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Concentrated Salt Effects on the Solvolysis Reaction Rates in Methanol–Water Solution

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The solvolysis rates of aliphatic halides and related compounds (RX) were determined in an 80 vol% MeOH–20 vol% H_2O solvent in the presence of very highly concentrated salts (0.25—5.0 $\mathrm{mol\,dm^{-3}}$) at 25—75 °C. For typical S_N1 substrates, such as 1-adamantyl bromide and *t*-butyl chloride, the pseudo-first-order reaction rates ($k/\mathrm{s^{-1}}$) increased exponentially with increasing concentration of $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, and $Ba(ClO_4)_2$. The cation effects increased as $Na^+ < Li^+ < Ba^{2+} \leq Mg^{2+}$. A nonmetallic salt, Et_4NBr, caused the $k/\mathrm{s^{-1}}$ value for 1-adamantly bromide to be slightly increased at lower concentrations ($< 1.0\ \mathrm{mol\,dm^{-3}}$), but to be greatly decreased at higher salt concentrations ($\geq 2.0\ \mathrm{mol\,dm^{-3}}$). The large positive effects of metal perchlorates were explained by a change in the solvent structure and the formation of "stable" carbocations through a "chemical" interaction between X^- (Cl^-, Br^-, or I^-) and M^+ (Li^+, Na^+) or M^{2+} (Mg^{2+}, Ba^{2+}) in the "modified" solvent. On the other hand, for S_N1–S_N2 intermediates, the solvolysis reaction rates were decreased by a decrease in the activity of the solvent containing a large amount of salts. The apparent rate constant ("$k/\mathrm{s^{-1}}$") for isopropyl bromide at 75 °C remained an almost constant value in the presence of 0—5.0 $\mathrm{mol\,dm^{-3}}$ $LiClO_4$. The rate constant for ethyl bromide was decreased substantially by the addition of the alkali metal and alkaline-earth metal perchlorates. A good linearity was observed between $\log(k_1/k_0)$ and the *m* values for RX by Grunwald and Winstein, where k_1 and k_0 are the solvolysis rates in the presence of 1.0 $\mathrm{mol\,dm^{-3}}$ $LiClO_4$ and in the absence of the salt, respectively. Upon the solvolysis of neophyl chloride (1-chloro-2-methyl-2-phenylpropane), the change in the reaction scheme (e.g., methyl shift) was suspected during the increase in the $LiClO_4$ or $Ba(ClO_4)_2$ concentration.

The "indifferent" salts affect the chemical equilibria or reaction kinetics in solution. The effects of a lower salt concentration ($<$ ca. 0.1 $\mathrm{mol\,dm^{-3}}$) in aqueous solution may be explained by the Debye–Hückel theory. New models[1,2] have been proposed to calculated the activities of ions in concentrated solutions. The salt effects in nonaqueous solution are so complicated that no theory has been successful in describing them quantitatively and comprehensively. The alternation between the contact ion pair (CIP) and the solvent separated ion pair (SSIP)[3] may seem to be a useful idea for explaining some salt effects.

We have demonstrated[4] the presence of higher ion aggregates, such as triple ions (M_2X^+, MX_2^-) and quadrupoles (M_2X_2), from uni-univalent salts (MX) in relatively high permittivity media ($20 < \varepsilon_r < 65$) of low solvating abilities. The motive forces for ion aggregation must be based on the hydrogen bonding, coordination or covalent bonding as well as a reduced Coulombic attraction between ions in such higher permittivities. For the first time,[5] in lower permittivity media ($\varepsilon_r < 10$) was observed the linearity (the slope of -1) between the triple ion formation constants and the salt concentrations at the minima appeared in conductometric curves (Λ–$C^{1/2}$), except for some systems where remarkable quadrupole formation occurred. Even higher permittivity solvents, acetonitrile and acetone, lithium 1-phenyl-3-methyl-4-benzoyl-5-pyrazolonate gave the minimum at $C =$ ca. 2×10^{-3} $\mathrm{mol\,dm^{-3}}$ in the conductometric curves.[6] These experimental results can be good evidence that strong "chemical" interactions are operating between Li^+ and the anion.

Previously, we explained quantitatively the specific salt effects of alkali metal and alkaline earth metal ions (M^+ and M^{2+}) on the indicator acidity with Methyl Yellow[7] and on the proton transfer from tropolone and nitrophenols[8] to amine bases in acetonitrile in terms of the formation of specific species, $(M^+)_2X^-$, $M^{2+}X^-$, or $H^+(X^-)_2$, where X^- stands for the tropolonate, nitrophenolate, or other anions. In acetonitrile solutions, by means of UV-visible absorption spectroscopy and ^{1}H NMR, we have observed the formation of stable carbocations from trityl halides and methoxy-substituted trityl chlorides by the addition of alkali metal or alkaline-earth metal perchlorates.[9] The formation of the trityl cations (Ph_3C^+) from trityl halides (Ph_3CX) has been attributed to the strong interaction between X^- and Li^+, Na^+ or M^{2+} ($M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, or Ba^{2+}). The crystals of $(4\text{-MeO})Ph_3CClO_4$ were isolated by the addition of $NaClO_4$ or $Ba(ClO_4)_2$ to 4-methyoxytrityl chloride in MeCN and following extraction with chloroform.[9] Thus, alkali metal or alkaline-earth metal ions in solution seem to have unexpectedly strong interactions with halide anions to cleave even (weak) covalent bonds or partially ionized covalent bonds (C^+–X^-).

In the present paper, we consider the concentrated salt effects on the solvolysis rates of several aliphatic halides and related compounds in a protic solvent, 80 vol% MeOH–20 vol% H_2O mixture. Positive salt effects on the solvolysis rate may be expected if "stable" carbocations can form in the "protic" media. It has been shown that the S_N1 solvolysis rates parallel the carbocation stabilities.[10] By the way, Marcus has pointed out[11] that Gutmann's donor numbers of H_2O and MeOH in bulk (40.3 and 31.3, respectively) differ greatly from those of "isolated solvent molecules" in an inert diluent (18.0 and 19, respectively). Unusual medium effects have been observed in 5—20 mol dm^{-3} aqueous quaternary ammonium salt solutions, media with excellent solvent power for organic nonelectrolytes.[12] Oelkers and Helgeson have suggested the formation of ion aggregates (multiple ion association) from very concentrated uni-univalent salts in supercritical aqueous solution with $\varepsilon_r \leq$ ca. 15.[13]

The salt effects on solvolysis reactions[14] and on many organic and organometallic reactions[15] have been extensively examined. Winstein et al.[16] discovered the "special salt effects" on the acetolysis of several substrates. Recently, Allen et al.[17] reported a large salt effect and ion pairing in trifluoroacetolysis. Salt effects on reaction rates are often examined at rather lower ionic strengths, although in moderately concentrated electrolyte aqueous solutions,[18] the effects of electrolyte on reaction rates and on the activity coefficient of the reaction substrate have been independently determined. Richard and Yeary[19] studied the importance of carbocation intermediates in bimolecular nucleophilic substitution reactions in aqueous solution. Bunton et al. have reported on specific salt effects upon the rates of S_N1 solvolysis.[20] In the present study we examined the salt effects at higher concentrations, even close to the solubility limits of salts, where the structures due to the hydrogen bonding of the solvents are expected to be destroyed and no theoretical evaluation for the activities of ions may be valid.

Experimental

Reagents. Commercially obtained 1-adamantyl bromide ($C_{10}H_{15}Br$, TCI EP garde), *t*-butyl chloride (Aldrich 99%), adamantyl iodide (Aldrich 98%), isopropyl bromide (TCI GR garde), and ethyl bromide (Wako Pure Chem. 98%) were used as received. Benzyl chloride (TCI GR > 99%) and bromide (TCI EP), 1-phenylethyl chloride, TCI EP > 97%), and 1-chloro-2-methyl-2-phenylpropane (neophyl chloride, TCI GR) were used without further purification. Lithium perchlorate (anhydrous, Wako GR) and sodium, magnesium, and barium perchlorates from Aldrich (all A.C.S. reagents) were used as received. Tetraethylammonium bromide was prepared[7] and recrystallized twice from methanol. Methanol (Wako GR) and benzene (Wako GR) were used without further purification. Acetonitrile (Wako GR) was distilled from CaH_2. Deionized and distilled water was used after being decarbonated.

Procedure and Apparatus. The solvolysis rates were determined by titration with 0.0025 mol dm^{-3} standard aqueous sodium hydroxide using phenolphthalein as the indicator. A sample was taken by removing 5 ml of the solution from the reaction flask (50 ml, containing a 0.01 mol dm^{-3} substrate) and adding it to an ice-cooled system composed of 25 ml of benzene and 50 ml of water. Titration was done after stirring the sample with a magnetic stirrer for 5 min. The 50 ml of a substrate + salt–80 vol% MeOH–20 vol% H_2O solution contained, actually, 1.0 mol of acetonitrile for dissolving the substrate completely, except for adamantyl iodide (in this case 2.0 ml). The reaction temperatures were controlled with a Yamato constant-temperature water bath (Model BK-15) or a Taitec (Model DX-10).

Results and Discussion

Concentrated Salt Effects on Typical S_N1 Reaction. It has been regarded that the solvolysis reaction of 1-adamantyl bromide ($C_{10}H_{15}Br$) occurs through a typical (or ideal) S_N1 scheme[21] ($RX \longrightarrow R^+ + X^-$ (slow), $R^+ + HS \longrightarrow RS + H^+$ (fast)). For the bridgehead substrate, a backside nucleophilic solvent attack and an elimination are both impossible. In 80 vol% MeOH–H_2O solutions, the "pseudo"-first-order reaction rates of the solvolysis of 1-adamantyl bromide increased with increasing concentration of $LiClO_4$ at various temperatures (25—60 °C), as shown in Fig. 1. The log (k/s^{-1}) value was almost linear to the concentration of $LiClO_4$ (0.25—4.0 mol dm^{-3}): The rate constants (k/s^{-1}) increased exponentially with the $LiClO_4$ concentration. For instance, in the presence of 1.0 mol dm^{-3} $LiClO_4$, the k value increased to 2.82×10^{-5} s^{-1} from $k_0 = 3.57 \times 10^{-6}$ s^{-1} without $LiClO_4$ at 35 °C. Similar large salt effects of $LiClO_4$ have been reported for the methanolysis of a chloronorbonane.[20] Figure 2 shows Arrhenius plots for the solvolysis reaction of 1-adamantyl bromide in 80 vol% MeOH–H_2O solutions with and without $LiClO_4$. From the slopes, the activation energies (E_a) were evaluated to be ca. 110 kJ mol^{-1} for all cases

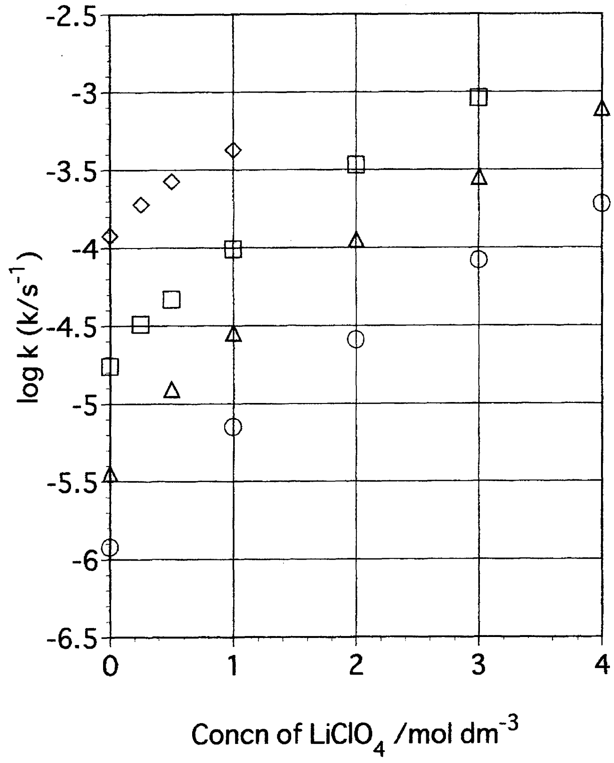


Fig. 1. Changes in rate constants of the solvolysis reaction of 1-adamantyl bromide ($C_{10}H_{15}Br$) with the addition of $LiClO_4$ in 80 vol% MeOH–H_2O solution at various temperatures: (○) 25; (△) 35; (□) 45; (◇) 60 °C.

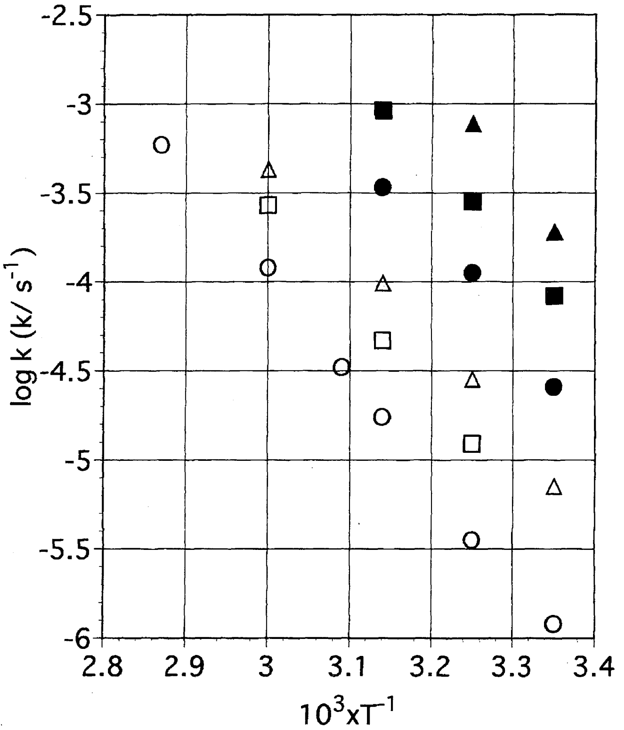


Fig. 2. The Arrhenius plots for the solvolysis reaction of 1-adamantyl bromide in 80 vol% $MeOH–H_2O$ with $LiClO_4$ of various concentrations: (○) 0; (□) 0.5; (△) 1.0; (●) 2.0; (■) 3.0; (▲) 4.0 mol dm^{-3} $LiClO_4$.

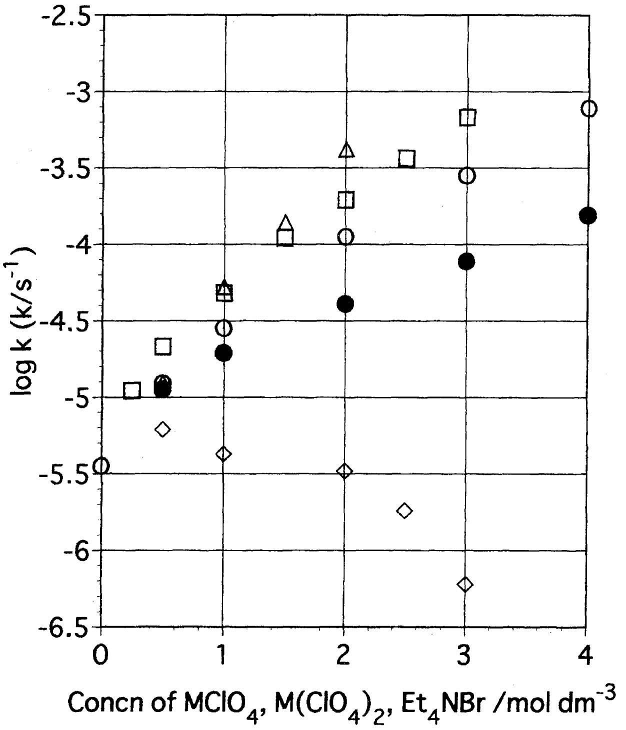


Fig. 3. Changes in the solvolysis rates of 1-adamantyl bromide with the addition of various salts in 80 vol% $MeOH–H_2O$ at 35 °C: (○) $LiClO_4$; (●) $NaClO_4$; (△) $Mg(ClO_4)_2$; (□) $Ba(ClO_4)_2$; (◇) Et_4NBr.

($[LiClO_4]$ = 0—4.0 mol dm^{-3}), suggesting no change in the reaction scheme (S_N1).

Figure 3 shows the effects of various alkali metal (M^+) and alkaline earth metal (M^{2+}) perchlorates on the solvolysis of 1-adamantyl bromide in 80 vol% $MeOH–H_2O$ at 35 °C. Sodium perchlorate at low concentrations gave effects similar to those of $LiClO_4$; however, at higher concentrations, the increase in the k values in the presence of $NaClO_4$ became smaller than that in the presence of $LiClO_4$. The effects of $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ were larger than those of $LiClO_4$. The cation effects increased as $Na^+ < Li^+ < Ba^{2+} \leq Mg^{2+}$. On the other hand, a nonmetallic salt, Et_4NBr, caused results much different from those of the metal salts. Although the rate constant was increased slightly by the presence of lower concentrations of Et_4NBr (up to 1.0 mol dm^{-3}), it was greatly decreased by the presence of higher concentrations of the salt ($\geq$2.0 mol dm^{-3}): The k values were 3.57×10^{-6}, 4.23×10^{-6}, 3.33×10^{-6}, 1.81×10^{-6}, and 5.97×10^{-7} s^{-1} at 0, 1.0, 2.0, 2.5, and 3.0 mol dm^{-3} Et_4NBr. The remarkable decrease in the k value should be caused by the common ion (Br^-) effects or by a decrease in the activities of the solvent molecules along with increased concentration of the salt. In 90 vol% acetone–10 vol% H_2O, the k value of t-butyl chloride decreased by the addition of > 0.5 mol dm^{-3} Et_4NClO_4, which suggested a decrease in the activity of H_2O in a solvent mixture with an increased concentration of salts. The small increase in the k values at lower concentrations of Et_4NBr in the present case could not be explained well, apart from the increase in the ionic strength. Bentley and Carter[22] have observed a slight increase (10.9% in the k value) in the hydrolysis rate of 1-adamantyl bromide by added Et_4NBr (0.1 mol dm^{-3}) in 50% acetone–H_2O at 50 °C.

In spite of the great decrease in activities of $MeOH–H_2O$ upon the addition of concentrated metal salts, the "pseudo"-first-order reaction rate (k/s^{-1}) of the solvolysis of 1-adamantyl bromide in 80 vol% $MeOH–H_2O$ increased exponentially. We do not think that these phenomena can be explained merely by the Debye–Hückel theory and its extended theories, which take only electrostatic effects into account. At higher ionic strength (μ), the reaction rate (k) can be expressed by

$$\log k = \log k_0 + b\mu, \tag{1}$$

were k_0 is the rate constant at infinite dilution (or μ=0); b is an empirical coefficient.[23] Our observation concerning the k values can follow Eq. 1, just apparently: The b values were estimated to be 0.56, 0.31, 0.35, 0.24, and ca. −0.4 for $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, and Et_4NBr at 25 °C. We would like to propose the solvolysis reaction mechanism in concentrated solutions ($\geq$ca. 1.0 mol dm^{-3} salts) as follows: A partially ionized C–Br bond (i.e., $C^+–Br^-$) in $MeOH–H_2O$ solution could be cleaved by an interaction between Br^- and M^+ or M^{2+} to give a "stable" adamantyl cation. The adamantyl cation can react with MeOH or H_2O immediately. However, the methanol and water mixture is not an aprotic solvent, but a protic solvent, in which the Br^- ion is not likely to interact strongly with alkali metal or alkaline-earth metal ions, except for the Coulombic attraction. We think that in a highly concentrated salt solution (>ca. 5 mol dm^{-3}), ions are present too much to be solvated fully by H_2O and MeOH molecules. Under such conditions, the structures by hydrogen bonding of the solvent (mixture) are almost destroyed; therefore, no "bulk" waters (or methanols) remain in solution; isolated molecules of H_2O or MeOH are very different from bulk water (H–O–H) or bulk methanol (Me–O–H); we think that they could behave just as ethers (R–O–R). The above idea is visualized in Scheme 1.

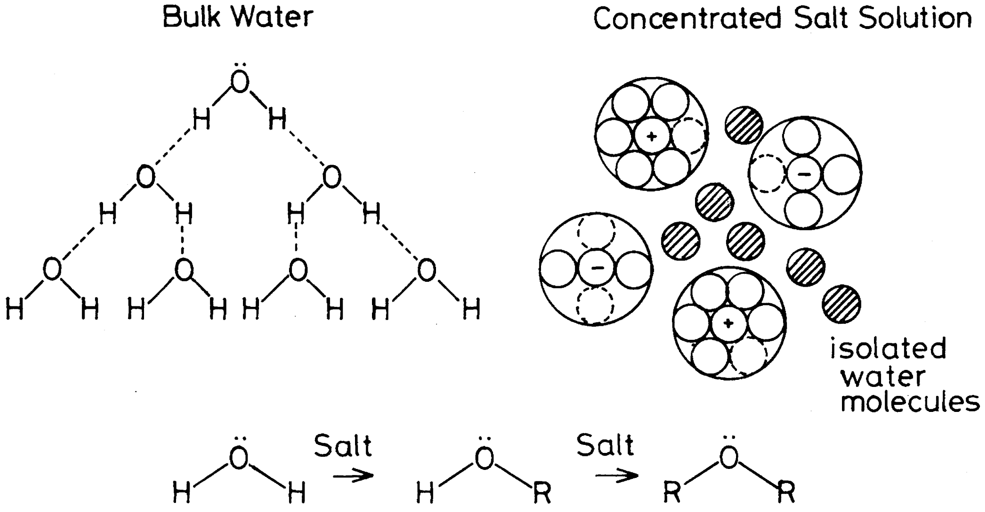
We note that Gutmann's donor numbers of "isolated" water and methanol have been reported to be 18.0 and 19, respectively, which are very close to 19.2 of diethyl ether.[24)] Large values have been proposed for "bulk" water, e.g., ca. 33 by ^{23}Na NMR (0.5 mol dm^{-3} NaCl in H_2O)[25)] or 40.3 by UV-visible spectral data[11)] of VO(acac)$_2$. In the (partly) isolated molecules of the solvent (the ether-like solvent), a "stable" carbocation can be formed by the interaction between Br^- and M^+ or M^{2+}. Even a triple cation ($(M^+)_2Br^-$) would be formed in addition to an ion pair (M^+Br^-) with extremely higher salt concentrations. Bateman et al.[26)] reported that in the hydrolysis of *t*-butyl bromide in a 90% acetone–water solvent at 50 °C, the first-order rate constant was found to increase ca. 40% by the addition of 0.1 mol dm^{-3} LiCl or LiBr; the rate-determining step was probably $(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-$. Rudakov and Kozhevniko have described that C–X bond heterolysis (mechanism S_N1) due to the reaction $RX + M^+ \longrightarrow R^+ + MX$ is accelerated by metal ions, M^+ (Lewis acids).[27)]

The effects of $MClO_4$ and $M(ClO_4)_2$ on the solvolysis rate of *t*-butyl chloride were also examined in 80 vol% MeOH–H_2O at 25 °C. In the presence of 0.5—4.0 mol dm^{-3} $LiClO_4$, the k value with *t*-butyl chloride increased almost exponentially, although the slope of $\log(k/k_0)$ vs. ΔC(salt) was smaller than that with 1-adamantyl bromide at 25 °C (cf. Table 1). Although Raber et al.[21)] proposed a new standard (1-adamantly bromide) for the "ideal" S_N1 reaction, *t*-butyl chloride[28,29)] has been the reference compound for the typical S_N1 reaction. The cation effects increased as $Na^+ < Li^+ < Ba^{2+} \le Mg^{2+}$, once more. However, for $NaClO_4$, plots of $\log(k/s^{-1})$ vs. C(salt) make a convex curve: The k values were linear to the concentration of $NaClO_4$ (over 0—5.0 mol dm^{-3}).

The salt effects on the solvolysis of 1-adamantyl iodide ($C_{10}H_{15}I$) at 35 °C were very similar to those on 1-adamantyl bromide at 35 °C, except that the k_0 value (1.27×10^{-5} s^{-1}) of the iodide was much larger than that of the bromide, and that the slopes of $\log(k/k_0)$ vs. ΔC(salt) of the iodide were smaller than those of the bromide for all of the salts. Even in acetonitrile, a polarographic analysis has indicated that the iodide ion interacte with a lithium ion and not with two lithium ions.[4a)] In the 80 vol% MeOH–H_2O solution, the iodide ion would be pulled out from the adamantyl body through ion-pair formation between I^- and M^+ or M^{2+}. We point out Bunton et al.[20)] concluded that, upon the rates of S_N1 solvolysis in MeOH, MeOH–H_2O, etc., anion effects were important but cation effects were small for Li^+, Na^+, and Et_4N^+; the anion order was $ClO_4^- > OTs^- \approx NO_3^- \approx Br^- > Cl^- \approx$ no salt. We thus now suspect that the cation effects had been reduced by the interaction between M^+ (the metal ions) and X^- (except for ClO_4^-) in a modified medium.

S_N1–S_N2 Intermediates. In the previous section, exponential increases in the k values of the solvolyses with the addition of concentrated salts for typical S_N1 substrates were reported. It is well-known[30)] that the S_N1 reaction rates for aliphatic compounds increase as $CH_3X < CH_3CH_2X < (CH_3)_2CHX < (CH_3)_3CX$, while the S_N2 reaction rates decrease as $CH_3X > CH_3CH_2X > (CH_3)_2CHX > (CH_3)_3CX$. It is expected that S_N2 reactions are decelerated by the presence of concentrated salts because of the decrease in solvent (HS) activity: $RX + HS \longrightarrow RS + HX$. In the present section, the solvolysis reaction rates of isopropyl and ethyl bromides, benzyl halides, and other "S_N1–S_N2 intermediate" compounds were measured in 80 vol% MeOH–H_2O.

In Fig. 4 are shown the solvolysis reaction rates of isopropyl bromide in the presence of higher concentra-



Scheme 1. Alteration of bulk water to isolated water molecules.

Table 1. The (Apparent) First-Order Reaction Rates for Solvolysis of RX in 80 vol% MeOH–H_2O in the Absence and the Presence of $LiClO_4$

RX	Temp/C°	k_0[a]/s^{-1}	k_1[a]/s^{-1}	k_2[a]/s^{-1}	log (k_1/k_0)	log (k_2/k_1)	*m*-Value[b]
1-Adamantyl bromide	25	1.20×10^{-6}	7.13×10^{-6}	2.54×10^{-5}	0.77	0.56	1.20 (25 °C)[c]
1-Adamantyl iodide	35	1.27×10^{-5}	5.09×10^{-5}	1.31×10^{-4}	0.60	0.41	
t-Butyl chloride	25	2.55×10^{-5}	9.12×10^{-5}	2.02×10^{-4}	0.55	0.35	1.00 (25 °C)[c]
1-Phenylethyl chloride	25	4.43×10^{-5}	1.46×10^{-4}	3.43×10^{-4}	0.52	0.37	0.97 (25 °C)[d]
Neophyl chloride	75	6.14×10^{-7}	9.03×10^{-7}	9.15×10^{-7}	0.17	0	0.761 (75 °C)[e]
Benzyl chloride	75	6.17×10^{-5}	6.88×10^{-5}	7.46×10^{-5}	0.05	0.03	0.425 (50 °C)[f]
Isopropyl bromide	75	3.29×10^{-5}	3.44×10^{-5}	3.54×10^{-5}	0.02	0.01	0.52 (50 °C)[d]
Ethyl bromide	75	1.83×10^{-5}	1.13×10^{-5}	8.43×10^{-6}	−0.21	−0.12	0.34 (55 °C)[c]

a) The k_0, k_1, and k_2 values are the solvolysis rates at 0, 1.0, and 2.0 mol dm^{-3} $LiClO_4$, respectively b) The *m* value is a parameter characteristic of RX by Grunwald and Winstein, cf. Ref. 28 ($\log(k/k_0)=mY$ in EtOH–H_2O, unless otherwise noted). c) cf., Ref. 21. d) cf., Ref. 31. e) In 30—80 vol% MeOH–H_2O, cf., Ref. 32. f) cf. Ref. 28 b).

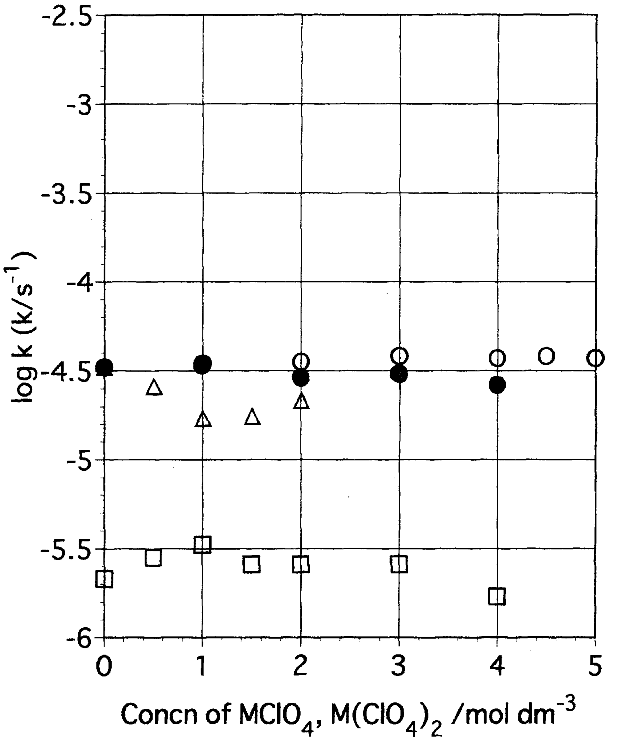


Fig. 4. Changes in the solvolysis rates of isopropyl bromide ($(CH_3)_2CHBr$) with the addition of various salts in 80 vol% MeOH–H_2O at 50 °C and 75 °C: (○) $LiClO_4$; (●) $NaClO_4$; (△) $Mg(ClO_4)_2$ at 75 °C; (□) $LiClO_4$ at 50 °C.

tions of $LiClO_4$, $NaClO_4$, and $Mg(ClO_4)_2$ at 75 °C. The "apparent" first-order reaction rate ("*k*/s^{-1}") remained almost constant over 0—0.5 mol dm^{-3} $LiClO_4$: The *k* values were 3.29×10^{-5}, 3.44×10^{-5}, 3.54×10^{-5}, 3.84×10^{-5}, 3.75×10^{-5}, and 3.69×10^{-5} s^{-1} at 0, 1.0, 2.0, 3.0, 4.0, and 5.0 mol dm^{-3} $LiClO_4$, respectively. The apparent effects of $NaClO_4$ (1.0—4.0 mol dm^{-3}) on the solvolysis reaction rate were also very small. Magnesium perchlorate (0.5—2.0 mol dm^{-3}) caused slight decreases in the *k* values at 75 °C. At 50 °C, the *k* value increased slightly upon the addition of 0.5—1.0 mol dm^{-3} $LiClO_4$, but became slightly smaller than k_0 upon the addition of 4.0 mol dm^{-3} $LiClO_4$. The concentrated salt effects of all the salts on the apparent first-order reaction rate for isopropyl bromide in 80 vol% MeOH–H_2O were quite small.

Figure 5 shows the change in the concentration of the substrate (isopropyl bromide) with time in the presence of various concentrations of $LiClO_4$. In the absence of $LiClO_4$, the value of $\ln(V_\infty - V_t)$ (corrected by the blank, V_b) vs. time was not linear, but concave, except for the early stage of solvolysis. As mentioned above, isopropyl bromide is solvolyzed by both S_N1 and S_N2 schemes. However, with increasing concentration of $LiClO_4$, the linearity between $\ln(V_\infty - V_t)$ and time was expanded, although the slope, ln [RX]/*t*, of the initial stage was unchanged, i.e., "*k*/s^{-1}" was unchanged. The above phenomena may indicate that the increase in the concentration of the carbocation, $[(CH_3)_2CH^+]$, and the de-

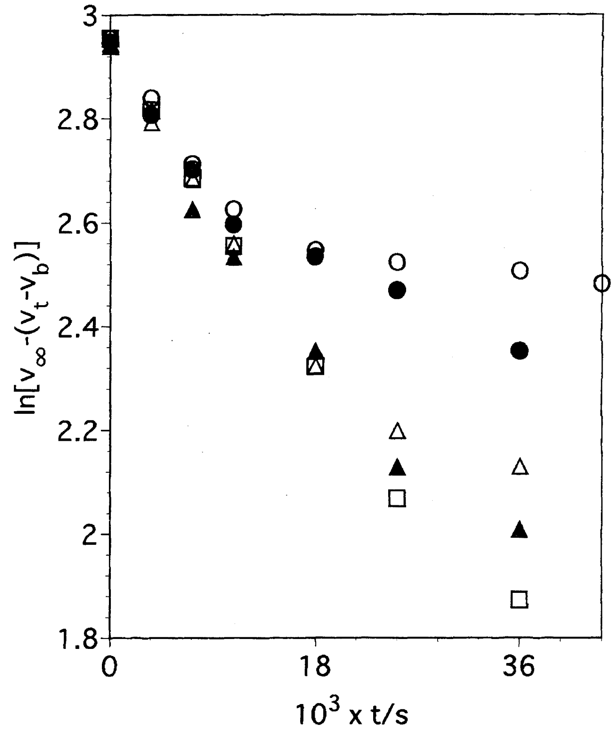


Fig. 5. The concentration change of RX (isopropyl bromide) during solvolysis in the presence of various concentrations of $LiClO_4$: (○) 0; (●) 1.0; (△) 2.0; (▲) 3.0; (□) 5.0 mol dm^{-3} $LiClO_4$.

crease in the activity of the solvent, a_{solvent} (or [solvent]), occurred at once in the presence of the concentrated salt.

However, the formation of the ethyl cation, $CH_3CH_2^+$, was less promoted in 80 vol% MeOH–H_2O by the addition of concentrated salts. The "apparent" first-order rate constant of the bromide was decreased by the presence of $LiClO_4$: at 75 °C, "k"=1.83×10^{-5}, 1.13×10^{-5}, 8.43×10^{-6}, 8.62×10^{-6}, 7.94×10^{-6}, and 6.54×10^{-6} s^{-1} at 0, 1.0, 2.0, 3.0, 4.0 and 5.0 mol dm^{-3} $LiClO_4$, respectively (cf. Fig. 6). Sodium perchlorate (1.0—4.0 mol dm^{-3}) caused almost similar decrease in the k values. The k values were greatly decreased by the presence of $Mg(ClO_4)_2$. The contribution in "k/s^{-1}" upon increasing [$CH_3CH_2^+$] was smaller than that of the decrease of the [solvent] with the concentrated salts. The rate constant of benzyl chloride at 75 °C showed a very gradual and small increase with increasing concentration of $LiClO_4$, while the k values of benzyl bromide at 35 and 50 °C showed small increases at 1.0—3.0 mol dm^{-3} and gradual decreases at $\geq$4.0 mol dm^{-3} $LiClO_4$. On the other hand, the salt effects of $LiClO_4$ on the k value of 1-phenylethyl chloride was close to those on *t*-butyl chloride.

Figure 7 shows a linear relationship between $\log(k_1/k_0)$ and the m value for RX, where k_1 and k_0 are the solvolysis rates in the presence of 1.0 mol dm^{-3} $LiClO_4$ and in the absence of the salt, respectively and the m value (by Grunwald and Winstein)[28] informs us about the extent of the S_N1 reaction. In the presence of 1.0 mol dm^{-3} $LiClO_4$, the activity of the solvent (80 vol% MeOH–H_2O) was greatly decreased; therefore, S_N2 reactions were decelerated, as clearly shown in the k values of CH_3CH_2Br. In spite of the decrease in the activity of solvent, the k values of the substrates (for which the S_N1 reaction is predominant) increased greatly. From Fig. 7, it can be read that for a substrate with m=0.5, the $\log(k_1/k_0)$ value is almost zero: no increase or decrease in the apparent solvolysis rate with the addition of 1.0 mol dm^{-3} $LiClO_4$. The $\log(k_2/k_1)$ (k_2: the rate at 2.0 mol dm^{-3} $LiClO_4$) values were smaller than the $\log(k_1/k_0)$ values by the factor of ca. 0.2 for substrates with larger m values (cf. Table 1). The $\log(k_2/k_1)$ or $\log(k_1/k_0)$ values for $LiClO_4$ represent the b values in Eq. 1. These values of *t*-butyl chloride (0.55 or 0.35) and 1-phenylethyl chloride (0.52 or 0.37) are very close to each other. A similar resemblance was observed between benzyl chloride (0.05 or 0.03) and isopropyl bromide (0.02 or 0.01). We can note that one phenyl group plays just as two methyl groups on the central carbon atom.

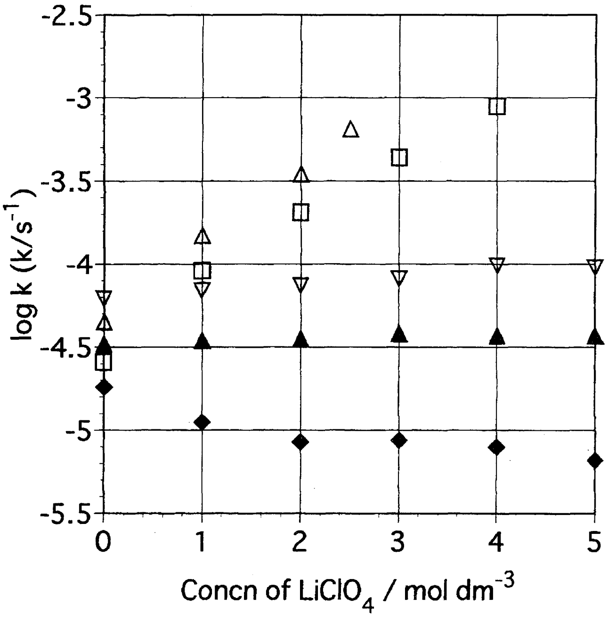


Fig. 6. Variations in the solvolysis rates of several substrates with increasing concentration of $LiClO_4$: (△) 1-phenylethyl chloride ($PhCHClCH_3$); (□) *t*-butyl chloride ($(CH_3)_3CCl$); (▽) benzyl chloride ($PhCH_2Cl$); (▲) isopropyl bromide ($(CH_3)_2CHBr$); (◆) ethyl bromide (CH_3CH_2Br).

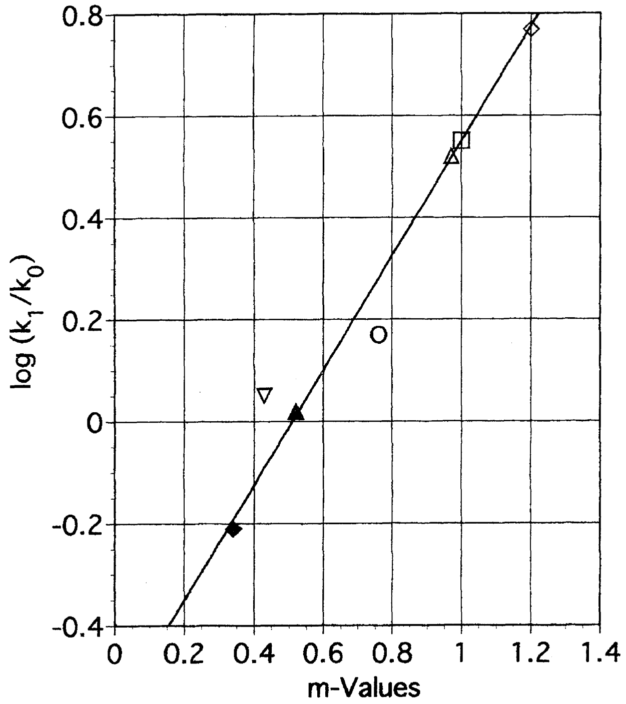


Fig. 7. The relation between $\log(k_1/k_0)$ and the m values of RX (cf. text for k_1 and k_0): (◇) $C_{10}H_{15}Br$; (□) $(CH_3)_3CCl$; (△) $PhCHClCH_3$; (○) $PhC(CH_3)_2CH_2Cl$; (▽) $PhCH_2Cl$; (▲) $(CH_3)_2CHBr$; (◆) CH_3CH_2Br.

Figure 8 shows a unique behavior in the effects of $LiClO_4$ on $\log(k/s^{-1})$ of neophyl chloride in 80 vol% MeOH–H_2O at 75 °C. The m value of neophyl chloride in 30—80% MeOH–H_2O at 75 °C has been reported to be 0.761.[32] Large positive salt effects can be expected from the larger m value (>0.5). However, $\log(k/s^{-1})$ did not increase very much at $\leq$2.0 mol dm^{-3} $LiClO_4$, and then increased suddenly after 2.5 mol dm^{-3} $LiClO_4$. Barium perchlorate of >1.0 mol dm^{-3} caused a sudden increase in the $\log(k/s^{-1})$ value. The unique salt effects can be explained as follows: Neophyl chloride may be solvolyzed through the neophyl cation, $PhC(CH_3)_2CH_2^+$, which is not so stable, resulting in an S_N1–S_N2 intermediate reaction. However, under concentrated salt conditions, more stable carbocations, such as $Ph(CH_3)C^+CH_2CH_3$, could be formed by a CH_3 shift; therefore, the S_N1 reaction becomes the predominant scheme.

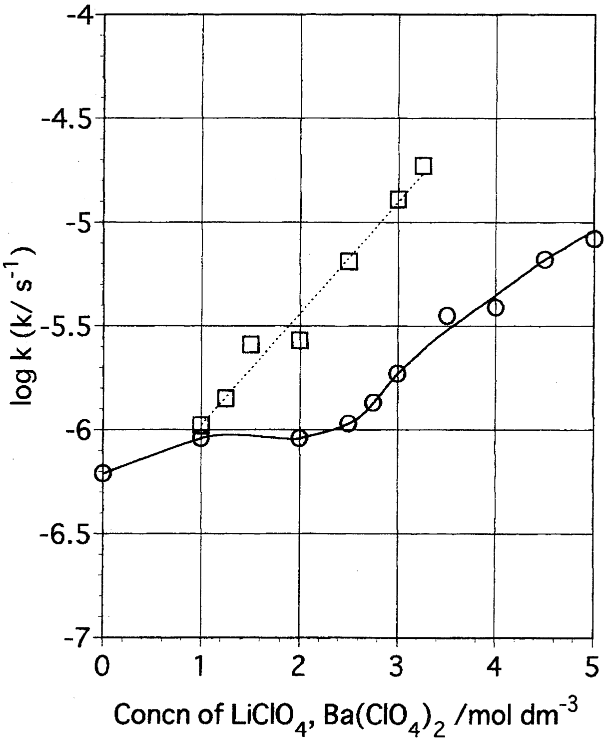


Fig. 8. Changes of the solvolysis rates of neophyl chloride ($PhC(CH_3)_2CH_2Cl$) with the addition of $LiClO_4$ (○) and $Ba(ClO_4)_2$ (□) in 80 vol% MeOH–H_2O at 75 °C.

Such changes in the reaction mechanisms could be possible because the properties of the protic solvent (MeOH–H_2O) should be converted to be "aprotic" characteristic by the addition of an extremely large amount of salts. Predominant productions of tertiary alcohols over primary alcohols have been reported[33] from a unimolecular hydrolysis of alkyl halides of the type R_2CHCH_2X (as the result of hydrogen migration during the reactions) in the presence of high salt concentrations, especially $LiClO_4$. Fainberg and Winstein[32] have suggested an anchimerically assisted ionization involving aryl participation for neophyl derivatives. The differentiation of the products must be done for confirming the proposed mechanism.

Similar or more distinct salt effects on the solvolysis rates of the substrates will be expected in other solvent systems, such as acetone–H_2O mixtures; extended examinations are being performed.

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