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Concentrated salt effects on the rates of solvolyses involving carbocations as reaction intermediates in acetone–water mixed solvents

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Extensive studies have been carried out on the concentrated salt effects on the solvolysis reaction rates of aliphatic halides and related compounds (RX) in acetone–water mixed solvents. In 90 vol% acetone–10 vol% water solution, the pseudo-first-order rate constant (k/s^{-1}) of a typical S_N1 substrate, *tert*-butyl chloride, at 50 °C was increased exponentially by the addition of $M^+ClO_4^-$ (M^+ = Li^+, Na^+: up to 4.0 mol dm^{-3}) and $M^{2+}(ClO_4^-)_2$ (M^{2+} = Mg^{2+}, Ba^{2+}: up to 2.0 mol dm^{-3}); the extent of the cation effects increased as $Na^+ \leqslant Li^+ < Mg^{2+} \leqslant Ba^{2+}$. However, the addition of Et_4NClO_4 (up to 1.0 mol dm^{-3}) decreased the solvolysis rate substantially. In 50 vol% acetone–water solution, the effects of the metal perchlorates on the solvolysis rates of 1-adamantyl chloride at 50 °C increased as $Na^+ < Li^+ < Ba^{2+} < Mg^{2+}$. Addition of >1.0 mol dm^{-3} Et_4NBr decreased the solvolysis rate markedly, whereas it was increased slightly by lower Et_4NBr concentrations. The positive effects of metal ions for typical S_N1 substrates were explained by the change of solvent structure and by a "chemical" interaction between the anions from the substrates ($R^+–X^-$) and M^+ or M^{2+} in the presence of very concentrated salts; the negative effects of nonmetallic salts should have been brought about by the decrease in activity of H_2O. The solvolysis rate of 2-adamantyl tosylate ($C_{10}H_{15}OTs$) in 50 vol% acetone–water solution at 50 °C was also increased exponentially by the addition of $LiClO_4$, whereas those of typical S_N2 substrates, methyl tosylate (CH_3OTs) and ethyl bromide, were decreased by the addition of $LiClO_4$. On the other hand, for isopropyl bromide and benzyl chloride, the solvolysis rates were not changed by the addition of $LiClO_4$. A good linearity was observed between the increase in log (k/s^{-1}) in the presence of 1.0 mol dm^{-3} $LiClO_4$ and the *m*-values of the substrates (by Grunwald–Winstein). It is proposed that one could simply distinguish S_N1 from S_N2 reactions merely by observing a substantial increase in the solvolysis rate constant at 1.0 mol dm^{-3} $LiClO_4$ in aqueous mixed solvents. The salt effects on the solvolysis rates of sulfonyl chlorides in 50% acetone–water at 35 °C were very different from those for substrates with carbocations as reaction intermediates.

Over many years, a number of studies have been performed to account for the salt effects on solvolysis reactions,[1] however, no theory has been successful in explaining comprehensively the effects of very high salt concentrations ($\geqslant 1.0$ mol dm^{-3}) on solvolysis reactions. Previously,[2] we explained quantitatively the concentrated salt effects on the solvolysis rates of aliphatic halides and related compounds in a protic $MeOH–H_2O$ solvent. The salt effects were examined at higher salt concentrations which approached the solubility limits of salts. We proposed that under such high salt concentrations, the structures due to hydrogen bonding of the solvents are destroyed beyond theoretical evaluation of their ionic activities, *i.e.*, some changes occur from bulk water (or MeOH–water) to isolated solvent molecules (H–O–H, R–O–H) which are supposed to behave just like ethers (R–O–R). In other words, the protic character of the solvent is altered to an "aprotic" one. The pseudo-first-order reaction rates (k/s^{-1}) for typical S_N1 substrates were found to increase exponentially with increasing concentrations of alkali metal or alkaline-earth metal perchlorates, whereas with a nonmetallic salt (Et_4NBr), the reaction rates decreased. We were able to conclude that the observed larger positive effects of the metal perchlorates were due to a change in the solvent structure and the formation of "stable" carbocations (R^+) through "chemical" interactions between the halides (X^-) and the metallic cations (M^+, M^{2+}) in the "modified" solvent.

In higher permittivity media (ε_r >10), it has been generally recognized that alkali metal ions do not interact with simple anions through "chemical" interactions beyond the Coulombic interaction. Snaith and Wright[3] have described how, although they are still the subject of some controversy, it is now generally agreed that alkali metal–X bonds (X = halogen, C, N, O, *etc.*) are essentially ionic. However, we have managed to demonstrate that lithium ions (or Na^+) and alkaline-earth metal ions in poorly solvating media can take part in chemical reactions directly.[4] Very recently,[5] the formation of trityl cations from (4-methoxy-substituted) trityl halides upon the addition of alkali metal (Li^+, Na^+) and alkaline-earth metal (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) perchlorates in acetonitrile was observed by means of UV–VIS spectroscopy and ^1H NMR. 4-Methoxy-substituted trityl perchlorates were simply prepared from the corresponding trityl chlorides by the addition of $NaClO_4$ or $Ba(ClO_4)_2$ in acetonitrile, instead of $AgClO_4$ in nitrobenzene. In acetonitrile (ε_r = *ca.* 36) or acetone (ε_r = 20.7), the conductometric curve (Λ *versus* $c^{1/2}$) gave a minimum of lithium β-diketonates (benzoyl- and 1-naphthoyl-pyrazolonates).[6] We do not think that these phenomena can be explained on the basis of mere ionic interactions between the anions and M^+ or M^{2+} in the reduced Coulombic field.

In the present study, extended examinations are performed on the concentrated salt effects on the solvolysis rates of aliphatic halides and related compounds in mixed solvents, 90 vol% and 50 vol% acetone–H_2O mixtures at 50 °C. The main purpose of this extended work is to compare the results in acetone–H_2O with those in the $MeOH–H_2O$ mixed solvent,

Table 1 (Apparent) first-order reaction rates for the solvolysis of RX in 50 vol% acetone–H$_2$O in the absence and presence of LiClO$_4$ at 50 °C

RX	$k_0{}^a$/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 chloride	5.42×10^{-6}	2.55×10^{-5}	6.94×10^{-5}	0.68	0.43	1.20 (25 °C)^c
1-Adamantyl bromide	2.21×10^{-4}	5.37×10^{-4}	—	0.39	—	1.20 (25 °C)^c
tert-Butyl chloride^d	4.55×10^{-6}	1.49×10^{-5}	3.83×10^{-5}	0.51	0.41	1.00 (25 °C)^c
2-Adamantyl tosylate	1.63×10^{-5}	2.96×10^{-5}	6.46×10^{-5}	0.26	0.34	0.78 (25 °C)^e
Isopropyl bromide	3.20×10^{-6}	3.22×10^{-6}	2.87×10^{-6}	0.00	−0.05	0.52 (50 °C)^f
Benzyl chloride	3.69×10^{-6}	3.19×10^{-6}	3.36×10^{-6}	−0.06	0.02	0.425 (50 °C)^g
Ethyl bromide	4.91×10^{-6}	3.09×10^{-6}	2.88×10^{-6}	−0.20	−0.03	0.34 (55 °C)^c
Methyl tosylate	1.69×10^{-5}	1.45×10^{-5}	1.11×10^{-5}	−0.07	−0.12	0.23 (75 °C)^h

^{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$_4$. ^{b} The m-value is a Grunwald–Winstein parameter characteristic of RX [log$(k/k_0) = mY$ in EtOH–H$_2$O]. ^{c} cf. ref. 8. ^{d} In 90 vol% acetone–H$_2$O. ^{e} cf. ref. 14. ^{f} cf. ref. 26. ^{g} cf. ref. 25. ^{h} cf. ref. 13.

containing higher salt concentrations approaching the solubility limits of the salts. Positive salt effects are again expected if "stable" carbocations can form as the result of a "chemical" interaction between the halide or other anions and metallic cations in the media. We also investigated the concentrated salt effects on the solvolysis reaction rates of sulfonyl chlorides in 50 vol% acetone–water.

Experimental

Commercially obtained 1-adamantyl chloride (C$_{10}$H$_{15}$Cl, TCI EP grade), 1-adamantyl bromide (C$_{10}$H$_{15}$Br, TCI GR grade), tert-butyl chloride (Aldrich 99%), isopropyl bromide (TCI GR grade) and ethyl bromide (Wako Pure Chem. 98%) were used as received. Benzyl chloride (TCI GR >99%), methyl toluene-p-sulfonate (methyl tosylate, MeOTs, TCI EP grade), benzenesulfonyl chloride (TCI EP grade), toluene-p-sulfonyl chloride (TCI EP grade) and dimethylsulfamoyl chloride (Aldrich 99%) were used without further purification. 2-Adamantyl tosylate was prepared as described previously.[7] Lithium perchlorate (anhydrous, Wako GR), sodium, magnesium and barium perchlorates (Aldrich, all A.C.S. reagents) were used as received. Tetraethylammonium bromide and perchlorate were prepared[4] and recrystallized twice from methanol and several times from water, respectively. Acetone (Wako GR) and benzene (Wako GR) were used without further purification. Deionized and distilled water was used after being decarbonated.

The solvolysis rates were determined by titration with 0.0025 mol dm^{-3} standard aqueous sodium hydroxide using phenolphthalein as the indicator. The details of the procedure were as described in our previous work.[2]

Results and discussion

Concentrated salt effects on the "limiting" S$_N$1 reaction

The solvolysis of tert-butyl chloride provided one of the earliest examples of an S$_N$1 reaction, and for many years this substance has been used as a reference substrate for "limiting" solvolysis though this classification has been criticized.[8] Fig. 1 shows that the log (k/s^{-1}) values for the solvolysis rates of tert-butyl chloride in 90 vol% acetone–10 vol% H$_2$O at 50 °C were almost linear with respect to the concentrations of metal perchlorates. The log (k/s^{-1}) values for sodium perchlorate were similar to those of lithium even at higher salt concentrations, and Mg(ClO$_4$)$_2$ showed slightly less positive effects than Ba(ClO$_4$)$_2$. These results are slightly different from those observed in 80 vol% MeOH–H$_2$O previously.[2] The effects of alkaline-earth ions were larger than those of alkali metal ions. The k_0 value (4.55×10^{-6} s^{-1} in Table 1) in the present system ($Y = \sim -1.856$)[9] was much smaller than that (2.55×10^{-5} s^{-1})[2] in 80 vol% MeOH–H$_2$O solution ($Y = 0.381$)[9] at 25 °C. On the other hand, for a non-metallic salt, Et$_4$NClO$_4$, though examined up to only 1.0 mol dm^{-3} due to limited solubility at 50 °C, the reaction rates decreased gradually. The presence of higher concentrations of
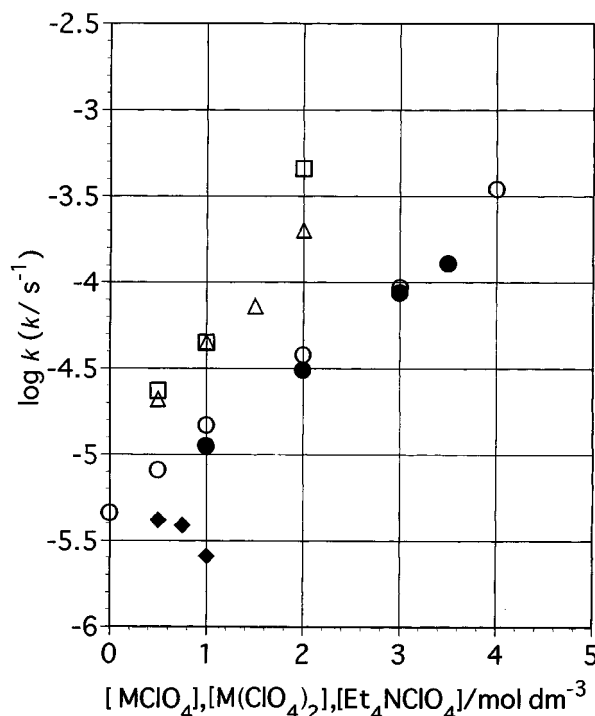

Fig. 1 Change in the rate constants of the solvolysis reaction of tert-butyl chloride with the addition of various salts in 90 vol% acetone–H$_2$O at 50 °C: (○) LiClO$_4$; (●) NaClO$_4$; (△) Mg(ClO$_4$)$_2$; (□) Ba(ClO$_4$)$_2$; (◆) Et$_4$NClO$_4$

Et$_4$NClO$_4$ in the solvent must have brought about a remarkable decrease in the activity of H$_2$O.

As in MeOH–H$_2$O solvent,[2] the increase in pseudo-first-order reaction rates of tert-butyl chloride solvolysis was also attributed to a change in the solvent structure and the formation of a "stable" carbocation through the "chemical" interaction between the halide ion (Cl$^-$) and the alkali metal M$^+$ (Li$^+$, Na$^+$) or alkaline-earth metal M^{2+} (Mg^{2+}, Ba^{2+}) in the "modified" solvent. The partially ionized C–Cl bond (C$^+$–Cl$^-$) in the concentrated salt solution would be cleaved as follows:

$$(CH_3)_3CCl \rightleftharpoons (CH_3)_3C^+\text{–}Cl^- \xrightarrow{M^+ \text{ or } M^{2+}}$$
$$(CH_3)_3C^+ + M^+Cl^- \text{ or } MCl^+ \quad (1)$$
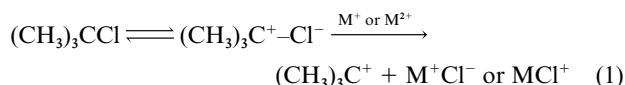
In the presence of extremely concentrated LiClO$_4$, a triple ion, (Li$^+$)$_2$Cl$^-$,[10] might be formed in addition to the ion pair, Li$^+$Cl$^-$. Oelkers and Helgeson[11] suggested the occurrence of multiple ion association from concentrated NaCl in supercritical aqueous solutions. In the present system, the effects of Na$^+$ and Ba^{2+} were larger than expected from the viewpoint of the ionic and/or coordination ability. Previously, we observed greater ability of Na$^+$ and Ba^{2+} than Li$^+$ and Mg^{2+}, respectively, in cleaving C$^+$–Cl$^-$ bonds in acetonitrile; the abnormal
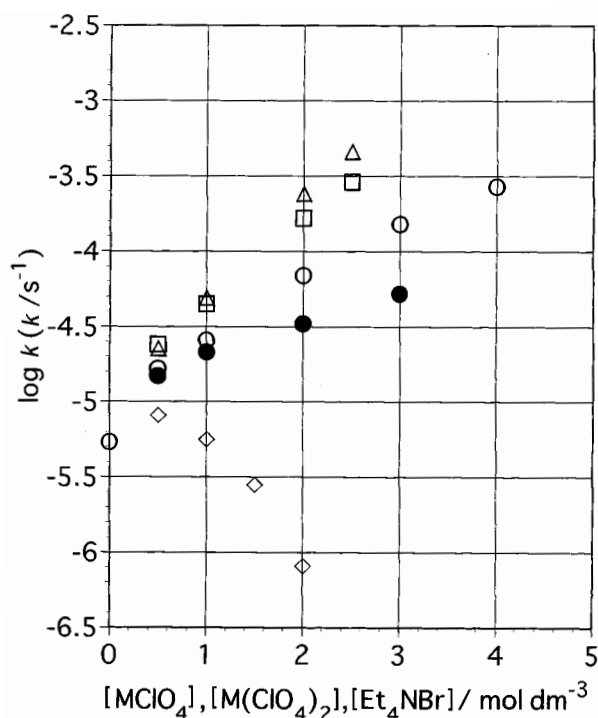
Fig. 2 Change in the rate constants of the solvolysis reaction of 1-adamantyl chloride with the addition of various salts in 50 vol% acetone–H$_2$O at 50 °C: (○) LiClO$_4$; (●) NaClO$_4$; (△) Mg(ClO$_4$)$_2$; (□) Ba(ClO$_4$)$_2$; (◇) Et$_4$NBr

Fig. 3 Variations of solvolysis reaction rates with different substrates in 50 vol% acetone–H$_2$O at 50 °C in the presence of LiClO$_4$: (△) C$_{10}$H$_{15}$OTs (2-adamantyl tosylate); (○) CH$_3$OTs; (▽) C$_6$H$_5$CH$_2$Cl; (▲) (CH$_3$)$_2$CHBr; (□) CH$_3$CH$_2$Br

phenomena were explained by assisted reactions including precipitation (*e.g.*, NaCl and BaCl$^+$ClO$_4^-$).[5]

1-Adamantyl chloride is an excellent substrate for defining a new scale (Y_{Cl}) of solvent ionization power.[12] The salt effects on the solvolysis of 1-adamantyl chloride in 50 vol% acetone–H$_2$O at 50 °C were greatly accelerated upon the addition of alkali metal and alkaline-earth metal perchlorates, as shown in Fig. 2. The log (k/s^{-1}) value of 1-adamantyl chloride increased exponentially with increasing metal salt concentrations. Upon the addition of a nonmetallic salt, Et$_4$NBr, the solvolysis reaction rate increased slightly up to ⩽1.0 mol dm^{-3}, and then decreased markedly with >1.0 mol dm^{-3} of the salt. The effects of LiClO$_4$ and Et$_4$NBr on the solvolysis of 1-adamantyl bromide were similar to those on the chloride compound. These salt effects in the acetone–H$_2$O solution were very similar to those observed for 1-adamantyl bromide at 35 °C in MeOH–H$_2$O solution.[2] By the way, Bentley and Carter suggested that S$_N$1 reactions of 1-adamantyl halides should be more rapid than those of *tert*-butyl halides, *i.e.*, equilibria between stable 1-adamantyl and *tert*-butyl cations favour the adamantyl cation:[12]

$$RX + R'^+ \rightleftharpoons R^+ + R'X$$

The decrease in the solvolysis reaction rate upon the addition of nonmetallic salt was attributed to a decrease in solvent activity as the salt concentration increased, while a slight increase of ⩽1.0 mol dm^{-3} might be explained by the increase in ionic strength.

The effects of LiClO$_4$ on the solvolysis rate of 2-adamantyl tosylate were also examined in 50 vol% acetone–H$_2$O at 50 °C. Tertiary compounds have been traditionally used to provide a model for "limiting" (carbocation) behaviour. A secondary substrate, 2-adamantyl tosylate, disposed toward "limiting" behaviour has been used as a new standard, against which the behaviour of other secondary systems can be calibrated and reevaluated.[13,14] Fig. 3 shows that the pseudo-first-order reaction rates of the solvolysis of 2-adamantyl tosylate increased with increasing concentration of LiClO$_4$. The log (k/s^{-1}) values were almost linear with respect to the concentration of
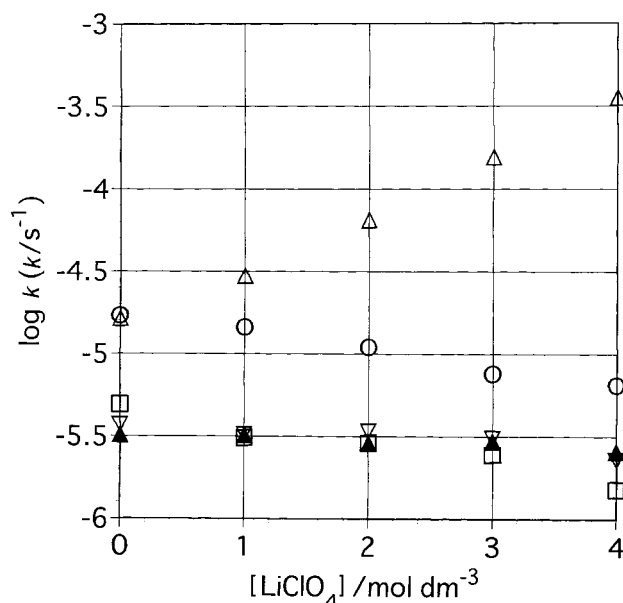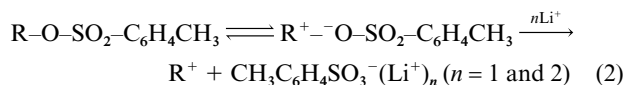
LiClO$_4$ (1.0–4.0 mol dm^{-3}). Since both anchimeric assistance and rearrangement are unlikely during the solvolysis of 2-adamantyl tosylate, the observed salt effects can be attributed again to the formation of a "stable" adamantyl cation through a "chemical" interaction between the tosylate ion and Li$^+$ ions. We think that the partially ionized covalent bond (C$^+$–O$^-$) can be cleaved by Li$^+$ to give an adamantyl cation (R$^+$).

$$R\text{–}O\text{–}SO_2\text{–}C_6H_4CH_3 \rightleftharpoons R^+\text{–}{}^-O\text{–}SO_2\text{–}C_6H_4CH_3 \xrightarrow{n\text{Li}^+}$$
$$R^+ + CH_3C_6H_4SO_3^-(\text{Li}^+)_n \ (n = 1 \text{ and } 2) \quad (2)$$

Ion pair (CH$_3$C$_6$H$_4$SO$_3^-$Li$^+$) and, perhaps, triple ion [CH$_3$C$_6$H$_4$SO$_3^-$(Li$^+$)$_2$] formation would shift the equilibrium to the right hand side in eqn. (2). In Winstein's terms,[15] "ion pair return" or "external ion return" for the substrate is inhibited by the ion pair (X$^-$Li$^+$) and, under extreme conditions, also by the triple ion [X$^-$(Li$^+$)$_2$]. The formation of such a triple ion, PhSO$_3^-$(Li$^+$)$_2$, in the presence of LiClO$_4$ (>0.02 mol dm^{-3}) in acetonitrile has been already reported.[16] We do not think that the reaction mechanism in a typical S$_N$1 reaction is basically altered by the presence of metal perchlorates: the formation of the carbocation is just promoted by the metal ions as "catalysts". Cox and Maskill[17] have reported a large enhancement in the solvolysis rate of *tert*-alkyl iodides by the addition of I$_2$ (I$_2$ + I$^-$⇌I$_3^-$). Chemical interactions seem to act between X$^-$ and I$_2$ or M$^+$, M^{2+} to promote the formation of carbocations in both their and our systems.

Wyatt *et al.*[18] reported a large decrease in the hydrolysis reaction rate of substituted-trityl ions (R$_3$C$^+$) by the addition of rather concentrated alkali metal and alkaline-earth metal perchlorates. They tried interpreting the phenomena in terms of an association between R$_3$C$^+$ and ClO$_4^-$. Here, we would like to point out that anions (except for ClO$_4^-$ *etc.*) can associate with alkali metal and alkaline-earth metal ions in concentrated salt solutions. However, according to our conductivity data[19] which show that a 4-methoxy-substituted trityl perchlorate is a strong electrolyte in acetonitrile [$K_a = ca.$ 20 and $\Lambda_0 = 165$ for (4-MeOC$_6$H$_4$)$_2$PhCClO$_4$], we can understand that the interaction between R$^+$ and ClO$_4^-$ is small in the acetone–water solvent, allowing that the ClO$_4^-$ ion is rather "unstable" in aqueous media. The broad peak in ^{19}F NMR spectra suggested that some interactions were possible between Ph$_3$C$^+$ and BF$_4^-$ in
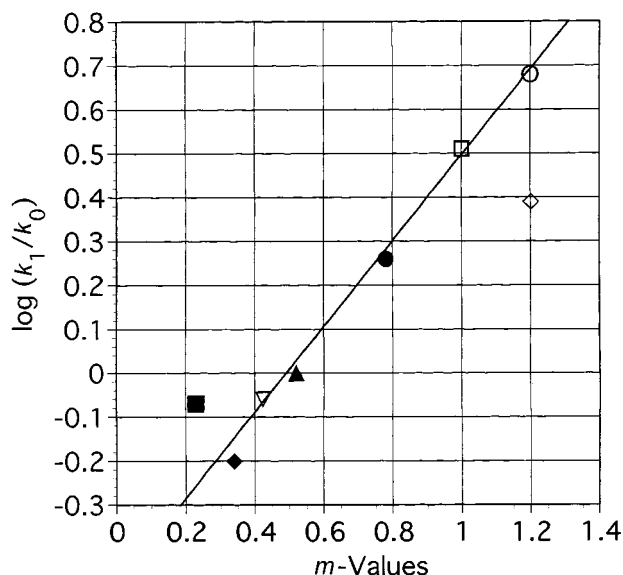
Fig. 4 Correlation between the increases in solvolysis rates [log (k_1/k_0)] on the addition of 1.0 mol dm^{-3} LiClO$_4$ in 50 vol% acetone–H$_2$O at 50 °C and the Grunwald–Winstein m-values (○) C$_{10}$H$_{15}$Cl; (◇) C$_{10}$H$_{15}$Br; (□) (CH$_3$)$_3$CCl; (▽) C$_6$H$_5$CH$_2$Cl; (▲) (CH$_3$)$_2$CHBr; (◆) CH$_3$CH$_2$Br; (●) C$_{10}$H$_{15}$OTs; (■) CH$_3$OTs
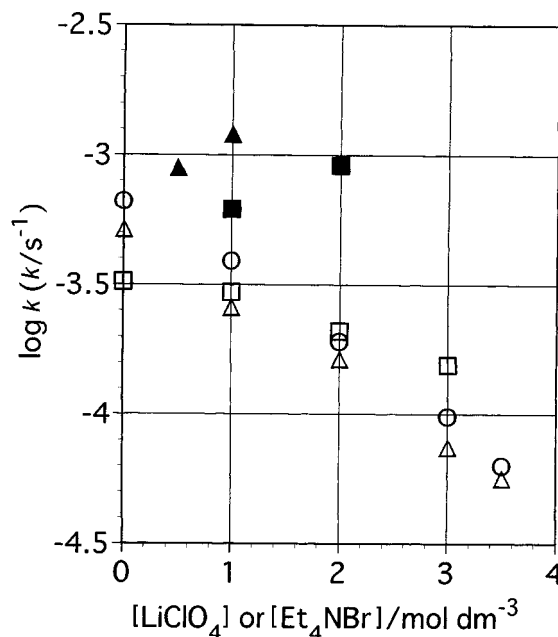

Fig. 5 Variations of solvolysis reaction rates of sulfonyl chlorides in the presence of LiClO$_4$ (open symbols) and Et$_4$NBr (solid symbols) in 50 vol% acetone–H$_2$O at 35 °C: (○) C$_6$H$_5$SO$_2$Cl; (△, ▲) CH$_3$C$_6$H$_4$-SO$_2$Cl; (□, ■) (CH$_3$)$_2$NSO$_2$Cl

acetonitrile.[20] Our conductivity data for (4-MeOC$_6$H$_4$)$_2$PhCCl in acetonitrile showed apparently abnormal behaviour: the molar conductivities (Λ) for $c = 4 \times 10^{-4}$–6×10^{-3} mol dm^{-3} were explained not by the 1:1 association alone but by higher aggregations.[19] Indeed, clear evidence was supplied for a chemical interaction in addition to the mere Coulombic interaction between the cation and the Cl$^-$ ion. The carbon centre of a carbocation (R$_3$C$^+$) is essentially an active site, therefore, we suppose, even (substituted) trityl cations can interact chemically with anions except for "inert" anions (no or very poor coordinating ability), such as ClO$_4^-$.

Very recently, solvolyses of 2-adamantyl bromide in alcohol–water were examined to determine the selectivity, $k_{\text{ether}}/k_{\text{alcohol}}$ under various conditions.[21] Coplanarity changes in the formation of 1,1-diaryl-2,2,2-trifluoroethyl cations from the tosylates have been discussed.[22]

On the S$_N$1–S$_N$2 intermediates
Salt effects on solvolysis reaction rates for S$_N$1–S$_N$2 intermediate compounds were also examined in 50 vol% acetone–H$_2$O solution. The variation of behaviour along the series methyl, ethyl, isopropyl, and *tert*-butyl groups has always played an important role in mechanistic studies of the solvolysis reaction. For S$_N$2 processes, the rates fall along the series, whereas they rise sharply for S$_N$1 reactions.[23]

The salt effects of LiClO$_4$ on the solvolysis reaction rates of benzyl chloride, isopropyl bromide, ethyl bromide and methyl tosylate at 50 °C are also shown in Fig. 3. The apparent "k/s^{-1}" values for benzyl chloride and isopropyl bromide remained almost constant with increasing concentration of LiClO$_4$, except for a slight decrease beyond 3.0 mol dm^{-3} salt concentration. On the other hand, the solvolysis rates of ethyl bromide and methyl tosylate were greatly decelerated upon the addition of LiClO$_4$; *e.g.*, the "k" values for methyl tosylate were 1.69×10^{-5}, 1.45×10^{-5}, 1.11×10^{-5}, 7.82×10^{-6} and 6.45×10^{-6} s^{-1} at 0, 1.0, 2.0, 3.0 and 4.0 mol dm^{-3} LiClO$_4$, respectively.

In Fig. 3, a big difference was observed between the salt effects on the solvolyses of 2-adamantyl tosylate (a typical S$_N$1 substrate) and methyl tosylate (a typical S$_N$2 substrate) upon the addition of LiClO$_4$. Bentley *et al.*[24] used 2-adamantyl tosylate and methyl tosylate as reference substrates for S$_N$1 and S$_N$2, respectively, to describe tosylate correlations in evaluating the applicability of a three-parameter equation for both S$_N$1

and S$_N$2 solvolyses. Incidentally, we would like to note that solvolysis rates of methyl tosylate were much decelerated and less decelerated depending on the concentration of Et$_4$NBr (not LiClO$_4$): "k" = 5.34×10^{-6}, 5.42×10^{-6} and 1.25×10^{-5} s^{-1} at 1.0, 2.0 and 3.0 mol dm^{-3} Et$_4$NBr.

Fig. 4 shows a linear relationship between log (k_1/k_0) and the m-value[25,26] of 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. The S$_N$1 substrates with m-values of >0.5 showed distinct increases in solvolysis reaction rates upon the addition of LiClO$_4$, whereas for S$_N$1–S$_N$2 intermediates, the solvolysis rates were decelerated. The m-values obtained in EtOH–H$_2$O systems were adapted for the present acetone–H$_2$O work because of the lack of data on acetone–H$_2$O systems (at least from our survey of the literature). It was rather surprising that the correlation of 1-adamantyl bromide was less satisfactory in 50% acetone–water. The log (k_2/k_1) values (in Table 1) *vs.* m-values also gave a linear relationship. Despite the limited data, it may be concluded that one can simply distinguish S$_N$1 from S$_N$2 reactions if a substantial increase in the solvolysis rate constants (k/s^{-1}) for organic halides or related compounds (RX) is observed on the addition of 1.0 and/or 2.0 mol dm^{-3} LiClO$_4$ in aqueous mixed solvents.

Solvolysis of sulfonyl chlorides
The solvolyses of sulfonyl chlorides in organic solvent–water mixtures have been recognized to proceed *via* an S$_N$2 scheme,[27] although some ionic character has been suggested.[28] Fig. 5 shows the effects of LiClO$_4$ on the solvolysis rate constant of toluene-*p*-sulfonyl chloride (CH$_3$C$_6$H$_4$SO$_2$Cl) in 50 vol% acetone–H$_2$O at 35 °C. Upon the addition of 1.0–3.5 mol dm^{-3} LiClO$_4$, the solvolysis rate of the substrate was decelerated: log $(k_1/k_0) = -0.30$, *cf.* Table 2. The decrease in the "k/s^{-1}" value of the S$_N$2 substrate can be explained by the decrease in the H$_2$O activity in the presence of concentrated LiClO$_4$. On the other hand, the effects of Et$_4$NBr were very curious; the rate constant was increased, *e.g.*, log $(k_1/k_0) = 0.37$ at 1.0 mol dm^{-3} Et$_4$NBr. A large decrease in the H$_2$O activity was expected on the addition of concentrated Et$_4$NBr. We think that the increase in the rate constant may be due to the nucleophilic attack of Br$^-$ at the S atom of the sulfonyl chloride, followed by H$_2$O substitution. The positive effects of Et$_4$NCl were also observed, not so large

Table 2 (Apparent) first-order reaction rates for the solvolysis of sulfonyl chlorides in 50 vol% acetone–H_2O in the presence of $LiClO_4$, Et_4NCl and Et_4NBr at 35 °C

| Substrate | $k_0{}^a$/s^{-1} | $LiClO_4$ | | Et_4NCl | | Et_4NBr | |
		$k_1{}^b$/s^{-1}	log (k_1/k_0)	$k_1{}^b$/s^{-1}	log (k_1/k_0)	$k_1{}^b$/s^{-1}	log (k_1/k_0)
Benzenesulfonyl chloride	6.67×10^{-4}	3.88×10^{-4}	-0.23	—	—	—	—
Toluene-p-sulfonyl chloride	5.02×10^{-4}	2.56×10^{-4}	-0.30	6.89×10^{-4}	0.13	1.21×10^{-3}	0.37
Dimethylsulfamoyl chloride	3.23×10^{-4}	2.94×10^{-4}	-0.04	3.35×10^{-4}	0.02	6.22×10^{-4}	0.28

^{a} The k_0 values are the solvolysis rates without salts. ^{b} The k_1 values are the solvolysis rates at 1.0 mol dm^{-3} of $LiClO_4$, Et_4NCl and Et_4NBr.

as those by Et_4NBr. The effects of halide ions on the sulfonyl chloride solvolysis (S$^+$: sulfur centre) seemed to be very different from those on the solvolysis of aliphatic halides and related compounds, in which rather stable carbocations are involved as the reaction intermediates. Similar salt effects in negative and positive directions have been reported in the presence of $LiClO_4$ and Me_4NCl, respectively, for the alkaline hydrolysis of 2,4-dinitrochlorobenzene.[29]

Benzenesulfonyl chloride (PhSO$_2$Cl) also gave an exponential decrease in the solvolysis rate constant in the presence of 1.0–3.5 mol dm^{-3} $LiClO_4$. A slight decrease has been reported with 0.1 mol dm^{-3} $LiClO_4$ in 50% acetone–water at 25 °C.[30] For dimethylsulfamoyl chloride (Me$_2$NSO$_2$Cl), the slope of log (k/s^{-1}) *vs.* c($LiClO_4$) was smaller than that for benzene- and toluene-p-sulfonyl chlorides; which is in accordance with the ionic character in the solvolysis reaction: $m = 0.69$, 0.5 and 0.54 for the sulfamoyl, benzene- and toluene-p-sulfonyl chlorides, respectively.[28] The presence of Et_4NBr caused the log (k/s^{-1}) value of dimethylsulfamoyl chloride to increase linearly. The kinetics of halide exchange using a ^{36}Cl label have been reported for dimethylsulfamoyl chloride.[31] Incidentally, the salt effects of R_4NCl and $NaClO_4$ on the solvolysis of covalent sulfonyl-methyl perchlorate (RSO$_2$CH$_2$OClO$_3$, including H$^+$ subtraction by bases) were explained by the structure-making and -breaking characters of the salts.[32] Brauman *et al.*[33] have reviewed the S$_N$2 reactions of ions in the gas phase, and compared the behaviour of the ionic reaction in the gas phase with that in solution.

Acknowledgements

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