthesized from (*S*)-ROH, $\{[\alpha]_D^{21.8}$ −21.72±0.04° (benzene)$\}$. d) In the presence of 2,6-di-*t*-butyl-4-methylpyridine (0.10 M). e) Cited from Ref. 5.

Reaction Pathway. For the solvolysis mechanism of ROPNB in phenol, the confirmed facts have been summarized as follows.

(1) The k_p–k_t pattern analysis method indicates that the phenolysis of ROPNB proceeds via multiple solvolysis intermediate stages ("*two ion pair intermediate stages*" or "*two ion pair and a dissociated carbocation intermediate stages*").[5,9]

(2) The comparison of the phenolysis reaction with the nucleophilic reactions on the in situ generated carbocation exhibits that *no dissociated (free)* carbocation intermediate intervenes in the solvolysis of ROPNB in phenol.[1]

(3) The formation of the partially retained products reveals that the solvolysis gives rise to the retained products at the stage of the ion pair intermediate, not the dissociated carbocation intermediate which provides the racemized products, under the reaction conditions.

(4) It demonstrates no intermediacy of the dissociated carbocation intermediate in the phenolysis system that the solvolysis product, *o*-RC_6H_4OH, is *not* less racemized in the presence of NaOPh[20] than that in the absence of NaOPh (Table 3).[5,9] If both Int-2 and the dissociated carbocation intermediate participated in the product formation, the phenoxide ion with higher nucleophilicity[21] should tend to attack Int-2 to afford the less recemized products before the dissociation of Int-2 to the dissociated carbocation intermediate.

All the reaction conditions for the phenolyses of ROPNB are identical with each other except the addition of a small amount of the salt ($(n\text{-Bu})_4N^+OPNB^-$ or NaOPh) which is much more nucleophilic than a solvent phenol molecule.[21] It is, consequently, concluded that no dissociated carbocation intermediate takes part in the solvolysis of ROPNB in phenol.

Accordingly, the common ion rate depression in the phenolysis of ROPNB does not arise at the stage of the dissociated (free) carbocation intermediate as generally expected until now,[3,11] but at the stage of the second ion pair intermediate (Int-2).

These experimental features can be expressed by the following reaction scheme, which contains two kinds of ion pair intermediate(Scheme 2).[5,9,17]

According to the Scheme 2, the total rate expressions for k_t and k_p can be derived as following Eqs. 1 and 2.

$$k_t = \frac{k_1}{1 + \frac{k_{-1}}{k_2k_3/(k_3+k_{-2})}}, \tag{1}$$

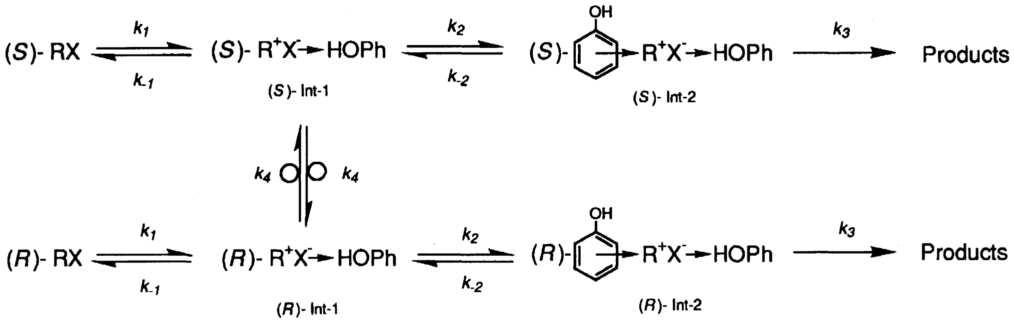
$$k_p = \frac{k_1}{1 + \frac{k_{-1}}{\{k_2k_3/(k_3+k_{-2})\}+2k_4}}, \tag{2}$$

where

$$k_{-2} = k_{-2'} + k_{-2''}[X^-].$$

The fact that the rate depression is not observed in the k_p values (vide supra) is most probably due to the much larger self-racemization rate (k_4) of Int-1 than the other elementary rate constants including k_{-2} (Eq. 2), which could be supported by the predominant racemization of solvolysis products (Eq. 2 and Scheme 2) and the large ratio of k_p/k_t (Eqs. 1 and 2).

As Int-2 in this system has a structure of *a rear-side shielded ion pair*[5] (Scheme 2), the nucleophilic attack by an added common ion salt should occur from the front side of Int-2. The nucleophilic attack should accelerate *the external ion pair return*[3,11] to generate *the rate depression* and might accompany "*a common anion exchange reaction*,"[3,7b,11a,11b,23] i.e., another common ion effect, which has been postulated to occur at the stage of Int-2 for the acetolyses of some systems.[11,23] For the mechanism of the common ion rate depression in the solvolysis of ROPNB, further examination is in



Scheme 2.

progress by the use of an isotope-labelled anion common to the leaving group of the substrate.

Contrary to the phenolysis of ROPNB, no common ion rate depression has been reconfirmed[11,16] in the acetolysis of 2-(*p*-methoxyphenyl)-1-methylpropyl tosylate, which proceeds via multiple solvolysis intermediates.[8,9] On the basis of the stability(reactivity)-selectivity relationships for solvolysis intermediates,[24] the distinction in the common ion salt effect between the phenolysis of ROPNB and the acetolysis of the tosylate indicates that Int-2 in the former should be more stable than that in the latter. In conclusion, this novel example which is caused at the stage of Int-2 indicates that the observation of a common ion rate depression in S_N1 solvolysis cannot provide evidence for the intermediacy of the dissociated carbocation intermediate, but is an indicator for the stability of solvolysis intermediate including the ion pair intermediate. Now we are looking for evidence for the intervention of the dissociated carbocation intermediate in the S_N1 solvolysis.

Experimental

^{13}C and ^{1}H NMR spectra were taken with a JEOL model JNM FX-90Q Fourier transform instrument (^{1}H; 90 MHz) with a ^{13}C and ^{1}H dual probe. IR spectra were recorded with a Hitachi model 215 spectrophotometer. Optical rotations were measured with a JASCO model DIP-SL polarimeter. G.L.P.C. was performed with Hitachi model 163 instrument. M.P.L.C. was done with a Chemco chromatograph system composed of a FMI model RP-SY-2 pump and a Merck silica gel 60 column. Mp's were measured on a Yamato model MP-21 apparatus. Solvolysis products were identified by comparison of their IR, ^{13}C and ^{1}H NMR spectra, and chromatographic data with those of authentic samples.[5]

Materials. Tetrabutylammonium *p*-nitrobenzoate was prepared by a known method.[25] Preparation of 2,6-di-*t*-butyl-4-methylpyridine was accomplished by the use of a reported procedure.[26] 2,2-Dimethyl-1-(*p*-methoxyphenyl)-1-propanol was synthesized and resolved in the previously reported manner.[5] Optically active and racemic 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoates were prepared by the usual method.[5] All the other organic reagents were of an analytical grade, dried, and fractionated prior to use.

Solvolysis Rate Measurements. The usual aliquot technique[5,14] was employed for measurements of k_p and k_t. The rate data against the added salt concentration are shown in Table 1 and Fig. 1.

Product Distribution Analysis. Product distribution for the solvolysis was analyzed by G.L.P.C. in a similar manner to those reported earlier.[27] The data are summarized in Table 2.

Isolation of Solvolysis Products. The previous procedures[5] were followed. ROPNB (6.86 g, 20.0 mmol; $[\alpha]_D^{24}$ +77.04±0.12° (c 1.67, benzene), synthesized from (S)-ROH, $[\alpha]_D^{22}$ −21.72±0.04° (c 5.01, benzene)) was solvolyzed in a phenol solution (200 ml) containing $(n\text{-Bu})_4N^+OPNB^-$ (8.18 g, 20.0 mmol) and 2,6-di-*t*-butyl-4-methylpyridine (3.92 g, 20.0 mmol) at 75.0±0.1°C for 22 h. After the usual workup, the products were separated by MPLC (silica gel) to afford ROPh (4.66 g; $[\alpha]_D^{24}$ +0.187±0.019° (c 9.97, benzene)), $o\text{-RC}_6H_4OH$ (0.0190 g; $[\alpha]_D^{24}$ −2.36±0.59° (c 4.24, benzene)), and $p\text{-RC}_6H_4OH$ (0.0973 g; $[\alpha]_D^{24}$ +0.661±0.190° (c 7.05, benzene)). The stereochemical outcomes are summarized in Table 3 along with the previously reported ones.[5]

References

1) Part 1: T. Kinoshita, T. Yokoi, K. Takeuchi, and K. Okamoto, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 101.

2) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954); and *Chem. Ind. (London)*, **1954**, 664; for a brief review: P. D. Bartlett, *J. Am. Chem. Soc.*, **94**, 2161 (1972).

3) For leading reviews: a) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, in "Ions and Ion Pairs in Organic Reactions," ed by M. Szwarc, John Wiley & Sons, New York (1974), Chap. 3, p. 249; b) J. P. Richard, in "Advances in Carbocation Chemistry," ed by X. Creary, JAI Press Inc., Greenwich (1989), p. 121; c) K. Okamoto, Ref. 3b, p. 171; and references cited therein.

4) Although Int-1 and Int-2 signify a contact (tight or intimate) and a solvent-separated ion pair intermediate, respectively, in the Winstein ion pair mechanism,[2,3] various other types of model have been experimentally found,[5,6] or proposed[7] for the structure of the ion pair intermediate, especially for that of Int-2.

5) For rear-side shielded ion pair model: T. Kinoshita, K. Komatsu, K. Ikai, T. Kashimura, S. Tanikawa, A. Hatanaka, and K. Okamoto, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1875; and references cited therein.

6) For four-center ion pair model: a) K. Okamoto, T. Kinoshita, and H. Shingu, *Bull. Chem. Soc. Jpn.*, **43**, 1545 (1970); b) K. Okamoto, K. Takeuchi, and K. Inoue, *J. Chem.*

Soc., Perkin Trans. 2, **1980**, 2785; and references cited therein.

7) a) For rear-side coordinated ion model: P. B. D. de la Mare, D. M. Hall, and E. Mauger, *Recl. Trav. Chim. Pays-Bas*, **87**, 1394 (1968); b) for anion-cation-stabilized ion pair model: L. S. Miller, D. Zazzaron, J. J. Dannenberg, R. Metras, and M. Gillard, *J. Org. Chem.*, **45**, 641 (1980); c) for ion-triplet model: J. Koskikallio, *Acta Chem. Scand.*, **26**, 1201 (1972); d) for quadruplet ion pair model: R. D. Topsom, in "Structure and Mechanism in Organic Chemistry," 2nd ed, ed by C. K. Ingold, Cornell Univ. Press, Ithaca (1969), p. 500; and references cited therein.

8) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

9) a) T. Kinoshita, K. Shibayama, K. Ikai, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **61**, 2917 (1988); b) T. Kinoshita, K. Ikai, T. Kashimura, M. Fujiwara, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **59**, 2843 (1986).

10) a) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, **1940**, 979; b) O. T. Benfey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, **1952**, 2488; c) G. Kohnstam and B. Shillaker, *J. Chem. Soc.*, **1959**, 1915; and references cited therein.

11) a) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956); b) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961); c) Z. Rappoport, Y. Apeloig, and J. Greenblatt, *J. Am. Chem. Soc.*, **102**, 3837 (1980); d) J. P. Richard, *J. Org. Chem.*, **57**, 625 (1992); and references cited therein.

12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York (1940), p. 52.

13) H. Shingu and K. Okamoto, *Nippon Kagaku Zasshi*, **81**, 111 (1960); *Chem. Abstr.*, **56**, 380b (1962).

14) K. Okamoto, T. Kinoshita, Y. Takemura, and H. Yoneda, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1426.

15) H. L. Goering and B. E. Jones, *J. Am. Chem. Soc.*, **102**, 1628 (1980).

16) The rate measurement was done only at a single concentration of the added common ion salt.[8)] Our exact reexamination confirms that our new rate data exhibit a larger normal salt effect (characterized using $b=0.75$ instead of $b=-0.35$, calculated from the reported data,[8)] in Winstein's equation[2)] $k_t=k_t^0\ (1+b[\text{salt}])$) but no common ion rate depression.[17)]

17) T. Kinoshita, M. Takemoto, and T. Takeuchi, unpublished work.

18) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2743 (1956); and references cited therein.

19) The concentration of $(n\text{-Bu})_4\text{N}^+\text{OPNB}^-$ corresponds to ca. 6 wt%.

20) In the absence of NaOPh, *o*-alkylphenol with the retention of configuration might be formed via a six-center transition state[6a)] between R^+X^- of Int-2 (see Scheme 2) and a phenol molecule, whereas, in the presence of NaOPh, *o*-alkylphenol could be produced both by the retentive phenoxide attack at Int-2 from the front-side and by the inversive phenoxide attack at the hydroxyl group of the shielding phenol molecule of Int-2 as a deprotonating reagent.[5)]

21) The added salt such as $(n\text{-Bu})_4\text{N}^+\text{OPNB}^-$ or NaOPh, $(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-$, $\text{Li}^+\text{ClO}_4^-$ etc. attacks nucleophilically the solvolysis intermediate to exert the common ion salt effect[10,11)] or the special salt effect[2,3,5,8,22)] in spite of the very small amount of the salt; 0.9—4 mol% in the solvolysis media.

22) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **19**, 109 (1965).

23) a) S. Winstein and E. Clippinger, *J. Am. Chem. Soc.*, **78**, 2784 (1956); b) S. Winstein, P. E. Klinedinst, Jr., and E. Clippinger, *J. Am. Chem. Soc.*, **83**, 4986 (1961); and references cited therein.

24) For leading reviews: a) A. Pross, *Adv. Phys. Org. Chem.*, **14**, 69 (1974); b) C. D. Johnson, *Chem. Rev.*, **75**, 955 (1975); c) E. M. Arnett and K. E. Molter, *Acc. Chem. Res.*, **18**, 339 (1985); d) C. D. Johnson and B. Stratton, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1903; and references cited therein.

25) Y. Pocker, *J. Chem. Soc.*, **1958**, 4322.

26) A. G. Anderson and P. J. Stang, *J. Org. Chem.*, **41**, 3034 (1976).

27) K. Okamoto, K. Matsubara, and T. Kinoshita, *Bull. Chem. Soc. Jpn.*, **45**, 1191 (1972).