PERKIN 2

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 $\mathrm{S_N1}$ substrate, *tert*-butyl chloride, at 50 °C was increased exponentially by the addition of $\mathrm{M^+ClO_4^-}$ ($\mathrm{M^+ = Li^+, Na^+}$: up to 4.0 mol dm^{-3}) and $\mathrm{M^{2+}(ClO_4^-)_2}$ ($\mathrm{M^{2+} = Mg^{2+}, Ba^{2+}}$: up to 2.0 mol dm^{-3}); the extent of the cation effects increased as $\mathrm{Na^+ \leqslant Li^+ < Mg^{2+} \leqslant Ba^{2+}}$. However, the addition of $\mathrm{Et_4NClO_4}$ (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 $\mathrm{Na^+ < Li^+ < Ba^{2+} < Mg^{2+}}$. Addition of >1.0 mol dm^{-3} $\mathrm{Et_4NBr}$ decreased the solvolysis rate markedly, whereas it was increased slightly by lower $\mathrm{Et_4NBr}$ concentrations. The positive effects of metal ions for typical $\mathrm{S_N1}$ substrates were explained by the change of solvent structure and by a "chemical" interaction between the anions from the substrates ($\mathrm{R^+–X^-}$) and $\mathrm{M^+}$ or $\mathrm{M^{2+}}$ in the presence of very concentrated salts; the negative effects of nonmetallic salts should have been brought about by the decrease in activity of $\mathrm{H_2O}$. The solvolysis rate of 2-adamantyl tosylate ($\mathrm{C_{10}H_{15}OTs}$) in 50 vol% acetone–water solution at 50 °C was also increased exponentially by the addition of $\mathrm{LiClO_4}$, whereas those of typical $\mathrm{S_N2}$ substrates, methyl tosylate ($\mathrm{CH_3OTs}$) and ethyl bromide, were decreased by the addition of $\mathrm{LiClO_4}$. On the other hand, for isopropyl bromide and benzyl chloride, the solvolysis rates were not changed by the addition of $\mathrm{LiClO_4}$. A good linearity was observed between the increase in log (k/s^{-1}) in the presence of 1.0 mol dm^{-3} $\mathrm{LiClO_4}$ and the *m*-values of the substrates (by Grunwald–Winstein). It is proposed that one could simply distinguish $\mathrm{S_N1}$ from $\mathrm{S_N2}$ reactions merely by observing a substantial increase in the solvolysis rate constant at 1.0 mol dm^{-3} $\mathrm{LiClO_4}$ 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 $\mathrm{MeOH–H_2O}$ 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 $\mathrm{S_N1}$ substrates were found to increase exponentially with increasing concentrations of alkali metal or alkaline-earth metal perchlorates, whereas with a nonmetallic salt ($\mathrm{Et_4NBr}$), 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 ($\mathrm{R^+}$) through "chemical" interactions between the halides ($\mathrm{X^-}$) and the metallic cations ($\mathrm{M^+}$, $\mathrm{M^{2+}}$) 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 $\mathrm{Na^+}$) 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 ($\mathrm{Li^+}$, $\mathrm{Na^+}$) and alkaline-earth metal ($\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Sr^{2+}}$, $\mathrm{Ba^{2+}}$) perchlorates in acetonitrile was observed by means of UV–VIS spectroscopy and ^{1}H NMR. 4-Methoxy-substituted trityl perchlorates were simply prepared from the corresponding trityl chlorides by the addition of $\mathrm{NaClO_4}$ or $\mathrm{Ba(ClO_4)_2}$ in acetonitrile, instead of $\mathrm{AgClO_4}$ 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 $\mathrm{M^+}$ or $\mathrm{M^{2+}}$ in the reduced Coulombic field.

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

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Table 1 (Apparent) first-order reaction rates for the solvolysis of RX in 50 vol% acetone–H_2O 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_2O]. [c] *cf.* ref. 8. [d] In 90 vol% acetone–H_2O. [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_N1 reaction

The solvolysis of *tert*-butyl chloride provided one of the earliest examples of an S_N1 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_2O 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_2O 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_2O solution ($Y = 0.381$)[9] at 25 °C. On the other hand, for a non-metallic salt, Et_4NClO_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 Et_4NClO_4 in the solvent must have brought about a remarkable decrease in the activity of H_2O.

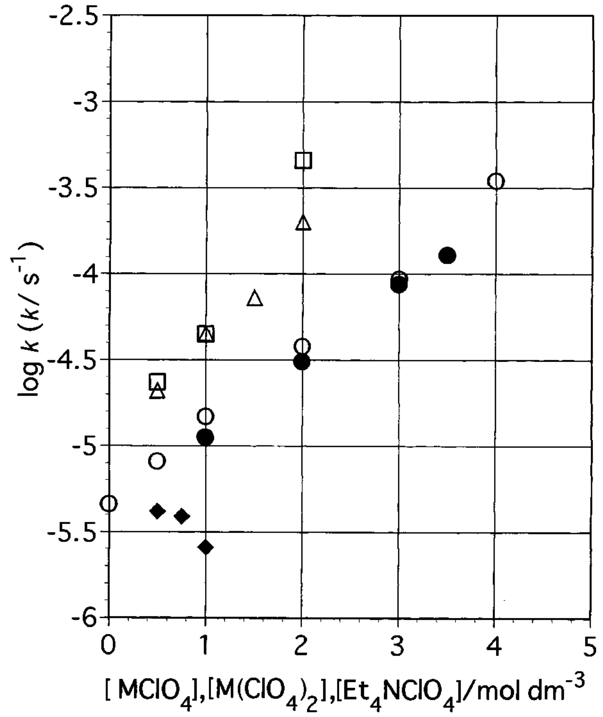

Fig. 1 Change in the rate constants of the solvolysis reaction of *tert*-butyl chloride with the addition of various salts in 90 vol% acetone–H_2O at 50 °C: (○) $LiClO_4$; (●) $NaClO_4$; (△) $Mg(ClO_4)_2$; (□) $Ba(ClO_4)_2$; (◆) Et_4NClO_4

As in MeOH–H_2O 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, $(Li^+)_2Cl^-$,[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

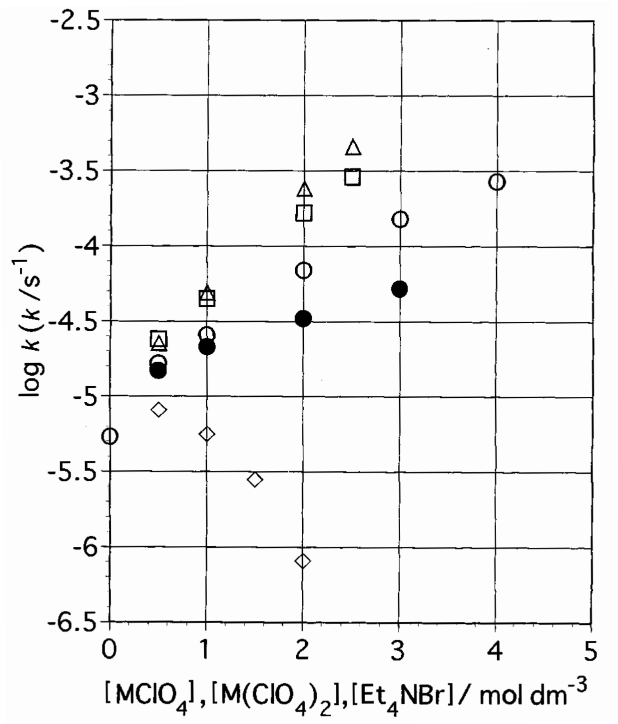

Fig. 2 Change in the rate constants of the solvolysis reaction of 1-adamantyl chloride with the addition of various salts in 50 vol% acetone–H_2O at 50 °C: (○) $LiClO_4$; (●) $NaClO_4$; (△) $Mg(ClO_4)_2$; (□) $Ba(ClO_4)_2$; (◇) Et_4NBr

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_2O 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_4NBr, the solvolysis reaction rate increased slightly up to $\leqslant 1.0$ mol dm^{-3}, and then decreased markedly with >1.0 mol dm^{-3} of the salt. The effects of $LiClO_4$ and Et_4NBr on the solvolysis of 1-adamantyl bromide were similar to those on the chloride compound. These salt effects in the acetone–H_2O solution were very similar to those observed for 1-adamantyl bromide at 35 °C in MeOH–H_2O solution.[2] By the way, Bentley and Carter suggested that S_N1 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 $\leqslant 1.0$ 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_2O 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^+).

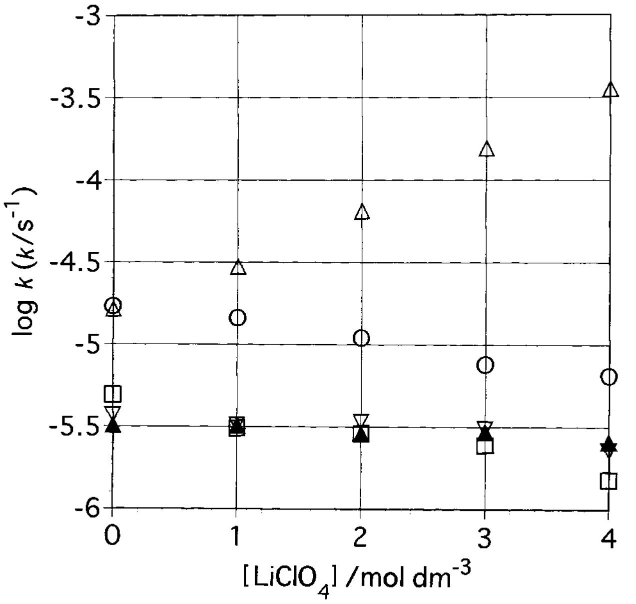

Fig. 3 Variations of solvolysis reaction rates with different substrates in 50 vol% acetone–H_2O at 50 °C in the presence of $LiClO_4$: (△) $C_{10}H_{15}OTs$ (2-adamantyl tosylate); (○) CH_3OTs; (▽) $C_6H_5CH_2Cl$; (▲) $(CH_3)_2CHBr$; (□) CH_3CH_2Br

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

Ion pair ($CH_3C_6H_4SO_3^-Li^+$) and, perhaps, triple ion [$CH_3C_6H_4SO_3^-(Li^+)_2$] 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_N1 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 ($I_2 + I^- \rightleftharpoons I_3^-$). 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_3C^+) 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_3C^+ 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 $(4\text{-}MeOC_6H_4)_2PhCClO_4$], 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_3C^+ and BF_4^- in

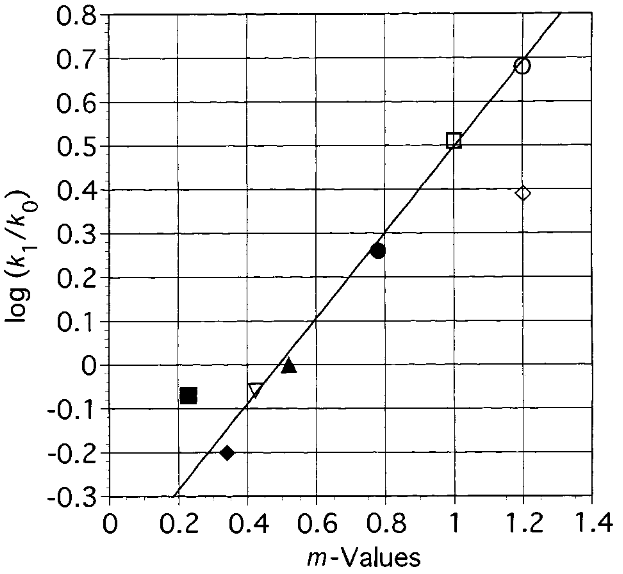

Fig. 4 Correlation between the increases in solvolysis rates [log (k_1/k_0)] on the addition of 1.0 mol dm^{-3} $LiClO_4$ in 50 vol% acetone–H_2O at 50 °C and the Grunwald–Winstein *m*-values (○) $C_{10}H_{15}Cl$; (◇) $C_{10}H_{15}Br$; (□) $(CH_3)_3CCl$; (▽) $C_6H_5CH_2Cl$; (▲) $(CH_3)_2CHBr$; (◆) CH_3CH_2Br; (●) $C_{10}H_{15}OTs$; (■) CH_3OTs

acetonitrile.[20] Our conductivity data for $(4\text{-}MeOC_6H_4)_2PhCCl$ 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_3C^+) 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_N1–S_N2 intermediates

Salt effects on solvolysis reaction rates for S_N1–S_N2 intermediate compounds were also examined in 50 vol% acetone–H_2O 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_N2 processes, the rates fall along the series, whereas they rise sharply for S_N1 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_N1 substrate) and methyl tosylate (a typical S_N2 substrate) upon the addition of $LiClO_4$. Bentley *et al.*[24] used 2-adamantyl tosylate and methyl tosylate as reference substrates for S_N1 and S_N2, respectively, to describe tosylate correlations in evaluating the applicability of a three-parameter equation for both S_N1 and S_N2 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_4NBr (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_4NBr.

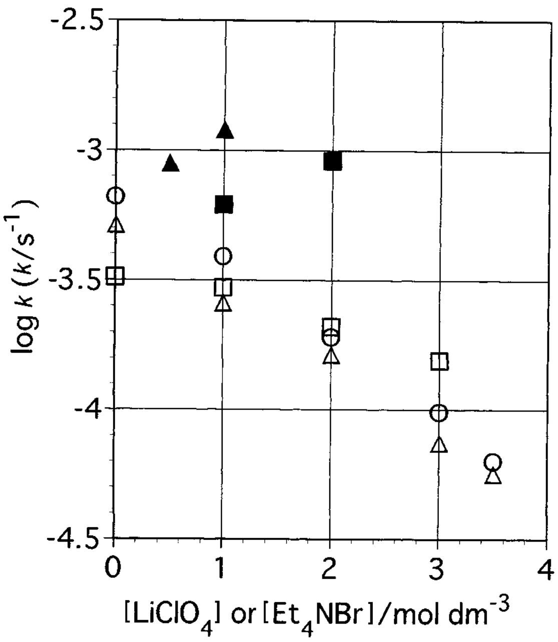

Fig. 5 Variations of solvolysis reaction rates of sulfonyl chlorides in the presence of $LiClO_4$ (open symbols) and Et_4NBr (solid symbols) in 50 vol% acetone–H_2O at 35 °C: (○) $C_6H_5SO_2Cl$; (△, ▲) $CH_3C_6H_4SO_2Cl$; (□, ■) $(CH_3)_2NSO_2Cl$

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_N1 substrates with *m*-values of >0.5 showed distinct increases in solvolysis reaction rates upon the addition of $LiClO_4$, whereas for S_N1–S_N2 intermediates, the solvolysis rates were decelerated. The *m*-values obtained in EtOH–H_2O systems were adapted for the present acetone–H_2O work because of the lack of data on acetone–H_2O 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_N1 from S_N2 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_N2 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 ($CH_3C_6H_4SO_2Cl$) in 50 vol% acetone–H_2O 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_N2 substrate can be explained by the decrease in the H_2O activity in the presence of concentrated $LiClO_4$. On the other hand, the effects of Et_4NBr were very curious; the rate constant was increased, *e.g.*, log (k_1/k_0) = 0.37 at 1.0 mol dm^{-3} Et_4NBr. A large decrease in the H_2O activity was expected on the addition of concentrated Et_4NBr. 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_2O substitution. The positive effects of Et_4NCl 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

		$LiClO_4$		Et_4NCl		Et_4NBr	
Substrate	k_0[a]/s^{-1}	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 ($PhSO_2Cl$) 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_2NSO_2Cl), 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 sulfonylmethyl perchlorate ($RSO_2CH_2OClO_3$, 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_N2 reactions of ions in the gas phase, and compared the behaviour of the ionic reaction in the gas phase with that in solution.

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