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NUMBER AND STRUCTURE OF SOLVOLYSIS INTERMEDIATES. PART 3.* S_N1 SOLVOLYSIS OF 2,2-DIMETHYL-1-(*p*-METHOXYPHENYL)PROPYL *p*-NITROBENZOATE: MECHANISM OF THE COMMON ION SALT EFFECTS ARISING AT THE STAGE OF THE SECOND ION-PAIR INTERMEDIATE

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2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) was subjected to solvolysis in phenol in the presence of tetrabutylammonium [carboxy-^{13}C]-*p*-nitrobenzoate, in which the 'common ion rate depression' was confirmed to arise at the stage of the second ion-pair intermediate (Int-2). The unchanged substrate recovered at 46% reaction contained the isotopically labelled leaving group, indicating the occurrence of common ion exchange to the extent of 41–46%. In the solvolysis of the optically active substrate under identical conditions, the unchanged substrate was recovered with 51·4% racemization and ROPh was produced with slightly (1·56%) retained configuration, similarly to the solvolysis in the absence of the common ion salt. These isotope-tracer and stereochemical outcomes indicate that the common ion exchange in this solvolysis system should be attributable to the retentive nucleophilic attack on Int-2 by the common ion salt via a quadrupole (four-centre ion pair) transition state, accompanying the common ion rate depression, and they suggest that the special salt effect also should proceed by an analogous anion-exchange mechanism to that for the common ion effects.

INTRODUCTION

The most direct method for demonstrating the presence of reactive intermediates with a very short life and characterizing the intermediates in S_N1 solvolysis reactions is the trapping of the intermediates, which appears as the special salt effect[2–8] and the common ion rate depression.[1,6,8–12] Although such salt effects have been generally and effectively utilized for the investigation of solvolysis reaction mechanisms,[1–12] all the mechanisms of the salt effects themselves, including common ion salt effects, have not so far been thoroughly substantiated. As for the common ion salt effects, it was explained in the Winstein ion-pair mechanism for sequential ionization[2,3] involving two kinds of ion-pair intermediate (Int-1 and Int-2)[2,3,13–15] that the rate depression might be caused by the acceleration of 'external ion return'.[2–6,8,10,11] Accordingly, the observation of the 'common ion rate depression (mass law effect)' was assumed to give strong evidence for the occurrence of the dissociated (free) carbocation intermediate in the S_N1 solvolysis reaction.[2–6,8,10,11] However, we recently found that, in the solvolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) in phenol,[13] the common ion rate depression arises at the stage of the second ion-pair intermediate, and not at the stage of the dissociated carbocation intermediate.[1] This novel example demonstrates that the common ion rate depression cannot necessarily give evidence for the intermediacy of the dissociated carbocation intermediate, but is an indicator for the stability of solvolysis intermediates including the ion-pair intermediate in the S_N1 solvolysis. However, the mechanism was not examined in detail for the common ion rate depression in this solvolysis system.

We therefore decided to investigate the mechanism for the novel example of the common ion rate depression by the use of a salt with an isotopically labelled anion group common to the leaving group of the

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substrate. In this paper, we report the mechanism of the common ion rate depression in connection with the common ion-exchange reaction and also that for the special salt effect by perchlorate, a non-product-forming non-common-ion salt, in the solvolysis of ROPNB.

RESULTS AND DISCUSSION

Synthesis of tetrabutylammonium [carboxy-^{13}C]-*p*-nitrobenzoate

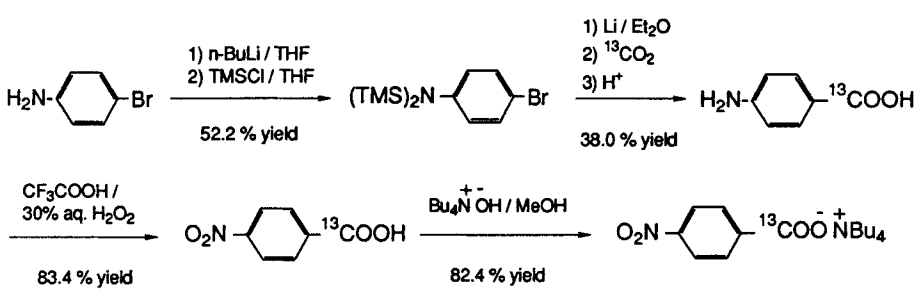
p-Bromoaniline was converted into tetrabutylammonium [carboxy-^{13}C]-*p*-nitrobenzoate by the four reaction steps shown in Scheme 1. After the protection of the amino group by two trimethylsilyl groups,[16] the bromine atom of the protected *p*-bromoaniline was lithiated, carbonylated with $^{13}CO_2$ (generated by addition of aqueous hydrogen chloride to 99% ^{13}C-enriched barium carbonate), and then the protecting groups were liberated to afford [carboxy-^{13}C]-*p*-aminobenzoic acid. Although the direct oxidation of aromatic amines to nitro compounds is usually carried out under much more vigorous conditions,[17] the oxidation of the ^{13}C-labelled aminobenzoic acid by CF_3COOH–30% aqueous H_2O_2 produced [carboxy-^{13}C]-*p*-nitrobenzoic acid, which was treated with an equivalent amount of tetrabutylammonium hydroxide[18] to give tetrabutylammonium [carboxy-^{13}C]-*p*-nitrobenzoate (^{13}C content 99 atom% excess) in an overall yield of 13·6%. A mixture ($Bu_4N^+OPNB^{*-}$; ^{13}C content 29·0 atom% excess) of the isotopically labelled quaternary ammonium salt and the unlabelled ammonium salt was used for the tracer study of the solvolysis reaction.

Solvolysis in the presence of the ^{13}C-labelled common ion salt

2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) was solvolysed in phenol in the presence of the ^{13}C-labelled common ion salt, tetrabutylammonium [carboxy-^{13}C]-*p*-nitrobenzoate (^{13}C content 29·0 atom% excess, 0·200 M), at 75 °C under conditions identical with those employed in previous work.[1,13] The solvolysis was interrupted at 46·4% reaction (reaction time 100 min) and the usual solvolysis products (ROPh, *o*-RC_6H_4OH and *p*-RC_6H_4OH) and the unchanged substrate were separated by MPLC (medium-pressure liquid chromatography) and preparative TLC (silica gel). The distribution (ROPh : *o*-RC_6H_4OH : *p*-RC_6H_4OH = 98·7 : 0·4 : 0·9, determined by GLPC) of the solvolysis products in the presence of the common ion salt is almost identical with that (ROPh : *o*-RC_6H_4OH : *p*-RC_6H_4OH = 96·6 : 1·1 : 2·3) in the absence of the added common ion salt,[1] within experimental error. The recovered substrate contained in part the isotopically labelled anion group and the ^{13}C content was determined by ^{13}C NMR spectroscopy to be 8·0 atom% excess (Table 1), indicating that the common anion exchange occurred to the extent of 41% in the course of the solvolysis. In the solvolysis in the presence of 0·300 M isotope-labelled quaternary ammonium salt, the substrate was recovered with a ^{13}C content of 10·0 atom% excess at 45·6% reaction, from which the extent of exchange was calculated to be 46%. It is demonstrated, as expected for the S_N1 solvolysis, that the extent of the anion exchange increases with increase in the concentration of the added common ion salt. The anion exchange including the common anion exchange had been observed in several solvolysis systems.[2,10,14a,19]

Solvolysis of the optically active substrate in the presence of the common ion salt

Optically active ROPNB was solvolysed in the presence of the unlabelled common ion salt ($Bu_4N^+OPNB^-$; 0·200 M) under conditions identical with those mentioned above.[1,13] At 51·7% reaction, the solvolysis was discontinued and the products and the unchanged ROPNB were separated by MPLC. The solvolysis produced ROPh with partially (1·56%) retained configuration and trace amounts of *o*- and *p*-RC_6H_4OH, and



Scheme 1

the unchanged substrate was recovered with 51·4% racemization. The stereochemical results are summarized in Table 2.

The extent (51·4%) of racemization for the recovered substrate is slightly (2·9%) larger in the presence of 0·200 M added salt than that (48·5%) in the absence of the salt, within experimental error. However, such a tendency could not be found for the ROPh which is produced with overwhelming (98·4%) racemization.

Reaction mechanism of the common ion salt effects

The results of the isotope-tracer and stereochemical experiments can be used to elucidate the mechanism of the common ion rate depression in this system, compared with those for the related salt effects, as follows.

Correspondence between the common ion exchange and the common ion rate depression

In the presence of the ^{13}C-labelled common ion salt, the unreacted substrate which was recovered at 46% conversion contained the ^{13}C-labelled leaving group, indicating the occurrence of the common ion exchange (Table 1). Under identical conditions, the phenomenon of common ion rate depression has been observed and found to arise at the stage of the second ion-pair intermediate (Int-2).[1] In the solvolysis of ROPNB in phenol, in addition, it has been confirmed that no dissociated (free) carbocation intermediate intervenes,[20] all the products are formed at the stage of Int-2,[1,13] and therefore the first ion pair intermediate (Int-1) is not nucleophilically attacked. Accordingly, the common ion-exchange reaction and the common ion rate depression

Table 1. ^{13}C content for the substrate recovered in the course of the solvolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) in the presence of tetrabutylammonium [carbonyl-^{13}C]-*p*-nitrobenzoate ($Bu_4N^+OPNB^{*-}$) in phenol at 75 °C[a]

$Bu_4N^+OPNB^{*-}$		Reaction			ROPNB recovered		
^{13}C content[a] (atom-% excess)	M	ROPNB (M)	Time (min)	%[b]	Recovery (%)	^{13}C content[a] (atom-% excess)	Exchange (%)
29	0·200	0·100	100	46·4	41·1	8·0[c]	41
29	0·300	0·100	113	45·6	42·4	10[d]	46

[a] Determined by ^{13}C NMR spectroscopy.
[b] Determined by titration.
[c] Equilibrium value = 19·4%.
[d] Equilibrium value = 21·8%.

Table 2. Stereochemical courses for the *O*-alkylation of the solvolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) in the presence of tetrabutylammonium *p*-nitrobenzoate ($Bu_4N^+OPNB^-$) in phenol at 75 °C[a]

$Bu_4N^+OPNB^-$ (M)	ROPNB		Reaction (%)[c]	ROPh		ROPNB recovered	
	$\{[\alpha]_D(^\circ)\}$[b]	M		Yield[d] (%)	Net stereochemical course (%)[a] $\{[\alpha]_D(^\circ)\}$[b]	Recovery[d] (%)	Racemization (%) $\{[\alpha]_D(^\circ)\}$[b]
0·200	{+77·04}[e] (±0·12)	0·100	51·7	37·8	1·56(±0·05)ret. {+0·340(±0·010)}	44·9	51·4(±0·1) {+37·43(±0·10)}
0·000	{+99·31}[f] (±0·02)	0·100	50·0	40·6	1·58(±0·07)ret. {+0·362(±0·015)}	44·4	48·5(±0·1) {+51·13(±0·07)}
0·100[g]		0·100	100	58·5	0·85(±0·09)ret.	0	—

[a] Calculated on the basis of the absolute configuration and the optical purity of the starting ROH from which ROPNB was synthesized and the ROPh produced; −44·83°, +161·4° and +45·0° for ROH, ROPNB and ROPh with *S*-configuration, respectively (from Ref. 13a).
[b] In benzene, c = 0·81–1·94 and 8·04–15·95 for ROPNB and ROPh, respectively.
[c] Determined by titration.
[d] Isolated value.
[e] Synthesized from (*S*)-ROH, $\{[\alpha]_D^{21\cdot8} - 21\cdot72 \pm 0\cdot04^\circ$ (benzene)$\}$.
[f] Synthesized from (*S*)-ROH, $\{[\alpha]_D^{26\cdot0} - 22\cdot80 \pm 0\cdot02^\circ$ (benzene)$\}$.
[g] From Ref. 1.

take place simultaneously at the same stage of Int-2 in this solvolysis system in the presence of the common ion salt in phenol.

The common ion exchange accompanies the rate depression also in the acetolyses of cholesteryl and 2-(2,4-dimethoxyphenyl)propyl systems,[2a,10a] whereas the exchange reaction does not cause rate depression in the acetolyses of *threo*-2-(*p*-anisyl)-1-methylpropyl[2a,4,21] and 1-(*p*-anisyl)methylethyl systems,[10a,22] and neither of the salt effects could be detected in the acetolysis of *exo*-2-norbornyl brosylate[10a] (Table 3). Consequently, it could be concluded that the common ion rate depression is accompanied by the anion exchange but the latter is not always accompanied by the former.

Comparison of the common ion salt effects and the special salt effect

A comparison of the common ion salt effects with the special salt effect, i.e. a non-common ion salt effect, could make each mechanism clearer.

Correspondence of the common ion salt effects and the special salt effect. In the solvolysis of ROPNB in PhOH, the common ion salt effects (the common ion rate depression and the common anion exchange) and the special salt effect arise at the same stage of Int-2, as mentioned above. Both the added common ion salt and the non-common ion salt capture Int-2 to result in the respective salt effect.

In several solvolysis systems in which both salt effects have been examined,[1,2a,3-5,10] there is an exact correspondence between the special salt effect and the anion-exchange reaction (Table 3). However, the special salt effect does not always correspond to the common ion rate depression; both the special salt effect and the common ion rate depression are observed in the solvolyses of 1-(*p*-anisyl)-2,2-dimethylpropyl,[12] cholesteryl and 2-(2,4-dimethoxyphenyl)ethyl systems in acetic acid,[5a,10] *p*-anisylmethyl bromide[6b] and benzal chloride[6c] in aqueous dioxane, and 1-(*p*-anisyl)-2,2,2-trifluoroethyl bromide in aqueous trifluoroethanol[8a] and water.[8b] Neither of the salt effects occurs in the acetolysis of *exo*-2-norbornyl brosylate[5a,10] whereas the

Table 3. Correspondence of the common ion rate depression, the anion exchange and the special salt effect in S_N1 solvolyses[a]

Substrate	Solvent	Common ion rate depression	Anion exchange	Special salt effect	k_p-k_t pattern[a]
AnCH(*t*-Bu)OPNB	PhOH	Yes[b]	Yes	Yes[a,c]	A
$CH_3CHAnCHXCH_3$[d] (*threo*-; X = OTs, OBs)	AcOH	No	Yes	Yes	A
$AnCH_2CH(OTs)CH_3$	AcOH	No[e]	Yes[f]	Yes[g,h]	A–B[i]
exo-2-NorbOBs	AcOH	No[e]	No[e]	No[j]	C
Cholesteryl-X (X = OTs, OBs)	AcOH	Yes[e]	Yes[e]	Yes[j]	A or B
$2,4\text{-}(CH_3O)_2C_6H_3CH_2CH_2OBs$	AcOH	Yes[e]	Yes[e]	Yes[j]	A or B
AnCH(*t*-Bu)Cl[k]	AcOH	Yes	—	Yes	A or B
$AnCH_2Br$[l]	Aq. dioxane	Yes	—	Yes	A or B
$AnCHCl_2$[m]	Aq. dioxane	Yes	—	Yes	A or B
$AnCHCF_3Br$	Aq. TFE[n]	Yes	—	Yes	A or B
	H_2O[o]	Yes	—	Yes	A or B

[a] Ref. 7a.
[b] Ref. 1.
[c] Ref. 24.
[d] Ref. 3.
[e] Ref. 10a.
[f] Ref. 5b.
[g] Ref. 22.
[h] Ref. 10b.
[i] Although the pattern B was previously reported for this system (Ref. 7), re-examination of the pattern has clarified that it follows a complex pattern of A and B.
[j] Ref. 5a.
[k] Ref. 12.
[l] Ref. 6b.
[m] Ref. 6c.
[n] Ref. 8a.
[o] Ref. 8b.

special salt effect alone is detected in the acetolyses of *threo*-2-(*p*-anisyl)-1-methylpropyl[4] and 1-(*p*-anisyl)methylethyl systems[10,22] (Table 3).

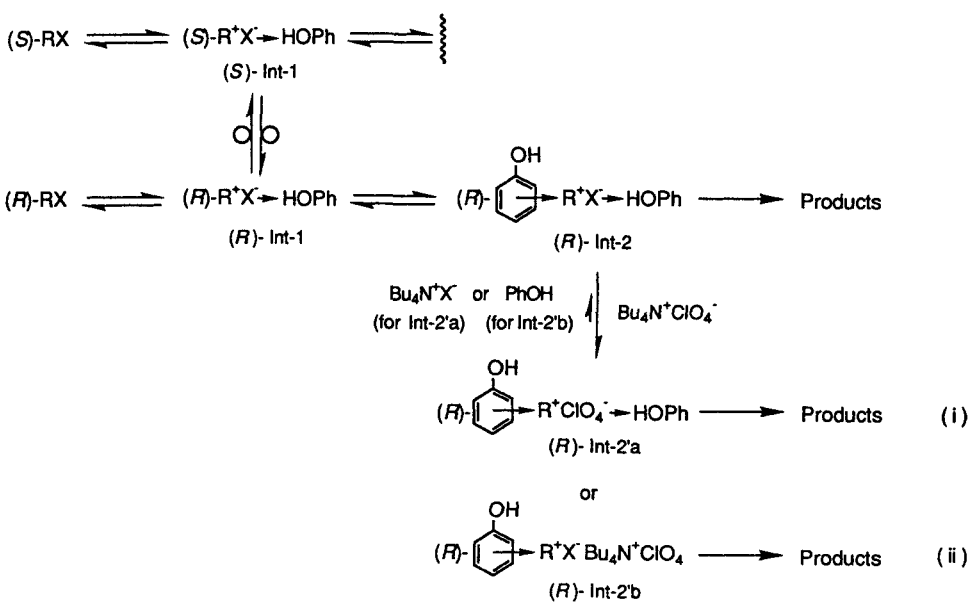
Action of an added salt as a nucleophilic anion (or its ion pair) or as an electrophilic ion pair. There were two possibilities for the behaviour of the added perchlorate salt towards Int-2 in the special salt effect (Scheme 2).[13] (i) A nucleophilic anion exchange of Int-2 might occur directly with ClO_4^- to form Int-2'a (a carbocation ion pair), in a way similar to the reaction pathway presented by Winstein and co-workers,[4,10] and it may be essentially identical with the anion-exchange mechanism of Hughes *et al.*[23] [(i) in Scheme 2]. (ii) Alternatively, an ion pair $Bu_4N^+ClO_4^-$ may exchange electrophilically, pulling the phenol molecule of Int-2 to give Int-2'b (a quadruplet ion pair) in the same way as Pocker's[18] and Topsom's[15d] pathways [(ii) in Scheme 2]. Corresponding to these two possibilities for the behaviour of perchlorate, two types of reaction mechanisms were formulated as depicted in Scheme 2.[13] In the case of the latter, a common ion salt such as $Bu_4N^+OPNB^-$ could have exhibited a special salt effect similarly to $Bu_4N^+ClO_4^-$ with a common cation block. However, the common ion salt $Bu_4N^+OPNB^-$ exerts the common ion effect (the common ion rate depression and the common ion exchange) and no special salt effect in this system.[1] This difference between the two kinds of quaternary ammonium ion salt demonstrates the significant role of the anion side of the added salt as a nucleophile.

Product-forming and non-product-forming non-common ion salts. Further support for the important function of the anionic part of salt in the special salt effect is that a non-product-forming non-common ion salt such as $Bu_4N^+ClO_4^-$ exerts the special salt effect similarly to a product-forming non-common ion salt such as NaOPh which could attack nucleophilically a solvolysis intermediate to give rise to the phenolysis products directly.[13,24]

Consequently, it can be concluded that the anion side of the added salt plays an essential role as a nucleophile in both the common ion salt effects and the special salt effect. The quaternary ammonium ion salts are present as ion pairs or their aggregates from 10^{-5} to 10^{-2} M, and even at 10^{-5} M a few parts per million of the salt are dissociated to the simple (free) ions in benzene.[25] Even in phenol with a small dielectric constant (10·73 at 50 °C[26]), which is larger than that (2·27[27]) for benzene, a salt such as $LiClO_4$ and NaOPh could be calculated to exist as ion pairs or their aggregates to the extent of 99·3% and 98·0%, respectively, at 0·1 M from their dissociation constants.[28] Accordingly, the added common ion salt will for the most part be present as ion pairs or their aggregates in the phenol solvent.

Nucleophilicity of an added salt

It has been confirmed that the common ion effects due to an added common ion salt and the special salt effect due to perchlorate salts in this system are exerted by nucleophilic attack of the respective salts themselves on



Scheme 2

Int-2. The common ion salt is much more nucleophilic than a solvent phenol molecule because the salt exercises distinct effects on the solvolyses in spite of a very small amount (0·9–4 mol% in the solvolysis media), similarly to the non-common ion salts.[1,7] On the other hand, the common ion salt and perchlorate are generally considered to be very weak as either a nucleophile or a base. However, the low basicity is based on its behaviour in more polar solvents and the relative basicities are strongly dependent on the solvent polarity.[29] Examples of nucleophilic[30] and basic[30a] intervention by perchlorate in solvents such as benzene,[30a] diethyl ether,[30b,c] dichloromethane,[30b] ethyl acetate[30b] and acetic acid[30d] are well documented.

From the collision theory of kinetics, the ion-pair intermediate and the added salt (ion pair or its aggregate) have a respective electrostatic force range, a collision radius, which is of the order of the spacings of their neighbours (the salt) at the practical salt concentrations (of the order of 0·1 M).[23] In addition, the high capturing efficiency of the salts in the solvolysis media could be ascribed also to the local increase in the salt concentration in the neighbourhood (the solvation shell) of the solvolysis intermediate owing to the electrostatic attraction force.

The stage of solvolysis intermediate attacked by an added salt

The common ion rate depression and the common ion exchange occur at the stage of Int-2, not at the stage of the dissociated carbocation intermediate in the solvolysis of ROPNB in phenol as described above,[1] although the former and the latter were generally assumed to arise at the stage of the dissociated (free) carbocation intermediate and Int-2, respectively, in the S_N1 reaction.[2–6,8,10,11,18] However, the stage of the solvolysis intermediate where the common ion effects generate have not been confirmed in the solvolysis systems except for the phenolysis of ROPNB in this work and the acetolyses of *threo*-2-(*p*-anisyl)-1-methylpropyl[4] and 1-(*p*-anisyl)methylethyl systems.[10a,22] In both acetolyses, the anion-exchange reaction was recognized to take place at the stage of Int-2 because the added perchlorate ion attacked Int-2 and no common ion rate depression was observed (Table 4).[4,10a,22]

The special salt effect also arises at the stage of Int-2 in this phenolysis system.[7] Nevertheless, the special salt effect does not occur only at the stage of Int-2 (A pattern in the k_p–k_t profile; Table 4) but also at the stage of Int-1 (B pattern in the k_p–k_t profile; Table 4)

Table 4. The number of solvolysis intermediate (Int.) stages via which the solvolysis proceeds and the special salt effect and the common ion salt effects arise[a]

Number of Int. stage	1			*2*	(≥)3
Product-forming Int.[b]	Int-1 (Ion pair)			*Int-2* (Ion pair)	R^+ (free ion)
k_p–k_t pattern[c]	D	C	B	*A*	A[d]
Special salt effect[c,e,f]	No	No	Yes	*Yes*	Yes[d]
	(←	No	→)	(Yes)	(Yes?)
Common ion rate depression[e,f]	No[d]	No[g]	?	No[h]-*Yes*	Yes?[d]
	(←	No	→)	(No)	(Yes)
Anion exchange[e,f]	No[d]	No[g]	?	*Yes*	Yes?[d]
	(←	No	→)	(Yes)	(Yes?)

[a] In italics: in the phenolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (this work).
[b] Int-1, the first ion-pair intermediate; Int-2, the second ion-pair intermediate; R^+, the dissociated carbocation intermediate (see text).
[c] See Ref. 7 for each profile.
[d] No example with an experimental confirmation has been found.
[e] Yes, arises; No, does not arise.
[f] In parentheses: assumed in Refs 2–6, 8, 10, 11 and 18.
[g] In the acetolysis of *exo*-2-norbornyl brosylate (Refs 5a and 10a).
[h] In the acetolyses of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl brosylate and tosylate and 1-(*p*-anisyl)methylethyl tosylate (see text; Refs 4 and 5b, respectively).

in the other S_N1 solvolyses.[7] Table 4 indicates that the common ion effects could provide an indicator for the stability of solvolysis intermediates in addition to the special salt effect in S_N1 solvolysis.

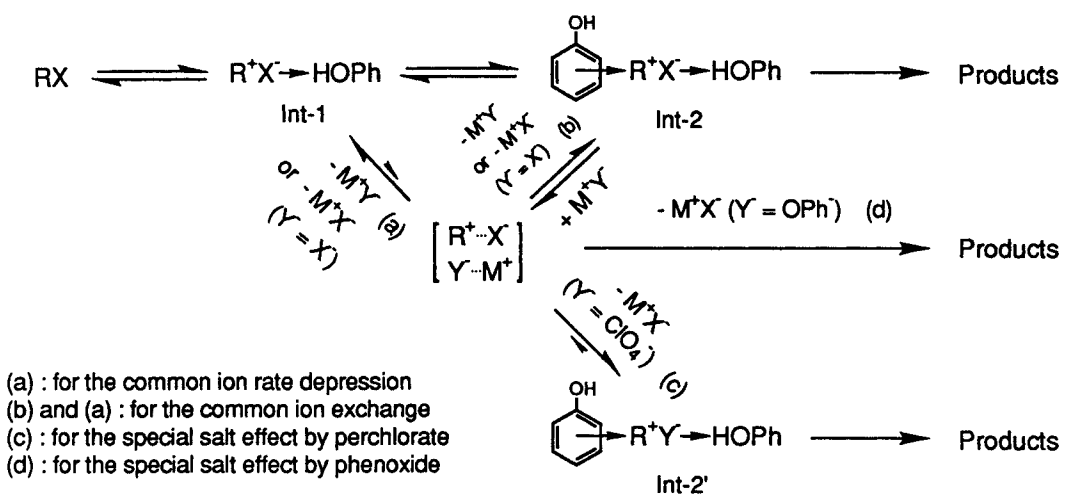
Mechanism of the common ion salt effects and the special salt effect

Since the common ion exchange, the common ion rate depression and the special salt effect have all been found to result from nucleophilic attack at the same stage of Int-2 by the ion pair of the respective added salt in this system, all the salt effects could be considered to be exerted via a quadrupole (four-centre ion pair) transition state[14,31] in a way similar to the reaction pathway originally proposed by Winstein and co-workers,[4,10] and it may be essentially identical with the anion-exchange mechanism of Hughes *et al.*[23] (Scheme 3). This could provide an explanation for each salt effect that, on collapse of the quadrupole arrangement at the transition state in Scheme 3, a predominant pathway should be a return to Int-1 resulting in external ion-pair return [(a) in Scheme 3] and a return to Int-2 and Int-1 leading to the common ion exchange [(b) and (a) in Scheme 3] in the case of the common ion salt, formation of Int-2′ which might be rapidly consumed by a phenol molecule to give the final products (ROPh, *o*- and *p*-RC_6H_4OH) in the case of the perchlorate salts [(c) in Scheme 3] and direct production of the final products in the case of the phenoxide salts [(d) in Scheme 3]. The collapse pathway would be dependent most probably on the nucleophilicity of the anion part of the added salt in the solvolysis medium.

The total expressions for k_p and k_t, which can be derived by application of the stationary-state treatment to Scheme 3, have been proved to be compatible with all the kinetic results for the common ion rate depression[1] and the special salt effect[13] in this phenolysis system.

An analogous reaction mechanism to that via a quadrupole transition state illustrated in Scheme 3 might be applied to the solvolysis systems in solvents other than phenol, in which the solvolysis would proceed via ion-pair intermediates with a different structure[2,3,14,15] from the rear-side shielded ion-pair intermediate[13] for Int-2 in phenol. By the use of the analogous mechanism, also, a reasonable explanation might be given for the changes in the kinetic α-deuterium isotope effects observed along with the common ion depression and the special salt effect in the solvolysis of *p*-anisylmethyl bromide, and the increase and decrease in α-deuterium isotope effects with increasing perchlorate ion concentration and with increasing concentration of common ion salt, respectively.[6b]

In a case such as this system, nucleophilic attack by the common ion salt not only gives rise to anion exchange but also accelerates the external ion-pair return to result in a rate depression, whereas in systems such as the acetolyses of *threo*-2-(*p*-anisyl)-1-methylpropyl and 1-(*p*-anisyl)methylethyl compounds the common ion attack causes only anion exchange.[4,5,10,22] The difference in the apparent phenomena for the common ion effects on both systems can probably be attributed to the difference in the stability of the solvolysis intermediate (Int-2). Consequently, the common ion salt effects could be affected by the stability of solvolysis intermediates similarly to the special salt effect (Table 4).



Scheme 3

Stereochemistry of the common ion salt effects

In spite of the occurrence of the common ion exchange to a significant extent in the course of the solvolysis of ROPNB in phenol in the presence of a common ion salt, the unchanged substrate is recovered with almost the same extent of racemization compared with that in the absence of the added salt. The racemization of ROPNB under these conditions could be ascribed to (a) the self-racemization of the ion pair intermediate (Int-1) and (b) the cancellation of the front-side and the rear-side nucleophilic attack on the ion-pair intermediate (Int-2)[1] by the added common ion salt. Although solvolysis mechanisms containing racemizable Int-2 have been proposed,[32] our previous results of systematic studies for the salt effect on the stereochemical courses could not be explained in terms of such a mechanism.[7,13] The stereochemical outcome mentioned above indicates that the nucleophilic attack by the common ion salt should occur predominantly from the front side of Int-2, presumably since Int-2 in this system has a structure of a rear-side shielded ion pair.[13]

In conclusion, the common ion rate depression in this solvolysis system is attributable to the retentive nucleophilic attack on Int-2 by the added common ion salt (ion pair) via a quadrupole transition state, accompanying the common anion exchange, and the special salt effect probably proceeds by an analogous anion-exchange mechanism to that for the common ion salt effects.

EXPERIMENTAL

^{13}C and ^{1}H NMR spectra were measured with JEOL Model GSX270 270 MHz and JEOL Model JNM FX-90Q 90 MHz Fourier transform instruments 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. GLPC was performed with Hitachi Model 163 instrument. Medium-pressure liquid chromatography (MPLC) was carried out with a Chemco chromatograph system composed of an FMI Model RP-SY-2 pump and a Merck silica gel 60 column. Melting points were measured on a Yamato Model MP-21 apparatus. Solvolysis products were identified by comparison of their IR and ^{13}C and ^{1}H NMR spectra and chromatographic data with those of authentic samples.[13]

Materials. Isotopically unlabelled tetrabutylammonium *p*-nitrobenzoate was prepared by a known method.[18] 2,2-Dimethyl-1-(*p*-methoxyphenyl)propanol was synthesized and resolved in the manner reported previously.[1,13] Optically active and racemic 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoates were prepared by the usual method.[1,13] All the other organic reagents were of analytical grade and were dried, and fractionated prior to use.

p-*Bromo*-N,N-*bis(trimethylsilyl)aniline.* The literature method[16] was adopted. To a solution of *p*-bromoaniline (20·4 g, 0·119 mol) in dry THF (100 ml), *n*-butyllithium–hexane solution (1·76 M, 135 ml, 0·237 mol) was added dropwise at 1·0–9·5 °C over 1·5 h. After stirring at ambient temperature for 80 min, trimethylsilyl chloride (32·0 ml, 0·295 mol) was added to the orange solution at 5–20 °C over 20 min. The dark-yellow suspension was stirred at room temperature overnight to give a mixture of an orange supernatant solution and a white precipitate. After filtration, the filtrate was distilled *in vacuo* to afford the protected *p*-bromoaniline (17·8 g, yield 52·2%; b.p. 97·0–101·0 °C/1 mmHg).

[*Carboxy-*^{13}C]-p-*aminobenzoic acid.* The known procedure[16] was applied. A mixture of *p*-bromo-*N,N*-bis(trimethylsilyl)aniline (2·46 g, 0·00850 mol) and lithium powder (0·354 g, 0·0510 mol) in diethyl ether (10 ml) was refluxed for 30 min and filtered through a glass filter under a nitrogen atmosphere. Into the filtrate cooled with a dry-ice–methanol bath, $^{13}CO_2$ gas, which was generated from 99% ^{13}C-enriched barium carbonate (3·12 g, 0·0160 mol) and 10% HCl, was continuously bubbled using a circulating pump (10 ml min^{-1}) and a gas stock bag for 3 h. After addition of cold water to the ether solution, the aqueous solution was extracted with diethyl ether, keeping the pH at about 3, to give the labelled aminobenzoic acid as slightly yellow needles [408 mg, yield 38·0%; ^{13}C NMR (CD_3OD), $\delta_{C=O}$ 168·0 ppm].

[*Carboxy-*^{13}C]-p-*nitrobenzoic acid.* To a mixture of trifluoroacetic acid (19·5 g, 0·171 mol), 35% H_2O_2 (2·67 g, 0·0270 mol) and concentrated H_2SO_4 (0·21 ml), [carboxy-^{13}C]-*p*-aminobenzoic acid (392 mg, 0·00290 mol) was added with trifluoroacetic acid (1 ml) at ambient temperature. The brownish yellow solution was heated at 73–76 °C. After 2 and 6 h, trifluoroacetic acid (10 and 5 ml) and 35% H_2O_2 (1·6 and 1·6 ml) were added, respectively. After heating for an additional 2 h, the yellow solution was treated with water to give the labelled nitrobenzoic acid as slightly yellow crystals [370 mg, yield 83·4%; ^{13}C NMR (CD_3OD), $\delta_{C=O}$ 167·6 ppm].

Tetrabutylammonium [*carboxy-*^{13}C]-p-*nitrobenzoate.* The method for the preparation of the unlabelled salt[18] was employed. A mixture of [carboxy-^{13}C]-*p*-nitrobenzoic acid (370 mg, 2·20 mmol) and 10% tetrabutylammonium hydroxide–methanol solution (5·70 g, 2·20 mmol) was evaporated and dried over P_2O_5 *in vacuo* for 5 days to give yellow crystals, which were recrystallized from benzene to afford the labelled ammonium salt as yellowish orange crystals [803 mg, yield 82·4%; ^{13}C NMR (CD_3OD), $\delta_{C=O}$ 167·9 ppm].

Isolation of solvolysis products. The previous procedures[4] were followed. As an example, the isolation of products in the solvolysis of ROPNB in the presence of tetrabutylammonium [carboxy-^{13}C]-*p*-nitrobenzoate (0·300 M) is described below. ROPNB (105 mg, 0·306 mmol) was solvolysed in phenol in the presence of $Bu_4N^+OPNB^{*-}$ (362 mg, 0·885 mmol; ^{13}C content 29·0 atom-% excess; 0·300 M) at 75·0 ± 0·1 °C for 113 min. The percentage reaction was determined by titration[1] (45·6%). After the usual work-up, the unchanged substrate and the products were separated by preparative TLC and MPLC (silica gel) to afford ROPNB (44·5 mg; ^{13}C content 10 atom-% excess, determined by ^{13}C NMR), ROPh (48·7 mg) and *o*- and *p*-RC_6H_4OH (4·5 mg).

All the isotopic and the stereochemical details are summarized in Tables 1 and 2, respectively.

Product distribution analysis. The product distribution for the solvolysis was analysed by GLPC in a similar manner to that reported earlier.[33]

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