Bull. Chem. Soc. Jpn. Vol. 83, No. 4, 401–414 (2010)

Salt Effects on the Rates and Mechanisms of Solvolysis Reaction of Organic Halides and Water Structure Distortion in *N*,*N*-Dimethylformamide– and *N*,*N*-Dimethylacetamide–Water Mixed Solvents

Masashi Hojo,* Tadaharu Ueda, Eriko Ueno, Tensei Hamasaki, and Toshiyuki Nakano

Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780-8520

Received December 11, 2009; E-mail: mhojo@cc.kochi-u.ac.jp

In 50% (v/v) DMF– and DMA–H_2O mixed solvents, salt effects on the solvolysis reaction rates of aliphatic halides and related compounds (RX) have been examined for further exploring. Compared with previous results obtained in other organic solvent systems, such as 50% (v/v) acetone–, 1,4-dioxane–, or sulfolane–H_2O, no exceptional behavior was observed in the "pseudo" first-order rate constants (k/s^{-1}) of all the typical S_N1 and S_N2 substrates by the addition of alkali metal and alkaline earth metal perchlorates or many kinds of tetraalkylammonium salts in 50% (v/v) DMF– and DMA–H_2O mixed solvents. The detailed examination of $\Delta\log(k/\mathrm{s}^{-1})/\Delta[\mathrm{LiClO_4}]$ for 1-adamantyl bromide vs. the contents of organic solvents (CH_3CN, DMA, and DMSO) suggested that the observed different salt effects were caused by the different solvation abilities of the solvents toward the leaving-group anion as well as the metal cation. As a new highlight in the present paper, we were able to demonstrate a proportionality or correlation between the $LiClO_4$ effects in the solvolysis rates and the carbocation stabilities expressed by the Gibbs free energy values (ΔG^o) of RX in the gas phase. Based on the Raman spectra of DMA–H_2O and DMA–D_2O as well as DMF–D_2O mixed solvents, we discuss the distortion of the bulk water structure.

The ionic strength influences the kinetics of reactions between ions and neutral molecules. It is believed that at higher ionic concentration, the rate constant may change because of changes in the activity coefficients of the ions (not given by the Debye–Hückel theory) and because the activity coefficients of neutral molecules are affected by higher ionic strengths.[1]

In organic chemistry, nucleophilic substitution reactions, especially solvolysis reactions have been vastly studied and discussed.[2] It is known that the rates of S_N1 solvolysis of alkyl halides and related compounds are subject to positive salt effects.[3] Bunton et al.[4] reported exponential increases in the methanolysis rates of S_N1 substrates with increasing concentration of salts and they insisted small cation effects (for Li^+, Na^+, and Et_4N^+). However, Allen et al.[5] have reported a great difference in the salt effects of $LiClO_4$ and $n\text{-}Bu_4NClO_4$ on the solvolysis of 4-methoxybenzyl chloride in 85% (v/v) aqueous dioxane. Many negative salt effects for unimolecular heterolysis have been reviewed.[6] Ingold and Hughes[7] carried out detailed kinetic and stereochemical investigations on nucleophilic substitution at saturated carbon and polar elimination reaction.

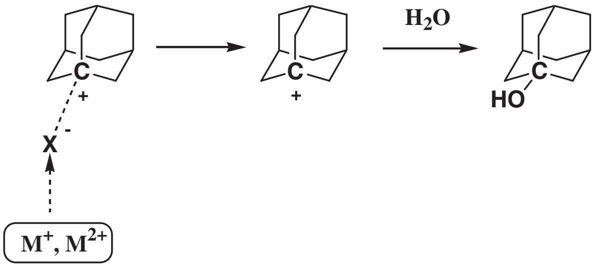
Winstein and co-workers[8] proposed an ion-pair scheme for solvolyses in an ionizing but only slightly dissociating solvent, especially, acetic acid ($\varepsilon_r = 6.2$). According to Winstein's interpretation, the "normal" salt effect on the acetolysis rate is due to acceleration of the substrate ionization step leading to the contact ion pair ($RX \rightleftharpoons R^+, X^-$) while the "special" salt effect is the result of an exchange reaction between two ion pairs as shown in eq 1,

$$R^+\|X^- + M^+\|ClO_4^- \rightleftharpoons R^+\|ClO_4^- + M^+\|X^- \qquad (1)$$

and his interpretation has been applied to so many salt effects on solvolysis reactions. Nevertheless, a quantitative and comprehensive treatment has never succeeded in accounting for the concentrated salt effects on solvolysis reactions. The solvent[9] and salt effects in organic reactions have been widely discussed.[10,11] The development of laser-flash photolysis supplied the necessary tool to study chemical systems on the nanosecond and picosecond time scales relevant to ion-pair dynamics. Bockman and Kochi[12] mentioned, however, the original goal of finding a spectroscopic distinction between contact ion pairs (CIPs) and solvent-separated ion pairs (SSIPs) remains unfulfilled.

In previous studies,[13–16] we have observed the solvolysis rate constant of typical S_N1 substrate, such as 1-adamantyl halides or *tert*-butyl chloride, increases with increasing concentration of alkali metal (M^+) and alkaline earth metal (M^{2+}) perchlorates: cation effects increase as $Na^+ < Li^+ < Mg^{2+}$, Ba^{2+} in 80% (v/v) MeOH–H_2O ($\varepsilon_r = 49$),[13] 50% (v/v) acetone–H_2O ($\varepsilon_r = 55$),[14] 50% (v/v) 1,4-dioxane–H_2O ($\varepsilon_r = 44$),[15] and 50% (v/v) sulfolane–H_2O[16] solvent systems. The main points proposed in our previous solvolytic studies[13–16] are summarized as: (1) The addition of highly concentrated salts as well as organic solvents would reduce the properties of bulk water (H–O–H) into those of a non-aqueous solvent, such as an alcohol (R–O–H) or even an ether (R–O–R). (2) In water-mixed organic solvents containing concentrated metal perchlorates

Published on the web March 26, 2010; doi:10.1246/bcsj.20090329



Scheme 1. Proposed mechanism for the metal cation effect on a typical S_N1 solvolysis.

(0–3.0 mol dm^{-3}), the exponential increases in solvolysis rates of S_N1 substrates are caused by the favorable formation of carbocations through direct "chemical" interaction between metal cations and the leaving group of a substrate in the modified solvent. (3) The solvolysis rates of S_N2 substrates are decelerated by concentrated salts because of the decrease in water activity. (4) Positive or negative salt effects by $LiClO_4$ can be correlated to the *m*-values (by Grunwald and Winstein)[17] of the substrates. The mechanism of the metal cation effects can be illustrated by Scheme 1.

At a first glance, however, the proposed scheme might be judged to be impossible because no one can deny that a diluted alkali metal halide (e.g., NaCl) in aqueous solution would dissociate completely. Difficulties involved in the mechanism arise from the following two points: (a) the coordination ability of alkali metal or alkaline earth metal ions must be quite small because of no d-electrons. Cotton and Wilkinson[18] describe that in main elements, s- and p-orbitals, especially p-orbitals, are the important key and d-orbitals play a secondary role, sometimes just a negligible role. (b) In aqueous solution, strong solvation (hydration) may shade completely the chemical interaction sites on alkali metal or alkaline earth metal cations as well as simple anions even though they have some potential for such chemical interaction in addition to Coulombic interaction.

Nevertheless, we have postulated that a very small but direct "chemical" interaction can operate between M^+ or M^{2+} and simple anions, such as halide, even in aqueous or organic–aqueous solutions if they are under the "dihydrogen ether" ([R](H)–O–(H)[R])[13–16] conditions. As for "dihydrogen ether," Reichardt et al.[19] described citing our papers[13,15] that, at high salt concentrations ($c > 5$ mol dm^{-3}), region **C** of ion solvations, according to Frank and Wen,[20] can be abolished and only regions **A** and **B** survive, resulting an aqueous solvent called "dihydrogen ether."

In addition, Reichardt et al.[19] have described that the adverse influence of tetramethylammonium chloride is more difficult to explain and that tetraalkylammonium salts are usually regarded as possessing structure-making properties. However, we have to stress that tetraalkylammonium halides at higher concentrations do distort the bulk water structure[15,21] even though the salt at low concentrations is regarded as possessing structure-making properties.

By means of voltammetry,[22] conductometry,[23,24] and UV–visible and NMR spectroscopies,[25–30] we have certainly demonstrated that alkali metal and alkaline earth metal cations possess "weak" but unexpectedly distinct chemical (i.e., covalent bonding or coordinating) as well as Coulombic interactions with many simple anions, not only in low permittivity media ($\varepsilon_r < 10$)[24] but also in higher permittivity media ($20 < \varepsilon_r < 65$) with poor solvating ability;[22,23] where the simple anions include halides, carboxylates, phosphates, sulfonates, etc. Coordination chemistry of the lithium ion with simple anions as well as cyclic ligands is reviewed.[31]

Olah[32] reviewed the significance of carbocations in chemistry; in general, stable carbocations are prepared in superacidic media. Schaller and Mayr[33] made it possible to monitor photometrically the formation of the carbocation of 4,4′-bis(morpholino)benzhydryl carboxylates in aqueous acetone and acetonitrile. However, we have discovered that stable carbocations can be produced from trityl halides by the addition of the perchlorates salts of Li^+, Na^+, Mg^{2+}, (Ca^{2+}, Sr^{2+},) and Ba^{2+} in acetonitrile;[25–27a] which have been detected by UV–visible,[25] ^1H and ^{13}C NMR spectroscopies.[26,27a] For a fluoran-based black color former in acetonitrile, the color has been developed by the addition of the alkali metal or alkaline earth metal perchlorates[27a] as well as phenol which is used as a normal color developer. In addition, reversible decolorization through the interaction between Mg^{2+} and polyamines (acyclic and macrocyclic) made it possible to reconfirm that the colored zwitterion is produced by the direct chemical interaction with $Mg(ClO_4)_2$ in the fluoran dye–acetonitrile solution.[27b]

In order to support our proposal of previous solvolytic studies[13–16] and to explore further, we examined the effects of various types of salts, $MClO_4$, $M(ClO_4)_2$, and R_4NX (R = Et, Pr, *n*-Bu, X = ClO_4, Cl, Br, OTs) on the solvolysis reactions of typical S_N1 and S_N2 substrates in 50% (v/v) DMF– and DMA–H_2O solvents. The basicities of DMF and DMA are rather large, i.e., Gutmann's donor numbers (DN) = 26.6 and 27.8,[34] respectively, while the acidities of the solvents are small, i.e., the acceptor numbers (AN) of DMF and DMA are reported to be 16.0 and 13.6, respectively.[34] Acetonitrile and DMSO were also used as solvents, and the role of the organic solvent in water mixed solvents was discussed. The substitution (or "anion exchange") of leaving groups with added salt anions for typical S_N2 substrates were examined thoroughly in the 50% (v/v) DMF– as well as the DMA–H_2O solvent system. The solvolyses accompanied by the anion exchanges for benzyl halides (S_N1–S_N2 borderline substrates) were examined also in the same solvent. A linear relationship was observed between the stabilities of carbocations and the $LiClO_4$ effects on the solvolysis rate constants of the various substrates in 50% (v/v) DMA–H_2O. Raman spectra of DMA–H_2O and DMA–D_2O in the presence of various salts were measured to evaluate the degree of distortion of bulk water properties. Raman spectra of DMF–D_2O were also measured to obtain further confident evidence.

Results and Discussion

Exponential Increases in the Solvolysis Rate of 1-Adamantyl Chloride by the Addition of Metal Perchlorates. Figure 1 shows the changes in the solvolysis rate of 1-adamantyl (=1-tricyclo[3.3.1.1^{3,7}]decyl) chloride with the addition of alkali metal or alkaline earth metal perchlorates in a 50% (v/v) *N*,*N*-dimethylacetamide (DMA)–water mixed

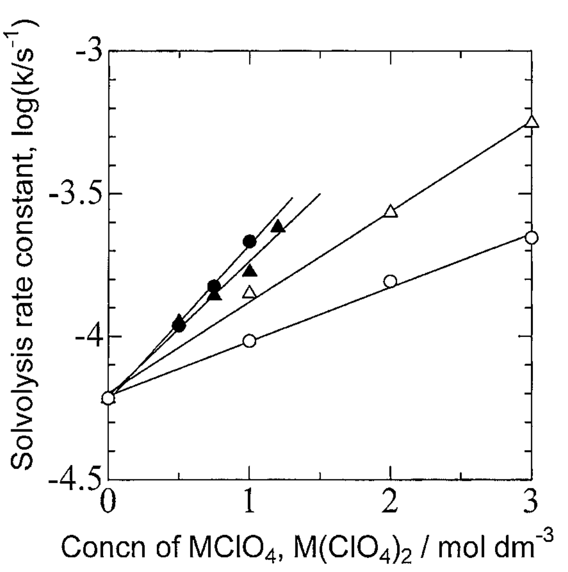


Figure 1. Exponential increases in the solvolysis rate constant of 1-adamantyl chloride with the addition of various metal perchlorates in 50% (v/v) DMA–H_2O at 65 °C: (○) $NaClO_4$, (△) $LiClO_4$, (●) $Mg(ClO_4)_2$, and (▲) $Ba(ClO_4)_2$.

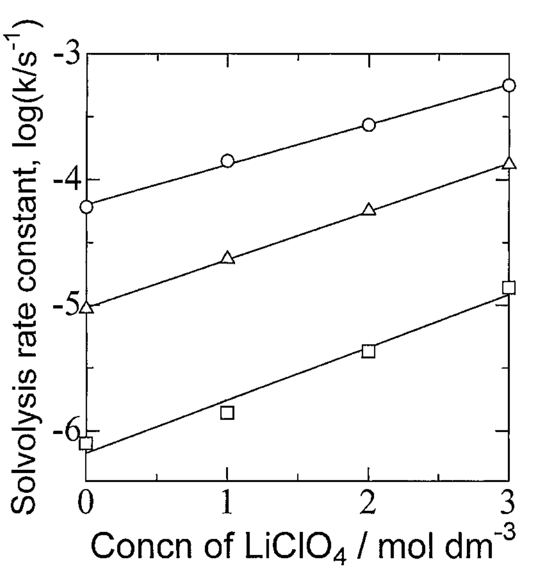


Figure 2. Differences of slopes in the solvolysis rate constant of 1-adamantyl chloride with $LiClO_4$ in various contents of DMA in DMA–H_2O mixed solvents at 65 °C: (○) 50, (△) 60, and (□) 75% (v/v) DMA.

solvent at 65 °C. The "pseudo" first-order reaction rate constant (k/s^{-1}) increased exponentially with increasing concentration of $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, or $Ba(ClO_4)_2$, i.e., linearity was observed between $\log(k/s^{-1})$ and the concentration of $MClO_4$ or $M(ClO_4)_2$. The effects of metallic ions increased as $Na^+ < Li^+ < Ba^{2+} < Mg^{2+}$. The difference in the salt effects between Mg^{2+} and Ba^{2+} is small and some contradictory results have been observed. In 50% (v/v) DMF–water or 50% (v/v) DMSO–water, obvious superiority of Ba^{2+} over Mg^{2+} was observed, while the superiority between Mg^{2+} and Ba^{2+} (of up to 1.5 mol dm^{-3} salt concentration) was not observed in 50% (v/v) sulfolane–water solvent.[16]

The Arrhenius plots of the solvolysis reaction (55–80 °C) of 1-adamantyl chloride in 50% (v/v) DMA–H_2O solvent gave 89.0, 94.3, and 109.1 kJ mol^{-1} activation energies (E_a) for no salt, 1.0 and 2.0 mol dm^{-3} $LiClO_4$, respectively. The values were 95.1 and 98.7 kJ mol^{-1} for 1.0 and 2.0 mol dm^{-3} $NaClO_4$, respectively.

Figure 2 shows exponential increases in the solvolysis rate constant (k/s^{-1}) of 1-adamantyl chloride with $LiClO_4$ in various contents of DMA (50, 60, and 75% (v/v)) in DMA–H_2O mixtures at 65 °C. In the absence of $LiClO_4$, the solvolysis reaction constants decreased with increasing content of DMA: $\log(k/s^{-1}) = -4.22$, -5.03, and -6.39 in 50, 60, and 75% (v/v) DMA–H_2O, respectively. The deceleration in the solvolysis should be caused by the decreases in the water activity with increasing contents of DMA. However, the slope of $\log(k/s^{-1})$ vs. the $LiClO_4$ concentration increased with increasing content of DMA: $\Delta\log(k/s^{-1})/\Delta[LiClO_4] = 0.32$, 0.38, and 0.51 for 50, 60, and 75% (v/v) DMA–H_2O, respectively. Increasing contents of the organic solvent cause the decrease of the activity of water, by which the solvolyses are decelerated. However, both Li^+ and Cl^- (of the leaving group) are so much less solvated in water mixed solvents of lesser water contents (e.g., 25%) that the chemical interaction between Li^+ and Cl^- may be encouraged to produce greater amount of carbocations at the higher $LiClO_4$ concentrations.

Similar phenomena were observed for 1-adamantyl bromide in 60, 70, and 90% (v/v) DMA–water mixed solvents. More and less distinct slope changes for 1-adamantyl bromide were obtained in CH_3CN– and DMSO–water systems, respectively. The solvation ability toward the metal cations of CH_3CN (DN = 14.1)[34] is much smaller than DMSO (DN = 29.8),[34] although the solvation abilities of both solvents toward anions must be similar, judging from the same acceptor numbers (AN = 19.3). The experimental results will be discussed in the next section.

Contents of Organic Solvents and the Role of Their Solvation Abilities. The effects of $LiClO_4$ on the solvolysis rate constant of 1-adamantyl bromide were examined in 60, 75, and 90% (v/v) DMA–H_2O mixed solvents: the linear increases in $\log(k/s^{-1})$ with the increasing concentration of $LiClO_4$ indicated the positive salt effect. However, the value of $\Delta\log(k/s^{-1})/\Delta[LiClO_4]$ varied with increasing DMA contents: 0.30, 0.46, and 0.51 in 60, 75, and 90% (v/v) DMA, respectively. As described above, for the chloride substrate, $\Delta\log(k/s^{-1})/\Delta[LiClO_4] = 0.32$, 0.38, and 0.51 in 50, 60, and 75% (v/v) DMA–H_2O mixed solvents (Figure 2). Obviously, the slopes for the bromide substrate are smaller than those for the chlorides. The interaction of Li^+ with Br^- should be smaller than that with Cl^- in those solvents. In 75 and 90% (v/v) DMSO–water mixed solvents, the $\Delta\log(k/s^{-1})/\Delta[LiClO_4]$ values were 0.32 and 0.39 for 1-adamantyl bromide.

In the 50% (v/v) CH_3CN–water mixed solvent, a linear increase in the solvolysis constant was observed for 1-adamantyl bromide with increasing $LiClO_4$ concentration up to 2.0 mol dm^{-3}. In 60, 75, and 90% (v/v) CH_3CN–water mixed solvents, however, the relation of $\log(k/s^{-1})$ vs. $LiClO_4$ concentration gave not linear but convex curves over lower $LiClO_4$ concentrations (Figure 3). For lower $LiClO_4$ concen-

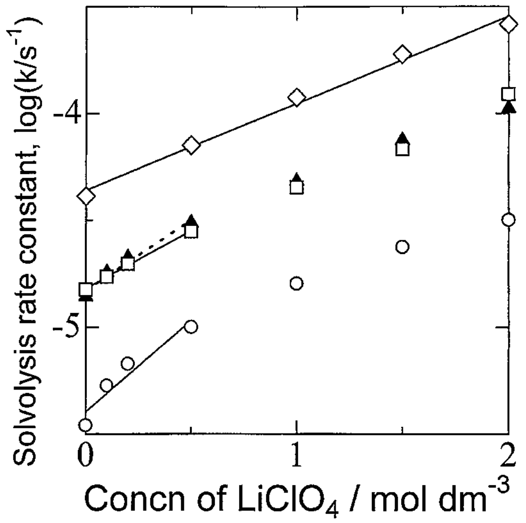


Figure 3. Changes in solvolysis rate constant of 1-adamantyl bromide with the addition of $LiClO_4$ in CH_3CN–H_2O mixed solvents: (◇) 50% (30 °C), (□) 60% (30 °C), (▲) 75% (45 °C), and (○) 90% (60 °C) CH_3CN.

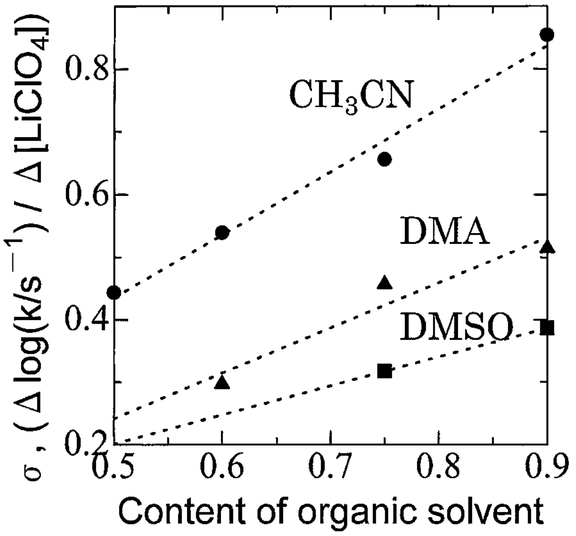
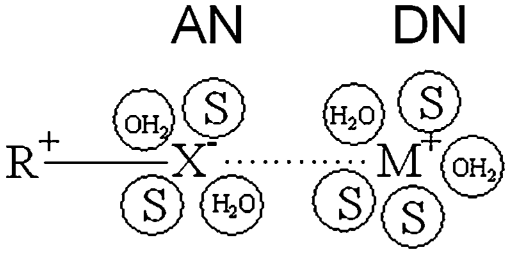


Figure 4. The changes in salt effects, $\Delta\log(k/\mathrm{s}^{-1})/\Delta[\mathrm{LiClO_4}]$ (σ), with increasing contents of organic solvents. The temperatures at which the rate constants were observed are 45, 60, and 80 °C for 60, 75, and 90% DMA–H_2O, 60 and 80 °C for 75 and 90% DMSO–H_2O, respectively; cf. Figure 3 for CH_3CN–H_2O.

tration ranges (0–0.5 mol dm^{-3}), the $\Delta\log(k/\mathrm{s}^{-1})/\Delta[\mathrm{LiClO_4}]$ values were evaluated to be 0.44, 0.54, 0.66, and 0.85 in 50, 60, 75 and 90% (v/v) CH_3CN–water solvents, respectively.

Figure 4 shows the relationship between the $\Delta\log(k/\mathrm{s}^{-1})/\Delta[\mathrm{LiClO_4}]$ (σ) values and the contents of the organic solvents (0.5, 0.6, 0.75, and 0.9) in the water mixed solvents. It is obvious that at 75% (v/v) organic solvent contents, for instance, the $\Delta\log(k/\mathrm{s}^{-1})/\Delta[\mathrm{LiClO_4}]$ (σ) value increases as DMSO < DMA < CH_3CN and also that the slope of $\Delta\log(k/\mathrm{s}^{-1})/\Delta[\mathrm{LiClO_4}]$ (σ) vs. contents of the organic solvents become more steep as DMSO (0.46) < DMA (0.73) < CH_3CN (1.0).



Scheme 2. Involvement of acceptor (AN) and donor (DN) numbers of an organic solvent toward the leaving-group anion as well as the metal cation.

It is true that in every solvent system the salt effect becomes more significant with increasing content of organic solvent. However, the fact that the slope of $\Delta\log(k/\mathrm{s}^{-1})/\Delta[\mathrm{LiClO_4}]$ (σ) vs. the content of an organic solvent differs one another suggests that the different salt effects are caused by the different solvation abilities of the solvents. Scheme 2 shows the involvement (or the solvation) of an organic solvent toward the leaving-group anion from the substrate as well as toward the cation of the salt. Both acceptor (AN) and donor (DN) numbers of an organic solvent should be involved for the metal salt effect, where the perchlorate ion is regarded to have no specific effect other than Coulombic interaction. An inverse proportional relationship between $\Delta\sigma/\Delta$ (contents of organic solvent) and the square roots of donor and acceptor numbers ($\sqrt{\mathrm{DN}\cdot\mathrm{AN}}$) for CH_3CN (16.5), DMA (19.4), and DMSO (24.0) supported our proposed mechanism illustrated in Scheme 2. Figure 4 provides us with the $\Delta\log(k/\mathrm{s}^{-1})/\Delta[\mathrm{LiClO_4}]$ (σ) values at 50% (v/v) organic solvents: 0.44, ca. 0.25, and ca. 0.2 for CH_3CN, DMA, and DMSO, respectively. Now, we can rather directly compare these values to previous data: $\log(k_1/k_0) = 0.39$ (at 50 °C)[14] and 0.48 (at 50 °C)[15] for 50% (v/v) acetone– and 1,4-dioxane–water mixed solvents, where the k_1 and k_0 values represent the solvolysis rate constants of 1-adamantyl bromide at 0 and 1.0 mol dm^{-3} $LiClO_4$, respectively. We may note that the $\sqrt{\mathrm{DN}\cdot\mathrm{AN}}$ values of acetone and 1,4-dioxane are 14.6 and 12.6, respectively.

Deceleration in the Solvolysis Rate of a Typical S_N1 Substrate by the Addition of Non-Metallic Salts. The effects of non-metallic salts on the S_N1 solvolysis rate were examined in the 50% (v/v) DMA–H_2O solvent. Figure 5 shows the change in the solvolysis rate of 1-adamantyl chloride with increasing concentration of $Et_4N^+X^-$ ($X^- = ClO_4^-$, Cl^-, Br^-, and TsO^-) at 65 °C. All the tetraethylammonium salts caused the deceleration in the solvolysis rate; the tosylate with the greatest bulk among the four anions caused the most remarkable decrease in the $\Delta\log(k/\mathrm{s}^{-1})$ value of −0.59, i.e., the solvolysis rate decreased to one-fourth at 1.0 mol dm^{-3} of the salt, compared with that in the absence of the salt [$\log(k/\mathrm{s}^{-1}) = -4.22$] at 65 °C. The tetraethylammonium salts caused the deceleration effect in the order of $ClO_4^- \approx Br^- < Cl^- < TsO^-$ for the anions. A similar and distinct order ($ClO_4^- < Br^- < Cl^- < TsO^-$) of Et_4N^+ salts has been observed in 50% (v/v) sulfolane–water.[16] In 50% (v/v) DMF–H_2O, the order of $ClO_4^- < Br^- < Cl^-$ was observed for 1-adamantyl chloride at 70 °C and also for 1-adamantyl bromide at 45 °C: the deceleration effect by Et_4NCl was larger than that by Et_4NBr (Table S1).

The deceleration effect must be brought by the decrease in the activity of water mixed with DMF or DMA: the solvolyses of typical S_N1 substrates should be initiated by the attack of water molecules toward the substrates in order to produce the carbocations. The solvation abilities of the anions may result in the difference of "effective" water activities. The distortion of water structure with the presence of tetraalkylammonium salts will be discussed based on our Raman spectral data in the final section.

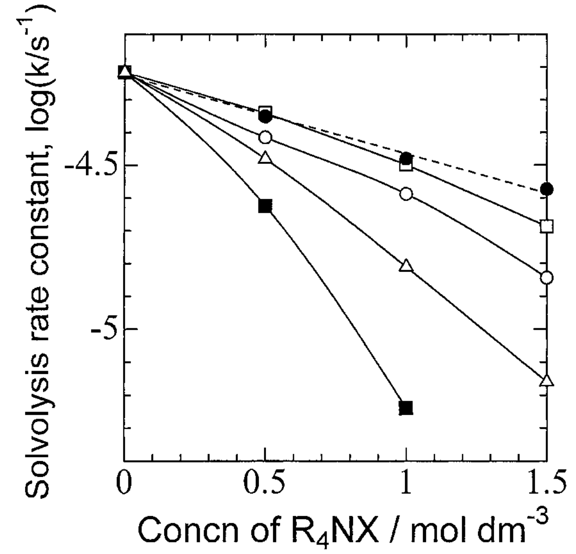


Figure 5. Decreases in the solvolysis rate constant of 1-adamantyl chloride with the addition of various salts in 50% (v/v) DMA–H_2O at 65 °C: (●) Et_4NClO_4, (□) Et_4NBr, (○) Et_4NCl, (△) Et_4NOTs, and (■) *n*-Bu_4NBr.

Similar but more remarkable deceleration in the solvolysis rate was observed with other tetraalkylammonium bromide (R_4NBr: R = Pr and *n*-Bu). The longer the chain in tetraalkylammonium bromide, the more remarkable deceleration was caused of the solvolysis rate as $Et_4N^+ < Pr_4N^+ < n\text{-}Bu_4N^+$: the changes in the logarithm factors [$\Delta\log(k/s^{-1})$] were −0.2, −0.63, and −1.02 with the 1.0 mol dm^{-3} salts at 65 °C, respectively. We noticed that the effect of Pr_4NBr was close to that of Et_4NOTs for the whole range of 0–1.5 mol dm^{-3} (e.g., −0.63 and −0.59 at 1.0 mol dm^{-3} for Pr_4NBr and Et_4NOTs, respectively, cf. Table 1).

On the Solvolysis Rate of 2-Adamantyl Bromide. Another typical S_N1 substrate, 2-adamantyl bromide, in the same solvent system was subject to similar acceleration and deceleration effects by added salts as shown in Figure 6. Without a salt, the solvolysis rate constant of the substrate was observed to be $\log(k/s^{-1}) = -5.50$ at 80 °C. The $\log(k/s^{-1})$ value increased linearly with increasing concentration of $LiClO_4$. The lithium ion should assist the formation of a stable carbocation from 2-adamantyl bromide in a manner similar to 1-adamantyl chloride. However, the carbocation of a secondary carbon may be less stable than of a tertiary carbon. Therefore, the degree in acceleration caused by the metal salts in the solvolysis rate for 2-adamantyl bromide should be less than that for 1-adamantyl chloride (apart from the difference in the leaving group). For instance, the solvolysis rates of the 1- and 2-derivatives increased with the logarithm factors [$\Delta\log(k/s^{-1})$] of +0.97 and +0.56 at 3.0 mol dm^{-3} $LiClO_4$, respectively. The deceleration effects on the solvolysis of 2-adamantyl bromide in the presence of non-metallic salts, Et_4NX (X = Cl and Br) and *n*-Bu_4NBr, were observed as $Et_4NBr \approx Et_4NCl < n\text{-}Bu_4NBr$: the $\Delta\log(k/s^{-1})$ values of −0.16, −0.16, and −0.79, respectively, for the 1.0 mol dm^{-3}

Table 1. "Pseudo" First-Order Reaction Rate Constants of the Solvolyses for Typical S_N1 Substrates in the Presence of Various Salts in the 50% (v/v) DMA–H_2O Solvent

Substrate	Temp/°C	Salt[a]	k/s^{-1}	$\log(k/s^{-1})$	$\Delta\log(k/s^{-1})$[b]
1-Adamantyl chloride	65	No salt	6.07×10^{-5}	−4.22	—
	65	$LiClO_4$	1.41×10^{-4}	−3.85	+0.37
	65	$NaClO_4$	9.62×10^{-5}	−4.02	+0.20
	65	$Mg(ClO_4)_2$	2.15×10^{-4}	−3.67	+0.55
	65	$Ba(ClO_4)_2$	1.68×10^{-4}	−3.77	+0.45
	65	Et_4NClO_4	3.31×10^{-5}	−4.48	−0.26
	65	Et_4NCl	2.58×10^{-5}	−4.46	−0.24
	65	Et_4NBr	3.79×10^{-5}	−4.42	−0.20
	65	Et_4NOTs[c]	1.55×10^{-5}	−4.81	−0.59
	65	Pr_4NBr	1.40×10^{-5}	−4.85	−0.63
	65	*n*-Bu_4NBr	5.77×10^{-6}	−5.24	−1.02
2-Adamantyl bromide	80	No salt	3.13×10^{-6}	−5.50	—
	80	$LiClO_4$	4.56×10^{-6}	−5.34	+0.16
	80	Et_4NCl	2.20×10^{-6}	−5.66	−0.16
	80	Et_4NBr	2.18×10^{-6}	−5.66	−0.16
	80	*n*-Bu_4NBr	5.07×10^{-7}	−6.29	−0.79
tert-Butyl chloride	20	No salt	1.41×10^{-4}	−3.85	—
	20	$LiClO_4$	1.87×10^{-4}	−3.73	+0.13

a) The salt concentration of 1.0 mol dm^{-3}. b) $\Delta\log(k/s^{-1}) = \log(k_1/s^{-1})$[with salt] − $\log(k_0/s^{-1})$[no salt] for each substrate. c) *p*-Toluenesulfonate (tosylate) salt.

salts. The solvolysis rates of typical S_N1 substrates, 1-adamantyl chloride and 2-adamantyl bromide, were decelerated by the non-metallic salts. The difference in deceleration effects of Cl^- and Br^- was not so clear for 2-adamantyl bromide while the deceleration effect of Cl^- on 1-adamantyl chloride was obviously larger than that of Br^-.

Now we may talk about the interaction between halide anions from substrates and other species in solution. Rudakov and Kozhevnikov[35] have reported exponential increases in solvolysis rates of *tert*-butyl halides in EtOH–H_2O mixed solvents with the complex formation constants (e.g., $K = [MX]/[M^+][X^-]$) of transition-metal halides. We have reported[16] an extremely large positive "salt" effect of $Ni(ClO_4)_2$ on the solvolysis rate constant of 1-adamantyl chloride in 50% (v/v) sulfolane–H_2O. Cox and Maskill[36] have discovered solvolyses of *tert*-butyl iodide catalyzed by I_2 in aqueous ethanol; the same effect, but to a smaller extent, is also found for *tert*-butyl bromide in the solvent. We would like to note that the polyhalogen ion formation, such as I_3^- and I_2Br^- (e.g., $I_2 + Br^- \rightleftharpoons I_2Br^-$), in the solution can account for the catalytic effects by I_2. The stability of the polyhalogen ions has been reported to decrease as $I_3^- > I_2Br^- > Br_3^-$.[37]

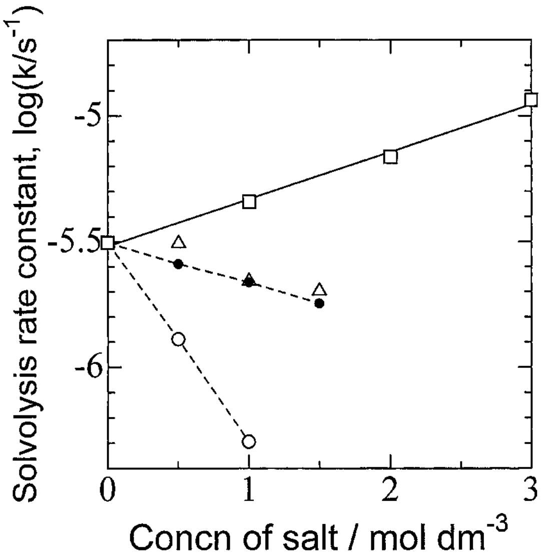


Figure 6. Changes in the solvolysis rate of 2-adamantyl bromide with the addition of various salts in 50% (v/v) DMA–H_2O at 80 °C: (□) $LiClO_4$, (●) Et_4NBr, (△) Et_4NCl, and (○) *n*-Bu_4NBr.

Effects of $LiClO_4$ on the Solvolyses of S_N2 Substrates, Hexyl Chloride, Bromide, and Tosylate. The changes in the solvolysis rates, $\log(k/s^{-1})$ were examined for hexyl chloride, bromide, and tosylate with 0–2.0 mol dm^{-3} $LiClO_4$ in 50% (v/v) DMA–H_2O at 80 °C. As contrasted with the cases of the typical S_N1 substrates, the solvolysis rates of the S_N2 substrates were not accelerated but decelerated by the addition of the metal perchlorate. The $\log(k/s^{-1})$ value (−3.68) of hexyl tosylate decreased linearly with increasing $LiClO_4$ concentration: $\Delta\log(k/s^{-1}) = -0.17$ and −0.33 at 1.0 and 2.0 mol dm^{-3} $LiClO_4$. The decrease for the bromide substrate was remarkable: $\Delta\log(k/s^{-1}) = -0.23$ and −0.50 at 1.0 and 2.0 mol dm^{-3} $LiClO_4$, respectively (Table 2 and Table S3). While the rate constant of the chloride substrate increased slightly up to 0.5 mol dm^{-3} $LiClO_4$, and then it began to decrease with increasing concentration of the salt. A similar minor increase was observed for hexyl chloride in 50% (v/v) DMF–H_2O at 80 °C; the rate constant of the substrate increased slightly up to 1.0 mol dm^{-3} $LiClO_4$ (Table S2), and then it decreased. The cause of these irregular increases for the chloride substrate is not clear but because of the long alkyl chain (causing some stability of the carbocation), the some S_N1 scheme might bring additional contribution to the very slow S_N2 solvolysis of the substrate.

Table 2. "Pseudo" First-Order Reaction Rate Constants of the Solvolyses for Typical S_N2 Substrates in the Presence of Various Salts in 50% (v/v) DMA–H_2O Solvent at 80 °C

Substrate	Temp/°C	Salt[a)]	k/s^{-1}	$\log(k/s^{-1})$	$\Delta\log(k/s^{-1})$[b)]
Hexyl chloride	80	No salt	1.01×10^{-6}	−5.99	—
	80	$LiClO_4$	1.16×10^{-6}	−5.94	(+0.05)[c)]
	80	Et_4NCl	1.29×10^{-6}	−5.89	+0.10
	80	Et_4NBr[d)]	1.56×10^{-5}	−4.81	+1.18
	80	Et_4NOTs[e)]	1.29×10^{-6}	−5.89	+0.30
Hexyl bromide	80	No salt	3.07×10^{-5}	−4.51	—
	80	$LiClO_4$	1.80×10^{-5}	−4.74	−0.23
	80	Et_4NCl[d)]	8.24×10^{-7}	−6.08	−1.57
	80	Et_4NBr	3.08×10^{-5}	−4.51	0
	80	Et_4NOTs[e)]	2.46×10^{-5}	−4.61	+0.10
Hexyl tosylate	80	No salt	2.09×10^{-4}	−3.68	—
	80	$LiClO_4$	1.41×10^{-4}	−3.85	−0.17
	80	Et_4NCl[d)]	6.98×10^{-7}	−6.16	−2.48
	80	Et_4NBr[d)]	2.50×10^{-5}	−4.60	−0.92
	80	Et_4NOTs[e)]	1.27×10^{-4}	−3.89	−0.21

a) The salt concentration of 1.0 mol dm^{-3}. b) $\Delta\log(k/s^{-1}) = \log(k_1/s^{-1})$[with salt] − $\log(k_0/s^{-1})$[no salt] for each substrate. c) The slope $\Delta\log(k/s^{-1})/\Delta[LiClO_4] = -0.14$ for whole the range of 0, 0.5, 1.0, 2.0, and 3.0 mol dm^{-3} $LiClO_4$, cf. Table 4. d) Only the linear part in the ln[S] vs. *t* plot was evaluated because an exchange reaction occurred between the leaving group and the added salt anion. e) *p*-Toluenesulfonate (tosylate) salt.

Solvolyses of S_N2 Substrates Accompanied by Anion-Exchange Reactions. Solvolyses accompanied by "anion exchange" reactions for typical S_N2 substrates, such as hexyl chloride, bromide, and tosylate were examined in the DMF–(Table S2) and DMA–H_2O solvents (Table 2 and Table S3). The anion-exchange reaction prior to or in parallel to the solvolysis of hexyl chloride, bromide, and tosylate has been suggested to cause remarkable acceleration or deceleration in the solvolysis rate, depending on the anion of added tetraethylammonium salts.[16] It is well known that the order of nucleophilicity for halide ions in aprotic solvents, such as acetone, is $Cl^- > Br^- > I^-$, whereas $Cl^- < Br^- < I^-$ in aqueous solution.[38]

The whole arguments for the solvolysis and exchange reactions for the S_N2 substrates in the 50% (v/v) DMA–H_2O solvent system has been verified also in the 50% (v/v) DMF–H_2O solvent system. In 50% (v/v) DMF–H_2O, we examined *n*-butyl bromide and tosylate as well as hexyl-compounds. However, *n*-butyl chloride was excluded because the boiling point of the compound (78.4 °C)[39] is lower than the reaction temperature. The possible formation of *n*-butyl chloride through the anion exchange of *n*-butyl bromide in the presence of the chloride ion (Et_4NCl) at 80 °C brought a partial escape of the chloride compound from the reaction vessel in order to give an imprecise value for the solvolysis rate constant: $\Delta\log(k/s^{-1}) = -0.99$ (too small) for *n*-BuBr, cf. -1.55 for *n*-HexylBr in the presence of $1.0\,mol\,dm^{-3}$ Et_4NCl (Table S2). In the 50% (v/v) DMA–H_2O system, however, $\Delta\log(k/s^{-1})$ was -1.57 for hexyl bromide in the presence of $1.0\,mol\,dm^{-3}$ Et_4NCl (Table 2).

The solvolyses in the presence of added salt anions were examined for phenacyl chloride and bromide (2-chloro- and 2-bromoacetophenone) in 50% (v/v) DMA–H_2O to demonstrate that another type of S_N2 substrate is subject to anion-exchange reactions. The detailed results will be reported in a paper. Now, we may go on to the solvolyses of S_N1–S_N2 borderline substrates.

Solvolyses of Benzyl Chlorides and Bromides, S_N1–S_N2 Borderline Substrates. Benzyl halides are regarded as S_N1–S_N2 borderline substrates in solvolysis reactions. Figure 7 shows the changes of solvolysis rate constants of benzyl halides in the presence of $LiClO_4$ in 50% (v/v) DMA–H_2O. The $\log(k/s^{-1})$ of benzyl chloride at 50 °C decreased linearly with increasing concentration of $LiClO_4$, giving a slope, $\Delta\log(k/s^{-1})/\Delta[LiClO_4] = -0.16$, cf. -0.19 at $1.0\,mol\,dm^{-3}$ $LiClO_4$ in Table 3. At 70 °C, 4-nitrobenzyl chloride, having more S_N2 tendency because of its electron-withdrawing group, gave a steeper slope (-0.23) than that of benzyl chloride (-0.16). The $\log(k/s^{-1})$ of 4-methylbenzyl chloride with greater S_N1 tendency, however, increased with increasing concentration of $LiClO_4$, after showing a minimum value at $0.5\,dm^{-3}$ $LiClO_4$. The slope, $\Delta\log(k/s^{-1})/\Delta[LiClO_4]$, over the range of 0–$2.0\,mol\,dm^{-3}$ $LiClO_4$ was small but definitely a positive value, $+0.04$. In 50% (v/v) DMF–H_2O, the substrate gave a similar minimum and a totally positive slope. We have discussed, in the previous sections, that typical S_N1 and S_N2 substrates give positive and negative slopes of rate constants, respectively, with increasing concentration $LiClO_4$.

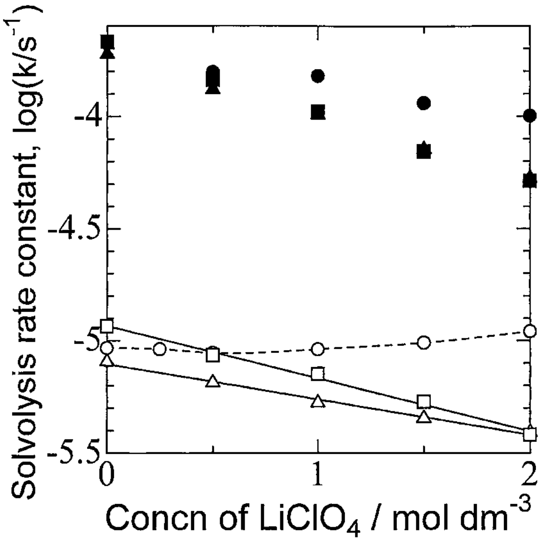


Figure 7. Changes in the solvolysis rate constant of S_N1–S_N2 borderline substrates with the addition of $LiClO_4$ in 50% (v/v) DMA–H_2O: (●) 4-methylbenzyl bromide, (○) 4-methylbenzyl chloride at 35 °C, (▲) benzyl bromide, (△) benzyl chloride at 50 °C, (■) 4-nitrobenzyl bromide, (□) 4-nitrobenzyl chloride at 70 °C.

As displayed in Figure 7, on the other hand, all the benzyl bromides gave negative slopes: -0.31, -0.27, and -0.16 for 4-nitrobenzyl (at 75 °C), benzyl (at 50 °C), and 4-methylbenzyl bromides (at 35 °C), respectively. Compared with chlorides, the bromides gave larger negative values. As shown above, a similar trend was observed for the typical S_N2 substrates, hexyl halides: the bromide gave a larger negative value than the chloride substrate.

In the previous study,[14] we observed that the solvolysis rate constants of *N*,*N*-dimethylsulfamoyl and *p*-toluenesulfonyl chlorides in 50% (v/v) acetone–H_2O decreased with increasing $LiClO_4$ concentration but increased with the presence of Et_4NBr. At that time, the phenomena were not fully interpreted. Recently, Kevill et al.[40] demonstrated that the pathways for solvolyses of *N*,*N*-dimethylsulfamoyl and *p*-toluenesulfonyl chlorides are indeed S_N2 and not S_N1 (earlier suggestions). Therefore, the acceleration in solvolysis rates of these substrates by the addition of Et_4NBr should be caused by the anion exchange between Cl^- from the substrates and Br^- of the added salt.

Solvolysis reactions of the S_N1–S_N2 borderline substrates, which may also be accompanied by anion exchange, were examined in 50% (v/v) DMA–H_2O. Figure 8 shows the changes in solvolysis rate constants of benzyl chloride and bromide at 50 °C. Almost no change in the rate constant was observed when Et_4NCl was added to benzyl chloride. Similarly, no change was observed when Et_4NBr was added to benzyl bromide. Upon the addition of a salt having a different type of anion, however, the solvolysis rates of the substrates altered remarkably. For instance, $\log(k/s^{-1})$ of benzyl bromide was decreased from -3.72 to -4.42 (to a one-fifth) and -5.00 (to ca. 1/20) by the addition of 0.05 and $0.2\,mol\,dm^{-3}$ Et_4NCl, respectively. In the presence of $1.0\,mol\,dm^{-3}$ Et_4NCl, at last, the rate constant, $\log(k/s^{-1})$ of benzyl bromide reached to that

Table 3. "Pseudo" First-Order Reaction Rate Constants of the Solvolyses for S_N1–S_N2 Borderline Substrates in the Presence of Various Salts in 50% (v/v) DMA–H_2O Solvent

Substrate	Temp/°C	Salt[a]	k/s^{-1}	$\log(k/s^{-1})$	$\Delta\log(k/s^{-1})$[b]
Benzyl chloride	50	No salt	8.07×10^{-6}	−5.09	—
	50	$LiClO_4$	5.30×10^{-6}	−5.28	−0.19
	50	Et_4NCl	7.71×10^{-6}	−5.11	−0.02
	50	Et_4NBr[c]	1.79×10^{-4}	−3.75	+1.34
Benzyl bromide	50	No salt	1.89×10^{-4}	−3.72	—
	50	$LiClO_4$	1.01×10^{-4}	−3.99	−0.27
	50	Et_4NCl[c]	7.82×10^{-6}	−5.11	−1.39
	50	Et_4NBr	2.07×10^{-4}	−3.69	+0.03
4-Methylbenzyl chloride	35	No salt	9.28×10^{-6}	−5.03	—
	35	$LiClO_4$	9.15×10^{-6}	−5.04	(−0.01)[d]
	35	Et_4NCl	7.54×10^{-6}	−5.12	−0.09
	35	Et_4NBr[c]	1.38×10^{-4}	−3.86	+1.17
4-Methylbenzyl bromide	35	No salt	2.10×10^{-4}	−3.68	—
	35	$LiClO_4$	1.51×10^{-4}	−3.82	−0.14
	35	Et_4NCl[c]	7.14×10^{-6}	−5.15	−1.47
	35	Et_4NBr	2.00×10^{-4}	−3.70	−0.02
4-Nitrobenzyl chloride	75	No salt	1.16×10^{-5}	−4.94	—
	75	$LiClO_4$	7.09×10^{-6}	−5.15	−0.21
	75	Et_4NCl	1.34×10^{-5}	−4.87	+0.07
	75	Et_4NBr[c]	2.47×10^{-4}	−3.61	+1.13
4-Nitrobenzyl bromide	75	No salt	2.14×10^{-4}	−3.67	—
	75	$LiClO_4$	1.05×10^{-4}	−3.98	−0.31
	75	Et_4NCl[c]	1.40×10^{-5}	−4.85	−1.18
	75	Et_4NBr	2.54×10^{-4}	−3.59	+0.08

a) The salt concentration of 1.0 mol dm^{-3}. b) $\Delta\log(k/s^{-1}) = \log(k_1/s^{-1})$[with salt] − $\log(k_0/s^{-1})$[no salt] for each substrate. c) Only the linear part in the ln[S] vs. t plot was evaluated because an exchange reaction occurred between the leaving group and the added salt anion. d) The slope $\Delta\log(k/s^{-1})/\Delta[LiClO_4] = +0.04$ for whole the range of 0, 0.25, 0.5, 1.0, and 2.0 mol dm^{-3} $LiClO_4$, see the text.

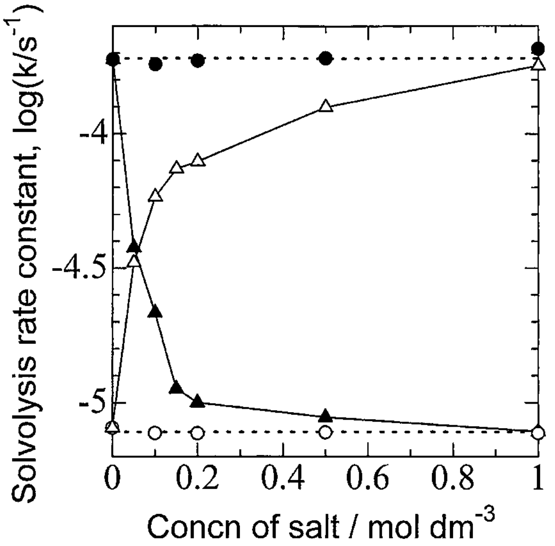


Figure 8. Changes in the solvolysis rates of benzyl halides with the addition of Et_4NX in 50% (v/v) DMA–H_2O at 50 °C: (●) Et_4NBr, (▲) Et_4NCl for benzyl bromide, (△) Et_4NBr, (○) Et_4NCl for benzyl chloride.

of benzyl chloride without a salt, i.e., −5.11 (to ca. 1/25). Just oppositely, the rate constant of benzyl chloride increased as high as ca. 25 times at 1.0 mol dm^{-3} Et_4NBr.

For the 4-methyl- and 4-nitro-derivatives of benzyl halides, solvolysis reactions accompanied by the anion exchange were also examined. The changes of rate constants at 35 °C of 4-methylbenzyl chloride and bromide with Et_4NX (X = Cl and Br) are shown in Figure 9. The rate constant, $\log(k/s^{-1})$, of 4-methylbenzyl bromide decreased to the value of 4-methylbenzyl chloride (intrinsic value) by the addition of 0.2 mol dm^{-3} Et_4NCl. In the presence of 0.5 and 1.0 mol dm^{-3} Et_4NCl, the rate constant of 4-methylbenzyl bromide further decreased to lower values than that of 4-methylbenzyl chloride. Conversely, the increases in the rate constant, $\log(k/s^{-1})$, of 4-methylbenzyl chloride were observed by the addition of Et_4NBr. However, the rate constant remained just below the value of 4-methylbenzyl bromide (−3.68) even at 1.0 mol dm^{-3} Et_4NBr.

The addition of even a small amount of Et_4NCl to the solvolysis system of 4-nitrobenzyl bromide (at 75 °C) caused a remarkable decrease in the rate constant (Table S4). On the other hand, a very remarkable increase was observed for 4-nitrobenzyl chloride upon the addition of a small amount of Et_4NBr, for instance, more than a three-fold rate constant at 0.01 mol dm^{-3} Et_4NBr. The greater S_N2 tendency, based on the nitro-group, may promote more sufficient anion-exchange

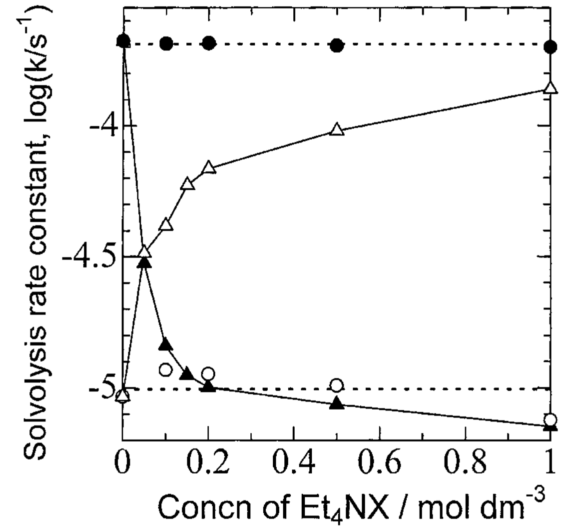


Figure 9. Changes in the solvolysis rates of 4-methylbenzyl halides with the addition of Et_4NX in 50% (v/v) DMA–H_2O at 35 °C: (●) Et_4NBr, (▲) Et_4NCl for 4-methylbenzyl bromide, (△) Et_4NBr, (○) Et_4NCl for 4-methylbenzyl chloride.

reactions. Contrastingly, the greater S_N1 tendency, based on the methyl-group on benzyl halides, caused less anion-exchange reaction. At last, the typical S_N1 substrates, *tert*-butyl or 1-adamantyl halides exhibit no apparent anion-exchange property (vide supra).

Relationship between Effects of $LiClO_4$ and Stabilities of Carbocations. Bingham and Schleyer[41] reported an attempt to rationalize the solvolysis rate constants of tertiary bridgehead halides (such as 1-adamantyl chloride) with the stabilities of carbocations by empirical calculation. Abboud and coworkers[42] have developed a method to determine the stability of carbocations in the gas phase by dissociative proton attachment (DPA) using Fourier transform ion cyclotron resonance (FTICR) spectroscopy. Carbocations are ranked according to their stabilities relative to the 1-adamantyl cation, based on eq 2,

$$\text{1-Ad–Cl(g)} + R^+\text{(g)} \rightarrow \text{1-Ad}^+\text{(g)} + \text{R–Cl(g)}, \Delta G^\circ \quad (2)$$

The Gibbs free energy values (ΔG°) of RX in the gas phase have been found to give excellent correlations with the $\log(k/s^{-1})$ values of RX in solution, where RX are not only bridgehead chlorides (such as 1-adamantyl) but also bi- and tricyclic secondary (such as 2-norbornyl and 2-adamantyl) chlorides.

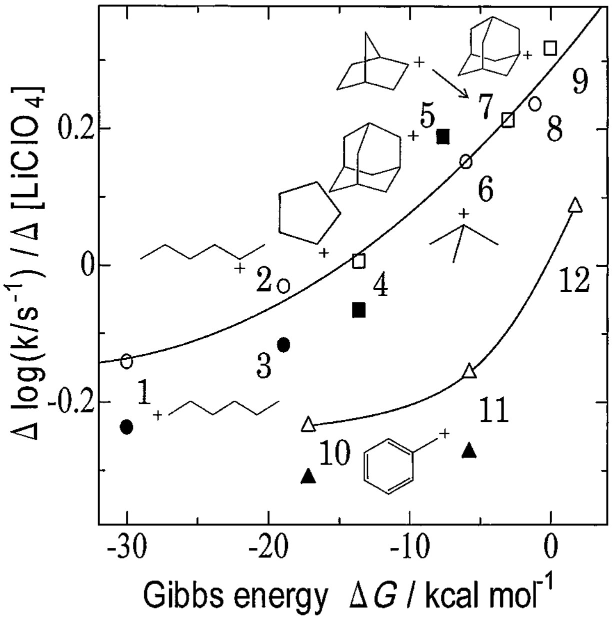


Figure 10. Relationship between the $LiClO_4$ effects on the solvolysis rate constants in 50% (v/v) DMA–H_2O and the stabilities of carbocations (the standard Gibbs energy changes for eq 2): (1) hexan-1-ylium, (2) hexan-2-ylium, (3) butan-2-ylium, (4) cyclopentylium, (5) adamantan-2-ylium, (6) 2-methylpropan-2-ylium, (7) norbornan-2-ylium, (8) 3-methylpentan-3-ylium, (9) adamantan-1-ylium, (10) 4-nitrobenzylium, (11) benzylium, (12) 1-phenylethan-1-ylium. The stability of 1-adamantyl cations is taken as the standard value ($\Delta G = 0$). Open and solid symbols represent chloride and bromide compounds, respectively. cf. Table 4 for the temperatures of solvolyses examined.

Figure 10 shows the relationship between the standard Gibbs energy changes for eq 2 and the $LiClO_4$ effects on the solvolysis rate constants of various chloride and bromide substrates in 50% (v/v) DMA–H_2O (Tables S3 and S5). Aliphatic chlorides gave a good proportionality or correlation between ΔG° and $\Delta\log(k/s^{-1})/\Delta[LiClO_4]$; aliphatic chlorides examined are 1-hexyl, 2-hexyl, cyclopentyl, *tert*-butyl (2-chloro-2-methylpropane), and *exo*-2-norbornyl (=*exo*-2-bicyclo[2.2.1]heptyl) chlorides, 3-chloro-3-methylpentane, and 1-adamantyl chloride. Aliphatic bromides, i.e., 1-hexyl, 2-butyl, and cyclopentyl bromides, gave a straight line below (the difference of ca. 0.1) the line of the corresponding or related chlorides. Just 2-adamantyl bromide was above the line of the chlorides. Benzyl halides and a benzyl-derivative (1-chloro-1-phenylethane) gave another correlation group below the group of aliphatic halides. Generally speaking, the more stable carbocation is apt to react through S_N1 rather S_N2 pathway. Therefore, it is obvious that $LiClO_4$ gives positive and negative effects on the solvolysis rate constants of S_N1 and S_N2 substrates, respectively. It must be quite natural that the salt effects on the S_N1–S_N2 borderline substrates are close to zero. The general principle may be that the faster solvolysis rate, the larger extent of the $LiClO_4$ effect.

Despite higher temperature ($\Delta T = 10$ °C), the $\log(k/s^{-1})$ of cyclohexyl chloride (−5.65) and bromide (−4.32) at 80 °C were still much smaller than those of cyclopentyl chloride (−4.93) and bromide (−3.52) at 70 °C. However, the $LiClO_4$ effects on the rate constant of the cyclohexyl substrates (0.07 for the chloride) were slightly larger (+0.06) than those of the cyclopentyl substrates (0.01 for the chloride), cf. Table 4. Now, we have to discuss in detail the relationship between the solvolysis rates, $\log(k/s^{-1})$, and the extent of $LiClO_4$ effects, $\Delta\log(k/s^{-1})/\Delta[LiClO_4]$.

It is well known that the solvolysis rate of *tert*-butyl chloride is much faster than that of 1-adamantyl chloride in polar solvents, hydrogen bonding donating solvents. For instance,

Table 4. The Stabilities of Carbocations in the Gas Phase and the $LiClO_4$ Effects on the Solvolysis Rate Constants of Various Chloride and Bromide Substrates in the 50% (v/v) DMA–H_2O Solvent

Cations	Standard Gibbs energy[a)], ΔG^{o}/kcal mol^{-1}	$LiClO_4$ effect[b)] $\Delta\log(k/s^{-1})/\Delta[LiClO_4]$
Hexan-1-ylium (**1**)	−30 (an arbitral value)[c)]	chloride: −0.14 (80 °C)
		bromide: −0.24 (80 °C)
Hexan-2-ylium (**2**)	−18.9 (a loaned value)[d)]	chloride: −0.03 (80 °C)
Butan-2-ylium (**3**)	−18.9	bromide: −0.12 (80 °C)
Cyclopentylium (**4**)	−13.6	chloride: 0.01 (70 °C)
		bromide: −0.07 (70 °C)
Cyclohexylium	data not found	chloride: 0.07 (80 °C)
		bromide: −0.01 (80 °C)
Adamantan-2-ylium (**5**)	−7.6	bromide: 0.19 (80 °C)
2-Methylpropan-2-ylium (**6**)	−6.0	chloride: 0.15 (20 °C)
Norbornan-2-ylium (**7**)	−3.0	chloride: 0.21 (60 °C)
3-Methylpentan-3-ylium (**8**)	−1.1	chloride: 0.24 (20 °C)
Adamantan-1-ylium (**9**)	0.00 (by definition)	chloride: 0.32 (65 °C)
4-Nitrobenzylium (**10**)	−17.2	chloride: −0.23 (75 °C)
		bromide: −0.31 (75 °C)
Benzylium (**11**)	−5.8	chloride: −0.16 (50 °C)
		bromide: −0.27 (50 °C)
1-Phenylethan-1-ylium (**12**)	1.7	chloride: 0.09 (20 °C)

a) Standard Gibss energy change for a reaction, $1\text{-}AdCl(g) + R^+(g) \rightarrow 1\text{-}Ad^+(g) + RCl(g)$, cf. Ref. 42b. b) The $LiClO_4$ effect ($\Delta\log(k/s^{-1})/\Delta[LiClO_4]$) for each substrate was evaluated over a concentration range of 0–2.0 mol dm^{-3} $LiClO_4$. c) Methylium: −77.4 kcal mol^{-1}. d) Butan-2-ylium: −18.9 kcal mol^{-1}.

solvolysis rate of *tert*-butyl chloride is roughly 1000 times faster than that of 1-adamantyl chloride in 80% ethanol–H_2O.[43] The solvolysis rate constant of 1-norbornyl derivative has been found significantly below the correlation line.[44] The cause of the much faster solvolysis of *tert*-butyl chloride has been explained by nucleophilic solvent participation[45] or other reasons, e.g., increased hydrogen bond donation to the leaving group of *tert*-butyl chloride.[43] In the present study, accordingly, the solvolysis experiment of *tert*-butyl chloride (20 °C) was performed at much lower temperature than that of 1-adamantyl chloride (Table 4). Regardless of the solvolysis rate of *tert*-butyl chloride is much faster than that of 1-adamantyl chloride, the extent of $LiClO_4$ effect on *tert*-butyl chloride was smaller than that on 1-adamantyl chloride in good accordance with the stabilities of their carbocations (Table 4).

Generally, the solvolysis rate of a bromide substrate is 20–30 times faster than that of the corresponding chloride (Tables 2, 3, and 4). Nevertheless, the effect of $LiClO_4$ on the solvolysis rate constants was found to be somewhat independent from the solvolysis rate constants themselves: the $\Delta\log(k/s^{-1})/\Delta[LiClO_4]$ value for a bromide substrate was smaller (ca. 0.1) than that of the corresponding chloride, as shown in Figure 10. The apparent difference in the $LiClO_4$ effects may be caused by the difference in the interaction of Li^+ (increasing concentration) with the leaving groups (Cl^- and Br^-) in 50% (v/v) DMA–H_2O.

In previous papers,[13–15] we reported the linearity between the $LiClO_4$ effects and the Grunwald–Winstein m values[17] for S_N1 to S_N2 substrates in methanol–water, acetone–water, and 1,4-dioxane–water mixtures. The salt effects were expressed by the changes in solvolysis rates, $\log(k_1/k_o)$, on the addition of 1.0 mol dm^{-3} $LiClO_4$. The m value is the reaction's sensitivity to ionizing solvent power Y ($m = 1$ or 1.2 for 1-AdCl),[46] and may vary not only with experimental conditions but also with the different definitions. In the present paper, however, we were able to demonstrate quantitatively the correlation between the $LiClO_4$ effects and the carbocation stabilities expressed by the Gibbs free energy values (ΔG^{o}) of RX in the gas phase, where RX are not only typical S_N1 halides but also non-, mono-, bi-, and tricyclic secondary (such as 2-hexyl, cyclopentyl, 2-norbornyl, and 2-adamantyl) and, finally, typical S_N2 halides.

Raman Spectra for Observing Water Structure Distortion. Raman spectroscopy is a technique preferably used for studies of water structure because the proportions of intensities of main OH stretching modes (around 3200 and 3400 cm^{-1}) are thought to reflect well a network of hydrogen bonds as well as its disturbance by the presence of some solute. Scherer et al.[47] have reported Raman spectra of liquid D_2O from −10 to 90 °C; the (isotropic) spectra show the development of a band around 2500 cm^{-1} at the expense of the band around 2400 cm^{-1} with increasing temperature. These bands have been attributed to the OD stretching vibration of the symmetrically hydrogen-bonded complex (tetrahedral: 2400 cm^{-1}) and of the single-handed complex (2500 cm^{-1}). Tokushima et al.[48] estimated a 2:1 ratio between distorted and tetrahedral species at room temperature by means of high-resolution X-ray emission spectroscopy of liquid water.

Figure 11 shows the change in Raman spectra of H_2O with increasing contents of DMA (25–90% (v/v)) at room temperature. The band intensity at ca. 3200 cm^{-1} decreased remarkably compared with that at ca. 3400 cm^{-1}. Both band shifted toward higher wavenumber with increasing contents of DMA and reached 3280 and 3460 cm^{-1}, respectively, at 90% (v/v) DMA. The increased distortion of water structure with the

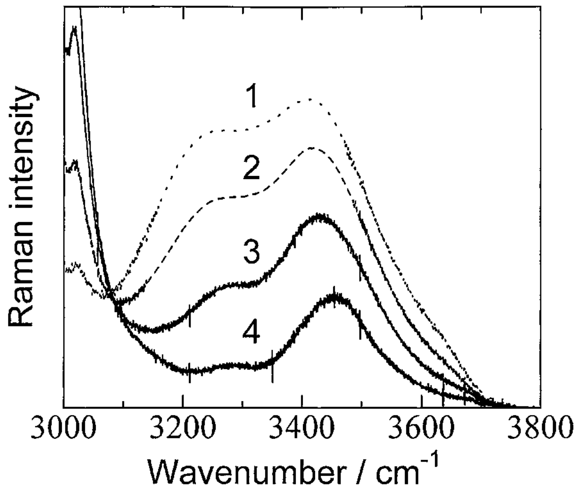


Figure 11. Raman spectra of DMA–H_2O mixture at room temperature: (1 ----) 0, (2 ---) 50, (3) 75, (4) 90% (v/v) of DMA.

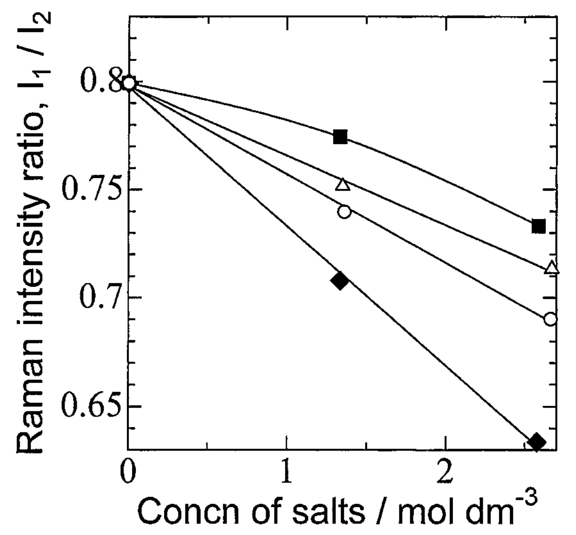


Figure 12. Relationship between the ratio of intensities in Raman OH stretching bands (I_1/I_2) and concentrations of metal perchlorates where I_1: ca. 3200 cm^{-1}, I_2: ca. 3400 cm^{-1}: (△) $LiClO_4$, (○) $NaClO_4$, (■) $Ma(ClO_4)_2$, (◆) $Ba(ClO_4)_2$.

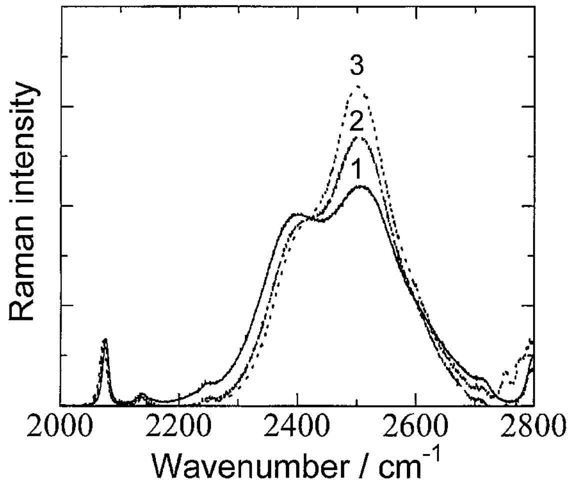


Figure 13. Raman spectra of 50% (v/v) DMA–D_2O mixed solutions containing concentrated Et_4NCl at room temperature: (1) $R = \infty$ (no salt); (2 ----) $R = 20$; (3 - - -) $R = 10$; where $R = [DMA + D_2O]/[Et_4NCl]$.

addition of DMA to H_2O was demonstrated by the remarkable decrease of the band intensity at ca. 3200 cm^{-1} compared with that at ca. 3400 cm^{-1}. Similar Raman band changes (2400 and 2500 cm^{-1}) were observed also for DMF–D_2O mixed solvents. We must just take into account that the intensity ratios of the main Raman components (around 3200 and 3400 cm^{-1}) of H_2O have been reported to alter with the different excitation wavelengths in Raman spectroscopy.[49] In the present work, a single wavelength (514.5 nm) was utilized for excitation of the Raman spectroscopy. Based on the IR spectra of H_2O containing various amount of DMF, Biliškov and Baranović[50] have evaluated the fraction of water OH oscillators that are hydrogen bonded to other water molecules.

Figure 12 shows the decreases in the ratio (I_1/I_2) of Raman OH band intensities around 3200 and 3400 cm^{-1} with increasing concentrations of various metal perchlorates (up to ca. 2.5 mol dm^{-3}) in 50% (v/v) DMA–H_2O. The decrease in the Raman intensity ratio (I_1/I_2) with the metal perchlorates was ordered as $Mg^{2+} < Li^{+} < Na^{+} < Ba^{2+}$. Barium perchlorate caused the most remarkable distortion in the water structure and $MgClO_4$ the least, and the effect of Li^{+} was smaller than that of Na^{+}. This order is not consistent with the order in the metal effect on the solvolysis rate of the typical S_N1 ($Na^{+} < Li^{+} < Ba^{2+} < Mg^{2+}$, cf. Figure 1). The coordination abilities of the metal ions in non-aqueous solvents, such as acetonitrile, have been found to be $Na^{+} < Li^{+} < Ba^{2+} < Mg^{2+}$.[27a,30] We have insisted that the metal effect on the S_N1 solvolysis rate of RX must be based on the direct interaction between X^{-} of the substrate and the added metal cation in organic solvent–H_2O mixtures. The degree in the chemical interaction of X^{-}–M^{+} or X^{-}–M^{2+} should depend on the intrinsic coordination ability of a metal ion as well as the trivialized solvation ability of water toward both anions (X^{-}) and cations (M^{+} and M^{2+}).

In Figure 13 are shown the Raman spectra of 50% (v/v) DMA–D_2O containing concentrated Et_4NCl. With increasing concentration of Et_4NCl, the intensity of the band at 2500 cm^{-1} increased at the expense of that at 2400 cm^{-1}, accompanied by almost no wavenumber shift. The intensity changes by the addition of the salt to the DMA–D_2O mixture were similar to those of D_2O with temperature increase reported by Scherer et al.[47] The change in the Raman intensity ratio (I_1/I_2) between ca. 2400 and ca. 2500 cm^{-1}, caused by the addition of Et_4NCl, is shown in Figure 14. Tetraethylammonium salts caused changes in the Raman intensity ratio (I_1/I_2) as $Cl^{-} < OTs^{-} < Br^{-}$. Tetrabutylammonium bromide caused much larger effect than Et_4NBr. The effect by $LiClO_4$ is also shown in Figure 14 as a reference. By the addition of all the tetraalkylammonium salts of higher concentrations, the water structure in the DMA–D_2O mixtures was found to be distorted at a great extent.

In principle, the decreases in the solvolysis rates of S_N1 substrates with the addition of tetraalkylammonium salts (R_4NX) are based on the decrease of water activity in DMA–H_2O. Therefore, the order shown in Figure 5 may indicate the true order of the water activity decrease in the DMA–H_2O

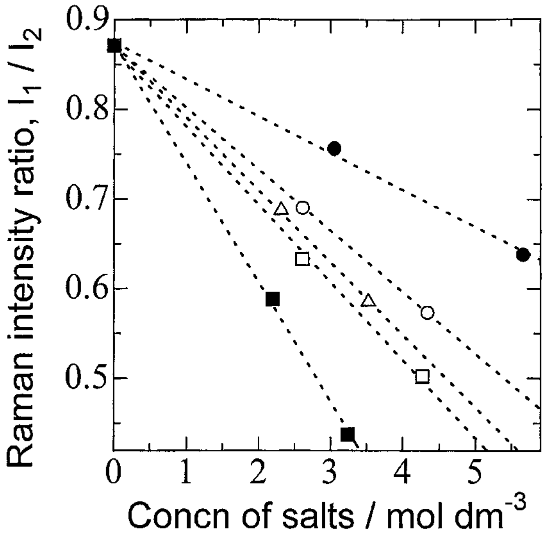


Figure 14. Relationship between the ratio of intensities in Raman OD stretching bands (I_1/I_2) and concentrations of R_4NX where I_1: ca. $2400\,cm^{-1}$, I_2: ca. $2500\,cm^{-1}$: (●) $LiClO_4$, (○) Et_4NCl, (□) Et_4NBr, (△) Et_4NOTs, (■) *n*-Bu_4NBr.

solutions containing concentrated R_4NX at 65 °C (Et_4NClO_4, Et_4NBr < Et_4NCl < Et_4NOTs < *n*-Bu_4NBr). The water activity in concentrated salt solution should be influenced by both the partial volume of a salt and the solvation of the anion. On the other hand, the degree of distortion of water structure evaluated by Raman intensity ratio (I_1/I_2) was different (Et_4NCl < Et_4NOTs < Et_4NOBr < *n*-Bu_4NBr) from the order in the solvolysis deceleration. The discrepancy between the orders based on the solvolysis deceleration $\Delta\log(k/s^{-1})$ and on Raman intensity ratio (I_1/I_2) might be caused by the fact that Cl^- can interact with the proton of H_2O to affect the OH stretching while the Br^- ion interacts weakly. Roscioli et al.[51] have reported the hydrogen-bonding interaction between anions and H_2O (X^-–H_2O: X = OH, F, Cl, and Br) in the gas phase. Takekiyo and Yoshimura[52] discussed the hydration structures of the tetraethylammonium cation in water.

One may accept that the properties of bulk water are based on the (huge) network of hydrogen bonding. As discussed above, the water structure (of bulk water) is distorted by the addition of organic solvents and concentrated salts and also by increasing temperature, which makes the bulk water turn to "dihydrogen ether" conditions. Note that all the salts concerned are not only alkali metal and alkaline earth metal salts but also tetraalkylammonium salts at higher concentrations. The distortion of bulk water structure may bring us unexpected high reactivity of solutes: we have reported a great enhancement in the oxidation ability of dilute HNO_3 as well as concentrated HNO_3 in nanoscale water-droplets of reverse micelle systems.[53] Hydrogen bond dynamics of both water in highly concentrated NaBr solution and in reverse micelle showed a similar behavior.[54]

Conclusion

We are confident that the proposed scheme for salt effects on solvolyses in the present work is never contradictory to Winstein's interpretation of "special" salt effect[8] but we have attempted to provide concrete evidence for the exchange reaction between two ion pairs without invoking the contact and solvent-separated ion pairs (CIP and SSIP). The obvious motive force for the ion-pair exchange should be based on the direct chemical interaction between the metal cations and the leaving-group anions of substrates under "dihydrogen ether" conditions, in which, solvation ability of H_2O should be weakened toward both anions and cations in the solution.

Experimental

Materials. *N*,*N*-Dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMA) as the solvents, purchased from Wako, were used as received. The substrates from TCI were used without further purification: 1-adamantyl chloride (>98%) and bromide (>97%), 2-adamantyl bromide (>97%), *tert*-butyl chloride (>98%), hexyl chloride (>95%), bromide (>98%), and *p*-toluenesulfonate (tosylate) (>98%), 2-bromobutane (>98%), 2-chlorohexane (>98%), cyclopentyl chloride (>98%) and bromide (>98%), cyclohexyl chloride (>98%) and bromide (>95%), benzyl chloride (>99%) and bromide (>98%), (1-chloroethyl)-benzene (>97%). Aldrich chemicals were used also as received: 4-methylbenzyl chloride (99%) and bromide (97%), 3-chloro-3-methylpentane (97%), *exo*-2-chloronorbornane (98%).

Salts of $NaClO_4$, Et_4NBr, Et_4NOTs, and Pr_4NBr from Aldrich as well as $LiClO_4$ and Et_4NCl from Wako, and *n*-Bu_4NCl form TCI were used. Tetraethylammonium perchlorate (Et_4NClO_4) was prepared by adding an equivalent amount of $HClO_4$ to Et_4NBr in water. The precipitates were filtered, washed with cold water and were recrystallized from water several times, followed by drying at 70 °C in vacuo. Tetrabutylammonium bromide was prepared as follows: tributylamine and butyl bromide in acetonitrile solvent were refluxed for 36 h, followed by evaporation of the solvent to dryness; the *n*-Bu_4NBr precipitates were recrystallized from ethyl acetate twice and dried at 70 °C in vacuo.

Kinetics and Raman Spectra. The solvolysis rates were determined by titration with $0.0025\,mol\,dm^{-3}$ standard aqueous sodium hydroxide using phenolphthalein as the indicator. The initial concentrations of the substrates were all kept at 0.010 $mol\,dm^{-3}$ in the reaction vessels. All the substrates were dissolved in acetonitrile (Aldrich, anhydrous 99.8%) at first. In principle, 0–90% consumption of a substrate was followed for evaluating the rate constant, except for some cases; in S_N2 substrates containing Et_4NX salts, only the linear parts in the ln[S] vs. *t* curve were utilized. Details for the other reagents and the procedure for the kinetic experiments have been described previously.[13–15] Raman spectra of H_2O and D_2O (99.9% atom D from Aldrich) mixed with DMF or DMA were recorded with a Horiba-Jobin Yvon LabRam Spectrograph HR-800 at room temperature (ca. 23 °C). Excitation for the Raman spectroscopy was provided by a 514.5 nm argon laser. The Raman intensity was standardized with the CD stretching band of 5% (v/v) CD_3OD–D_2O as an internal intensity standard; CD_3OD, 99.8 atom % D from Aldrich was used. For DMF–H_2O mixed solvents, signals of DMF were utilized as the Raman intensity standard.

We are grateful to Prof. Herbert Mayr, Ludwig-Maximilians University, Germany for his valuable comments to the effects of tetraalkylammonium salts on the solvolysis rates of S_N1 substrates. We are also deeply indebted to Professor Emeritus Tadashi Okuyama of Hyogo Prefectural University, Japan for

his encouraging us to examine the relationship between effects of $LiClO_4$ in solvolyses and stabilities of carbocations in gas phase.

Supporting Information

Solvolysis rate constants of typical S_N1 and S_N2 substrates in the presence of various salts in 50% (v/v) DMF–H_2O are given in Tables S1 and S2. Tables S3–S5 are some results in 50% (v/v) DMA–H_2O. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

References

1 A. A. Frost, R. G. Pearson, *Kinetics and Mechanism*, 2nd ed., John Wiley, New York, **1961**, p. 151.

2 e.g.: T. W. Bentley, P. R. Schleyer, *Medium Effects on the Rates and Mechanisms of Solvolytic Reactions*, in *Advances in Physical Organic Chemistry*, ed. by V. Gold, D. Bethell, Academic Press, London, **1977**, Vol. 14.

3 C. A. Bunton, S. K. Huang, *J. Am. Chem. Soc.* **1972**, *94*, 3536.

4 C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, K.-U. Yang, *J. Org. Chem.* **1971**, *36*, 887.

5 A. D. Allen, T. T. Tidwell, O. S. Tee, *J. Am. Chem. Soc.* **1993**, *115*, 10091.

6 G. F. Dvorko, E. A. Ponomareva, *Russ. J. Org. Chem.* **1998**, *34*, 487.

7 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, NY, **1953**; 2nd ed., **1969**.

8 S. Winstein, E. Clippinger, A. H. Fainberg, G. C. Robinson, *J. Am. Chem. Soc.* **1954**, *76*, 2597; A. H. Fainberg, S. Winstein, *J. Am. Chem. Soc.* **1956**, *78*, 2767; S. Winstein, P. E. Klinedinst, Jr., G. C. Robinson, *J. Am. Chem. Soc.* **1961**, *83*, 885; S. Winstein, P. E. Klinedinst, Jr., E. Clippinger, *J. Am. Chem. Soc.* **1961**, *83*, 4986.

9 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Weily-VCH, Weinheim, **2003**.

10 A. Loupy, B. Tchoubar, *Salt Effects in Organic and Organometallic Chemistry*, VCH, Weinheim, **1992**.

11 J. E. Gordon, *The Organic Chemistry of Electrolytes Solutions*, Wiley, New York, **1975**; *Ions and Ion Pairs in Organic Reactions*, ed. by M. Szwarc, Wiley-Interscience, New York, **1972**, Vol. 1 and **1974**, Vol. 2.

12 T. M. Bockman, J. K. Kochi, *J. Chem. Soc., Pekrin Trans. 2* **1994**, 1901.

13 L. C. Manege, T. Ueda, M. Hojo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 589.

14 L. C. Manege, T. Ueda, M. Hojo, M. Fujio, *J. Chem. Soc., Perkin Trans. 2* **1998**, 1961.

15 M. Hojo, T. Ueda, S. Inoue, Y. Kawahara, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1735.

16 M. Hojo, T. Ueda, E. Ueno, T. Hamasaki, D. Fujimura, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 751.

17 E. Grunwald, S. Winstein, *J. Am. Chem. Soc.* **1948**, *70*, 846.

18 F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry, A Comprehensive Text*, 4th ed., John Weily, New York, **1987**, Chap. 20.

19 C. Reichardt, D. Che, G. Heckenkemper, G. Schäfer, *Eur. J. Org. Chem.* **2001**, 2343.

20 H. S. Frank, W.-Y. Wen, *Discuss. Faraday Soc.* **1957**, *24*, 133.

21 A. Nose, M. Hojo, T. Ueda, *J. Phys. Chem. B* **2004**, *108*, 798.

22 M. Hojo, Y. Imai, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1963.

23 M. Hojo, T. Takiguchi, M. Hagiwara, H. Nagai, Y. Imai, *J. Phys. Chem.* **1989**, *93*, 955; M. Hojo, H. Hasegawa, Y. Miyauchi, H. Moriyama, H. Yoneda, S. Arisawa, *Electrochim. Acta* **1994**, *39*, 629; M. Hojo, H. Hasegawa, N. Hiura, *J. Phys. Chem.* **1996**, *100*, 891; M. Hojo, H. Hasegawa, Y. Morimoto, *Anal. Sci.* **1996**, *12*, 521; M. Hojo, T. Ueda, M. Nishimura, H. Hamada, M. Mastui, S. Umetani, *J. Phys. Chem. B* **1999**, *103*, 8965.

24 Z. Chen, M. Hojo, *J. Phys. Chem. B* **1997**, *101*, 10896; M. Hojo, T. Ueda, Z. Chen, M. Nishimura, *J. Electroanal. Chem.* **1999**, *468*, 110.

25 M. Hojo, H. Hasegawa, H. Tsurui, K. Kawamura, S. Minami, A. Mizobe, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1619.

26 M. Hojo, T. Ueda, M. Yamasaki, *J. Org. Chem.* **1999**, *64*, 4939.

27 a) M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, S. Tokita, M. Yanagita, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1569; b) M. Hojo, T. Ueda, A. Inoue, S. Tokita, *J. Mol. Liq.* **2009**, *148*, 109.

28 M. Hojo, H. Hasegawa, H. Yoneda, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 971.

29 M. Hojo, H. Hasegawa, H. Yoneda, *J. Chem. Soc., Perkin Trans. 2* **1994**, 1855.

30 M. Hojo, H. Hasegawa, A. Mizobe, Y. Ohkawa, Y. Miimi, *J. Phys. Chem.* **1995**, *99*, 16609.

31 U. Olsher, R. M. Izatt, J. S. Bradshaw, N. K. Dalley, *Chem. Rev.* **1991**, *91*, 137; *Lithium Chemistry*, ed. by A.-M. Sapse, P. v. R. Schleyer, John Wiley, New York, **1995**.

32 G. A. Olah, *J. Org. Chem.* **2001**, *66*, 5943.

33 H. F. Schaller, H. Mayr, *Angew. Chem., Int. Ed.* **2008**, *47*, 3958.

34 V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions*, Plenum, New York, **1978**.

35 E. S. Rudakov, I. V. Kozhevnikov, *Tetrahedron Lett.* **1971**, *12*, 1333.

36 B. G. Cox, H. Maskill, *J. Chem. Soc., Perkin Trans. 2* **1983**, 1901.

37 R. B. Heslop, P. L. Robinson, *Inorganic Chemistry, A: Guide to Advanced Study*, 3rd ed., Elsevier, Oxford, **1967**, p. 527.

38 S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, J. S. Gall, *Tetrahedron Lett.* **1960**, *1*, 24.

39 *CRC Handbook of Chemistry and Physics*, 70th ed., CRC Press, Boca Raton, Fl, **1989**, C-163.

40 D. N. Kevill, B.-C. Park, K.-H. Park, M. J. D'Souza, L. Yaakoubd, S. L. Mlynarski, J. B. Kyong, *Org. Biomol. Chem.* **2006**, *4*, 1580.

41 P. v. R. Schleyer, R. C. Bingham, *J. Am. Chem. Soc.* **1971**, *93*, 3189.

42 a) J.-L. M. Abboud, I. Alkorta, J. Z. Davalos, P. Müller, E. Quintanilla, J.-C. Rossier, *J. Org. Chem.* **2003**, *68*, 3786. b) J.-L. M. Abboud, I. Alkorta, J. Z. Davalos, P. Müller, E. Quintanilla, *Adv. Phys. Org. Chem.* **2002**, *37*, 57.

43 J. J. Gajewski, *J. Am. Chem. Soc.* **2001**, *123*, 10877.

44 P. Müller, J.-C. Rossier, J.-L. M. Abboud, *J. Phys. Org. Chem.* **2000**, *13*, 569.

45 K. Takeuchi, M. Takasuka, E. Shiba, T. Kinoshita, T. Okazaki, J.-L. M. Abboud, R. Notario, O. Castaño, *J. Am. Chem. Soc.* **2000**, *122*, 7351.

46 T. W. Bentley, G. E. Carter, *J. Am. Chem. Soc.* **1982**, *104*, 5741.

47 J. R. Scherer, M. K. Go, S. Kint, *J. Phys. Chem.* **1974**, *78*, 1304.

48 T. Tokushima, Y. Harada, O. Takahashi, Y. Senba, H. Ohashi, L. G. M. Pettersson, A. Nilsson, S. Shin, *Chem. Phys. Lett.* **2008**, *460*, 387.

49 M. Pastorczak, M. Kozanecki, J. Ulanski, *J. Phys. Chem. A* **2008**, *112*, 10705.

50 N. Biliškov, G. Baranović, *J. Mol. Liq.* **2009**, *144*, 155.

51 J. R. Roscioli, E. G. Diken, M. A. Johnson, S. Horvath, A. B. McCoy, *J. Phys. Chem. A* **2006**, *110*, 4943.

52 T. Takekiyo, Y. Yoshimura, *J. Phys. Chem. A* **2006**, *110*, 10829.

53 M. Hojo, T. Ueda, C. Daike, F. Takezaki, Y. Furuya, K. Miyamoto, A. Narutaki, R. Kato, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1215.

54 S. Park, D. E. Moilanen, M. D. Fayer, *J. Phys. Chem. B* **2008**, *112*, 5279.