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Formation of Stable Carbocations or Zwitterions by a Specific Interaction with Alkali Metal or Alkaline-Earth Metal Ions in Acetonitrile

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In an acetonitrile solution, the extents of ionization of trityl halides (Ph_3CX: $X = Cl, Br$) in the presence of various concentrations of alkali metal ($M^+ = Li^+, Na^+$) and alkaline-earth metal ($M^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$) perchlorates were examined by spectrophotometry. The promoted formation of the trityl ion (Ph_3C^+) in the presence of metal ions was attributed to "chemical" interactions, such as coordination or covalent bonding between the halide ions and M^+ or M^{2+} ions, and not merely the electrostatic interaction. The salt effects increased with methoxy-substituents on trityl chloride as non-substituted < 4-methoxy < 4,4′-dimethoxy < 4,4′,4″-trimethoxytrityl. At higher RX (or X^-) concentrations, not only "coordination", but also precipitation reactions between X^- and M^+ or M^{2+} (except for Li^+ and Mg^{2+}) seemed to promote the ionization of RX. In the co-presence of a small amount of CH_3SO_3H, trityl benzoate gave the Ph_3C^+ ion upon the addition of $LiClO_4$ or $Mg(ClO_4)_2$. A red color with strong fluorescence due to the zwitterion ($R^+–COO^-$) of Rhodamine (Rhodamine B base) was observed upon the addition of M^+ and M^{2+}, which should have been caused by an interaction between the metal ions and the intramolecule carboxylate (from the γ-lactone) of Rhodamine in the solution. The γ-lactone ring of Crystal Violet lactone in acetonitrile was cleaved by the addition of $Mg(ClO_4)_2$ to give a strong violet color, whereas, $LiClO_4$, $NaClO_4$, or $Ba(ClO_4)_2$ had no (or very small) effects in the solution. It was found that the interactions between X^- or $RCOO^-$ and M^+ or M^{2+} in acetonitrile were strong enough to promote the ionization of partly ionized covalent bonds.

It may be generally believed that in aqueous solutions precipitates of AgCl do not react with Ag^+ at a constant ionic strength, while $AgCl_2^-$ can be formed by the addition of an excess amount of NaCl, although the formation of polynuclear complexes, such as Ag_2Cl^+ in pyridine[1] and aqueous solution,[2] has been suggested. During the course of our studies, we have found strong abilities in coordination and "reverse-coordination" for the lithium ion in higher relative permittivity media ($20 < \varepsilon_r < 65$)[3—6] as well as low-permittivity media ($\varepsilon_r < 10$).[7] The term "reverse-coordination" was coined for the formation of $(M^+)_nX^-$-type species ($n \geq 2$) instead of $M^+(X^-)_m$ ($m \geq 2$): the interaction between multiple numbers of alkali metal ions ($M^+ = Li^+$ or Na^+) and a single charged anion (X^-). Very recently, we obtained distinct evidence for the triple ions of some lithium β-diketonates (acyl pyrazolonates: A^-) in acetonitrile and acetone:[8] the molar conductivities (Λ) of Li^+A^- gave the minimum ($c = $ ca. 2×10^{-3} mol dm^{-3}), and were quantitatively explained by the formation of an ion pair, "symmetrical" triple ions, and a quadrupole. Previously, we explained the large salt effects on the indicator acidity (or Hammett acidity function) using *p*-(dimethylamino)-azobenzene[9] and on the proton-transfer from tropolone or nitrophenols[10] to amine bases in acetonitrile in terms of a specific interaction between anions and M^+ and M^{2+}, and not merely the ion-exchange reactions nor the alternation between the contact ion pair (CIP) and the solvent-separated ion pair (SSIP). Bockman and Kochi[11] have reviewed the ion-pair dynamics by time-resolved spectroscopy, and noted that the original goal of finding a spectroscopic distinction between CIPs and SSIPs remained unfulfilled. Recently, we have reported[12] that concentrated salt effects on S_N1 solvolysis reactions of organic halides (RX) in MeOH–H_2O solution can be explained by changes in the solvent structure and the formation of "stable" carbocations through a "chemical" interaction between X^- and metal ions.

The stabilization of carbocations in solution is a matter of great interest in considering the mechanisms of organic reactions, especially S_N1 and S_N2 reactions in solvolysis. In some solvents,[13] such as 1,2-dichloroethane[14] and sulfur dioxide,[15] triphenylmethyl chloride (trityl chloride, Ph_3CCl) can be ionized by itself. However, the ionization constant is too low to be estimated in acetonitrile.[16] By the addition of metal chlorides, such as $HgCl_2$, $AlCl_3$, and $SnCl_4$ to Ph_3CCl solutions (MeCN[16] and $MeNO_2$[17] solvents), the trityl cation (Ph_3C^+) can be formed even quantitatively through the following reaction: $Ph_3CCl + MCl_m \rightleftarrows Ph_3C^+ + [MCl_{m+1}]^-$.

The chloro-complex formation must be the motive force of the reaction progress. Pocker and Buchholz[18] observed an exchange-rate increase by a very large factor for the ionization of Ph_3CCl in diethyl ether upon the addition of 1

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mol dm^{-3} $LiClO_4$. They have explained this kinetic effects by the presence of the species $LiClO_4$, $n$$Et_2O$ ($n = 1$ and 2).

In the present paper, we would like to demonstrate that the interactions between alkali metal (M^+) or alkaline-earth metal (M^{2+}) ions and simple anions are strong enough to cleave weak covalent bonds (or partly ionized covalent bonds: $C^+–X^-$). For this purpose, the formation of a stable carbocation (the trityl cation, Ph_3C^+) from Ph_3CX (X = Cl, Br) and $PhCOOCPh_3$ (trityl benzoate) by the addition of M^+ (Li^+, Na^+) and M^{2+} (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) in acetonitrile was observed spectrophotometrically. The effects of methoxy-substituents on trityl chloride were examined. The cleavage of γ-lactone rings of Rhodamine (Rhodamine B base) and Crystal Violet lactone in the presence of M^+ and M^{2+} in acetonitrile solutions was also examined. Direct evidence of strong interactions between M^{2+} and benzoate ions will be shown in the final section of the paper.

Experimental

Commercially obtained acetonitrile (Wako, GR grade) was distilled (water contents of < 0.05% by volume) with 50 cm column over freshly added CaH_2 after drying with CaH_2 for several days. Benzonitrile (Wako, GR grade) and THF (tetrahydrofuran: Wako, GR grade) were used as received. *N*,*N*-Dimethylformamide (DMF: Wako, GR grade) was distilled at a reduced pressure. 4-Methyl-2-pentanone (MIBK: Wako, GR grade) was distilled from freshly added molecular sieves 4A after treating the solvent with it for several days; acetone (Wako, SP grade) was distilled in a similar way from molecular sieves 4A. Triphenylmethyl (trityl) chloride and bromide (both TCl, GR grade), 4-methoxytrityl chloride (Aldrich, 97%), 4,4′-dimethoxytrityl chloride (Aldrich, 95%), 4,4′,4″-trimethoxytrityl chloride (Aldrich, tech. grade), and triphenylmethyl benzoate (Aldrich) were used without further purification. Triphenylmethyl hexafluorophosphate ($Ph_3C^+PF_6^-$) was kindly supplied by Dr. T. Kitagawa of Kyoto University. Commercially obtained Rhodamine (Rhodamine B base: HCl free, Aldrich) and Crystal Violet lactone (Aldrich) were used as received. Trifluoroacetic acid (Wako, GR garde), methanesulfonic acid (Wako, GR grade), trifluoromethanesulfonic acid (Wako or TCl, GR grade), and 1,1,3,3-tetramethylguanidine (Wako) were used as received.

Tetraethylammonium benzoate and *p*-nitrobenzoate were prepared as previously described,[3] or in a similar way. The resources and the purification methods of alkali metal, alkaline-earth metal, and tetraethylammonium perchlorates were previously described.[9] In adition, $NaClO_4$, $Mg(ClO_4)_2$, and $Ba(ClO_4)_2$ from Aldrich were also used as received.

UV-visible spectra were measured using a Hitachi double-beam spectrophotometer (Model U-2000) in 0.1 and 1.0 cm quartz cuvettes at room temperature (ca. 25 °C). The glassware was carefully dried in a dry-oven as well as by blowing nitrogen gas.

Results and Discussion

Formation of the Trityl Cation from Trityl Halides by the Addition of M^+ and M^{2+}. In dried acetonitrile, upon the addition of 1.0 mol dm^{-3} $LiClO_4$ to 1.0×10^{-3} mol dm^{-3} trityl chloride (Ph_3CCl), the solution color turned pale yellow to give a UV-visible absorption band of two peaks: λ_{max} of 403 and 430 nm, absorbance (with path-length, $l = 1.0$ cm) of 0.141 and 0.135, respectively. The yellow color was hardly observed for a 1.0×10^{-3} mol dm^{-3} solution of Ph_3CBr alone, even though trityl bromide (Ph_3CBr) is more easily ionized than the chloride. However, upon the addition of 1.0 mol dm^{-3} $LiClO_4$, the Ph_3CBr solution gave strong absorbances of 0.892 and 0.869 at $\lambda_{max} = 403.5$ and 431 nm, respectively (Fig. 1). Using $\varepsilon = 4.0\times10^4$ cm^{-1} mol^{-1} dm^3 at 403 nm of the trityl cation (Ph_3C^+)[13b] in acetonitrile, the yields of Ph_3C^+ from 1.0×10^{-3} mol dm^{-3} Ph_3CCl and Ph_3CBr by the addition of 1.0 mol dm^{-3} $LiClO_4$ were evaluated to be 0.36 and 2.28%, respectively (cf. Table 1). The effects of $NaClO_4$ were not so large as those of $LiClO_4$. We propose that the promoted ionization of Ph_3CX (X = Cl, Br) is caused by a "chemical" interaction, such as coordination or covalent bonding, between the lithium ions and the halide ions in a low-solvating solvent (Gutmann's donor number of 14.1 and acceptor number of 19.3)[19] with a higher permittivity (ε_r = ca. 36).

$$Ph_3CX \rightleftharpoons Ph_3C^+X^- \xrightarrow{n\,LiClO_4\ (n=1\text{ or }2)} Ph_3C^+(ClO_4^-) + Li^+X^- \quad\text{or}\quad (Li^+)_2X^-(ClO_4^-). \quad (1)$$

The 1 : 1 interaction (i.e., Li^+X^-) between Li^+ and Cl^- or Br^- in acetonitrile may also contribute to pulling out the halide ions from the partly ionized $C^+–X^-$ bonds, and to make the species completely free from Ph_3C^+. However, the formation constants of the ion pairs of LiCl and LiBr in acetonitrile are not very large: $\log K_1 = 3.0$ and ca. 2, respectively.[20] In addition to ion-pair formation, the overall formation constants of $(Li^+)_2Cl^-$ and $(Li^+)_2Br^-$ have been reported to be $\log K_2 = 5.5$[4] and 3.2,[21] respectively. Therefore, we think that both 1 : 1 and 2 : 1 interactions between Li^+ and X^- operate together in the system.

The addition of 1.0 mol dm^{-3} Et_4NClO_4 to 1.0×10^{-3} mol dm^{-3} Ph_3CBr caused the production of a small amount

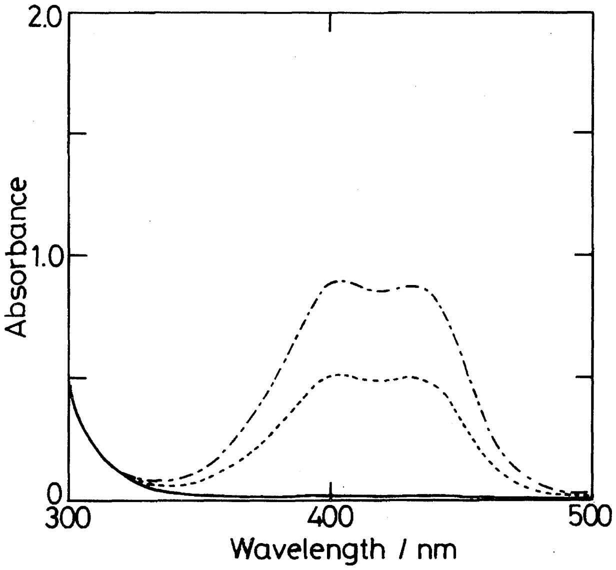


Fig. 1. Changes in UV-visible absorption spectra ($l = 1.0$ cm) of 1.0×10^{-3} mol dm^{-3} Ph_3CBr with the addition of $LiClO_4$ in acetonitrile at ca. 25 °C: (——) 0; (····) 0.5; (–·–) 1.0 mol dm^{-3} $LiClO_4$.

Table 1. The Formation of the Trityl Cation by the Addition of Alkali Metal and Alkaline-Earth Metal Perchlorates to 1.0×10^{-3} mol dm^{-3} Trtyl Chloride and Bromide in Acetonitrile at ca. 25 °C

	$[Ph_3CCl]=1.0\times10^{-3}$ mol dm^{-3} Yield/%		$[Ph_3CBr]=1.0\times10^{-3}$ mol dm^{-3} Yield/%	
[salts]	0.5 mol dm^{-3}	1.0 mol dm^{-3}	0.5 mol dm^{-3}	1.0 mol dm^{-3}
Et_4NClO_4		ca. 0		0.45
$LiClO_4$	0.13	0.36	1.28	2.28
$NaClO_4$				1.52
$Mg(ClO_4)_2$	1.80	1.65	3.03	2.81
$Ca(ClO_4)_2$	10.4	28.8	25.2	42.8
$Sr(ClO_4)_2$	3.50	15.5	6.08	27.9
$Ba(ClO_4)_2$	7.12	25.8	15.6	37.3

(0.45%) of Ph_3C^+, though no production of Ph_3C^+ from Ph_3CCl. Indeed, the increase in the ionic strength contributed slightly to the production of Ph_3C^+ from Ph_3CBr. However, the addition of 1.0 mol dm^{-3} Et_4NCl to 1.0×10^{-3} mol dm^{-3} Ph_3CCl and Ph_3CBr caused no effects, except that the tailing of Ph_3CBr around 300 nm showed a hypsochromic shift; the resultant Ph_3CBr spectrum was almost coincident with that of Ph_3CCl, itself. The effects of 0.01 mol dm^{-3} LiCl on 1.0×10^{-3} mol dm^{-3} Ph_3CCl or Ph_3CBr were negligibly small.

Much higher yields of Ph_3C^+ were observed by the addition of $Ba(ClO_4)_2$ to 1.0×10^{-3} Ph_3CBr in acetonitrile at ca. 25 °C. The absorbances at 403.5 and 431 nm of Ph_3C^+ increased with increasing concentration of $Ba(ClO_4)_2$: The yields of Ph_3C^+ were 15.6 and 37.3% with 0.5 and 1.0 mol dm^{-3}, respectively. The effects of alkaline-earth metal perchlorates decreased as $Ba^{2+}>Sr^{2+}\gg Mg^{2+}$; the effects of Ca^{2+} were exceptionally large (cf. Table 1), which can not be explained well at the moment. A disorder in the effects of M^{2+} was also observed for methoxy-substituted trityl chlorides (cf. the next section). The apparent effects of M^{2+} on Ph_3CCl were smaller than those on Ph_3CBr because of the smaller ionization of C^+–Cl^- without metal ions. The formation of Ph_3C^+ from Ph_3CX upon the addition of alkaline-earth metal ions (M^{2+}) could be explained by Eq. 2.

$$Ph_3C^+X^- + M(ClO_4)_2 \longrightarrow Ph_3C^+(ClO_4^-) + MX^+(ClO_4^-). \quad (2)$$

The stability of Ph_3C^+ in acetonitrile containing $Ba(ClO_4)_2$ was examined. As results, the Ph_3C^+ ion produced by the concentrated salt in acetonitrile was found to be very stable. The absorbance at 403 nm from 1.0×10^{-3} mol dm^{-3} Ph_3CBr with 1.0 mol dm^{-3} $Ba(ClO_4)_2$ decreased only 2% after 2 h, when stored in a 5 ml-flask. By the way, Brauman and Archie[22)] have reported the rate of the reaction between trityl ion and water in acetonitrile.

Figure 2 shows cyclic voltammograms of 2.0×10^{-3} mol dm^{-3} Ph_3CCl– MeCN solutions containing 1.0 mol dm^{-3} Et_4NClO_4 and 0.5 mol dm^{-3} $Ca(ClO_4)_2$. On a glassy carbon electrode, 2×10^{-3} mol dm^{-3} Ph_3CCl with an "indifferent" supporting electrolyte (Et_4NClO_4) gave no wave (from +0.3 to −1.0 V), whereas 2×10^{-3} mol dm^{-3} $Ph_3C^+PF_6^-$ gave quasi-reversible waves at $E_{pc}=-0.198$ V and $E_{pa}=-0.106$ V in acetonitrile. We believe that the appearance of CV waves ($E_{pc}=-0.20$ V and $E_{pa}=-0.12$ V) from Ph_3CCl upon the addition of 0.5 mol dm^{-3} $Ca(ClO_4)_2$ indicated the ionic dissociation of Ph_3CCl into $Ph_3C^+(ClO_4^-)$ and $CaCl^+(ClO_4^-)$.

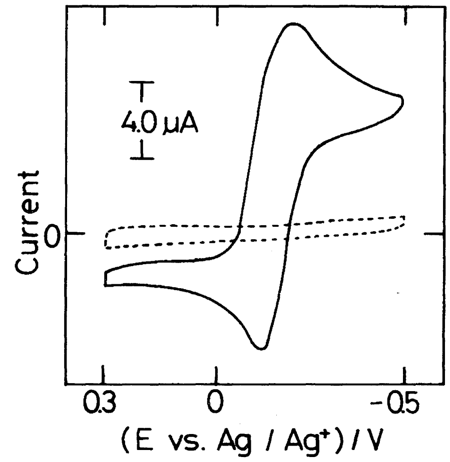


Fig. 2. Cyclic voltammograms of 2.0×10^{-3} mol dm^{-3} Ph_3CCl with and without $Ca(ClO_4)_2$ on a GC electrode (BAS) vs. a Ag/0.1 mol dm^{-3} $AgClO_4$–MeCN reference electrode: (——) 0.5 mol dm^{-3} $Ca(ClO_4)_2$; (····) 1.0 mol dm^{-3} Et_4NClO_4 as the supporting electrolyte.

Similar attempts to produce a stable Ph_3C^+ ion in benzonitrile, DMF, MIBK, and THF were not successful. However, in acetone, a small amount of Ph_3C^+ (0.1—0.2%) was produced from Ph_3CBr by the addition of 1.0 mol dm^{-3} $LiClO_4$ or $Ba(ClO_4)_2$. In conclusion, we propose that the ionization of Ph_3CCl and Ph_3CBr can be promoted by a specific interaction between the halide ions and alkali metal or alkaline-earth metal ions, and not merely the electrostatic interaction between them in acetonitrile.

Methoxy-Substituted Trityl Chlorides and Trityl Benzoate. The effects of methoxy-substituents on the production of trityl cations by the addition of metal ions were examined. It is well known that 4-methoxy, 4,4′-dimethoxy, and 4,4′,4″-trimethoxy-substituents stabilize the trityl cations in solution.[13b)] In acetonitrile, 4-methoxytrityl chloride ($4\text{-}MeOC_6H_4Ph_2CCl$) dissociated very slightly by itself: An apparent dissociation constants was evaluated to be $K_d=3.4\times10^{-9}$ (mol dm^{-3}). However, upon the addition of $LiClO_4$, an acetonitrile solution of 5.0×10^{-4} mol dm^{-3} 4-$MeOC_6H_4Ph_2CCl$ turned a strong yellow color to give two absorption bands at around 390 and 470 nm (Fig. 3). By the way, the addition of ≥0.2 mol dm^{-3} CH_3SO_3H to 2.0×10^{-4} mol dm^{-3}4-$MeOC_6H_4Ph_2CCl$ gave the 4-methoxytrityl cation quantitatively with the absorption band at around 390 and 470 nm: the molar absorptivity (ε/cm^{-1} mol^{-1} dm^3) of 6.1×10^4 at $\lambda_{max}=472$ nm in MeCN (cf., log $\varepsilon=4.75$ at $\lambda_{max}=476$ nm by Deno et al.[23]). The production yield of the 4-methoxytrityl cation from 4-$MeOC_6H_4Ph_2CCl$ with 1.0 mol dm^{-3} $LiClO_4$ was evaluated to be 49.3%, using the value of $\varepsilon=6.1\times10^4$ (cf. Table 2). The addition of $NaClO_4$, $Mg(ClO_4)_2$, and $Ba(ClO_4)_2$ also gave two absorption bands at around 390 and 470 nm; the production yields of the 4-methoxytrityl cation are shown in Fig. 4. At lower salt concentrations, the effects of salts increased as $Li^+<Na^+<Mg^{2+}<Ba^{2+}$. Strangely for $Mg^{2+}$the yield started to decrease at >0.1 mol dm^{-3}. Decrease in the yields with increasing concentration of $Mg(ClO_4)_2$ might be explained as follows: A small amount of MgO contained in dried $Mg(ClO_4)_2$ would produce $Mg(OH)_2$ by a reaction with H_2O in "dried" MeCN; the carbocations are ready to react with the hydroxide ion to form colorless triphenylmethanols. Decreases in the yields were also observed for >0.2 mol dm^{-3} $NaClO_4$ (an Aldrich reagent), suggesting that the $NaClO_4$ contained a minor amount of sodium oxide in $NaClO_4$. The addition of Et_4NClO_4 to 4-$MeOC_6H_4Ph_2CCl$ gave a small amount of the trityl cation, e.g., ca. 1.3% at 1.0 mol dm^{-3} Et_4NClO_4: The effects of Et_4N^+ were much smaller than those of metal cations, M^+ or M^{2+}.

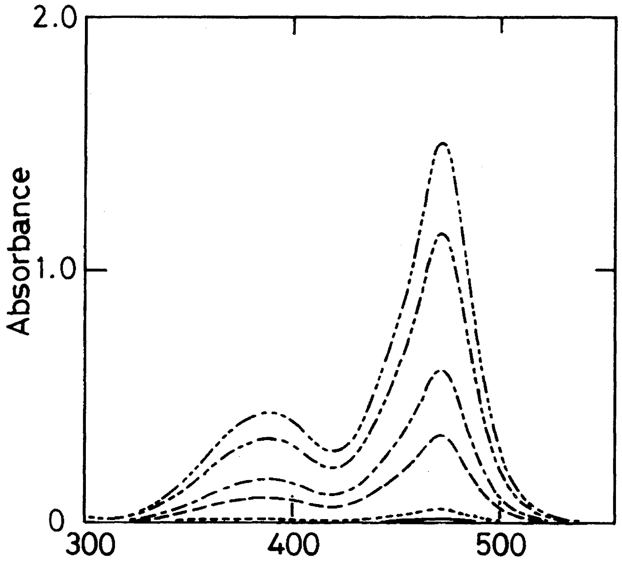


Fig. 3. Changes in UV-visible absorption spectra (l=0.1 cm) of 5.0×10^{-4} mol dm^{-3} 4-methoxytrityl chloride with increasing concentration of $LiClO_4$ in acetonitrile: (—) 0; (····) 1.0×10^{-2}; (- - -) 0.1; (-··-) 0.2; (-···-) 0.5; (-····-) 1.0 mol dm^{-3} $LiClO_4$.

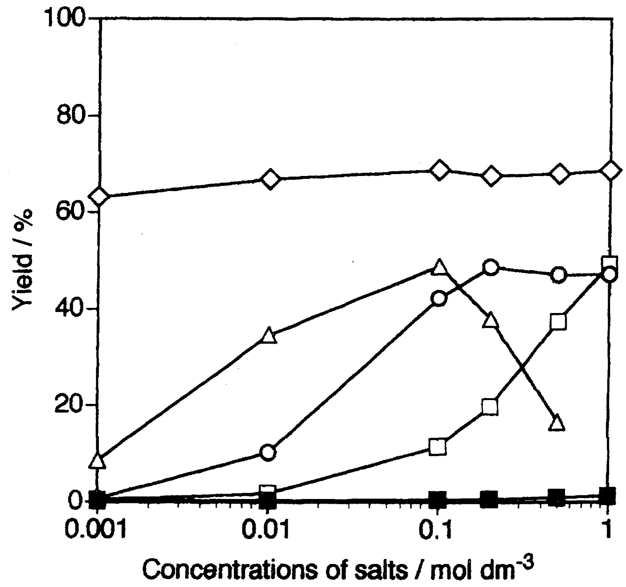


Fig. 4. The production yields of the 4-methoxytrityl cation by the addition of alkali metal and alkaline-earth metal perchlorates to 5.0×10^{-4} mol dm^{-3} 4-methoxytrityl chloride in acetonitrile: (□) $LiClO_4$; (○) $NaClO_4$; (△) $Mg(ClO_4)_2$; (◇) $Ba(ClO_4)_2$; (■) Et_4NClO_4.

Figure 5 shows the formation yields of the 4,4′-dimethoxytrityl cation ($\varepsilon=3.0\times10^4$ at 410 nm, cf. Table 2) upon the addition of alkali metal (M^+) and alkaline-earth metal (M^{2+}) perchlorates. The effects of the metal ions increased again as $Li^+<Na^+<Mg^{2+}<Ba^{2+}$ at lower metal concentrations. However, at higher concentrations, the effects of

Table 2. The Yields of the Trityl Cations from 4-Methoxy-Substituted Trityl Chlorides in the Presence of 1.0 mol dm^{-3} Salts in Acetonitrile

Methoxy-substituted	Concn	K_d[a)]	Yields of the trityl cations/%			λ_{max}	(ε/cm^{-1} mol^{-1} dm^3)
trityl chroride	mod dm^{-3}	mol dm^{-3}	None	Et_4NClO_4	$LiClO_4$		
$(4\text{-}MeOC_6H_4)Ph_2CCl$	5.0×10^{-4}	3.4×10^{-9}	0.21	1.3	49.3	390 nm 472 nm	(1.8×10^4) (6.1×10^4)[b)]
$(4\text{-}MeOC_6H_4)_2PhCCl$	5.0×10^{-4}	1.0×10^{-5}	15.0	37.5	78.4	410 nm 497 nm	(3.0×10^4) (ca. 8×10^4)[c)]
$(4\text{-}MeOC_6H_4)_3CCl$	2.0×10^{-4}	1.4×10^{-4} (4×10^{-3})[e)]	56.0	78.4	85.2	482 nm	(8.6×10^4)[d)]

a) Apparent dissociation constants ($RCl \rightleftarrows R^+ + Cl^-$, K_d) of the trityl chlorides in the absence of salts. b) cf. the literature value, as shown in the text. c) cf. Ref. 24. d) cf. the value in Ref. 23: log $\varepsilon=5.02$ at $\lambda_{max}=483$ nm. e) In nitrobenzene, cf., Ref. 13b.

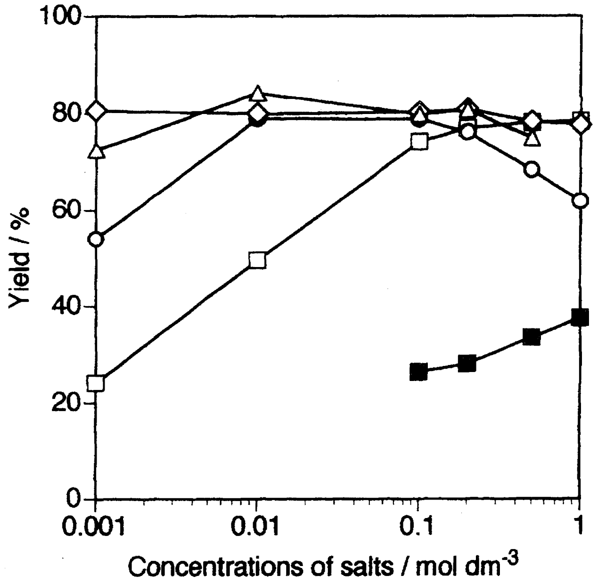


Fig. 5. The production yields of the 4,4′-dimethoxytrityl cation by the addition of alkali metal and alkaline-earth metal perchlorates to 5.0×10^{-4} mol dm^{-3} 4,4′-dimethoxytrityl chloride in acetonitrile: (□) $LiClO_4$; (○) $NaClO_4$; (△) $Mg(ClO_4)_2$; (◇) $Ba(ClO_4)_2$; (■) Et_4NClO_4.

metal ions were close to each other. Decreases in the yields of the trityl cation were observed for higher concentrations of $NaClO_4$ and $Mg(ClO_4)_2$. The presence of an "indifferent" salt Et_4NClO_4, caused an increase in yield from 15% (no salt) to 37.5% (at 1.0 mol dm^{-3}). Figure 6 clearly shows that the formations of the trityl cations from the corresponding chlorides were increased upon the addition of $LiClO_4$ as non-substituted < 4-methoxy < 4,4′-dimethoxy < 4,4′,4″-trimethoxytrityl chloride.

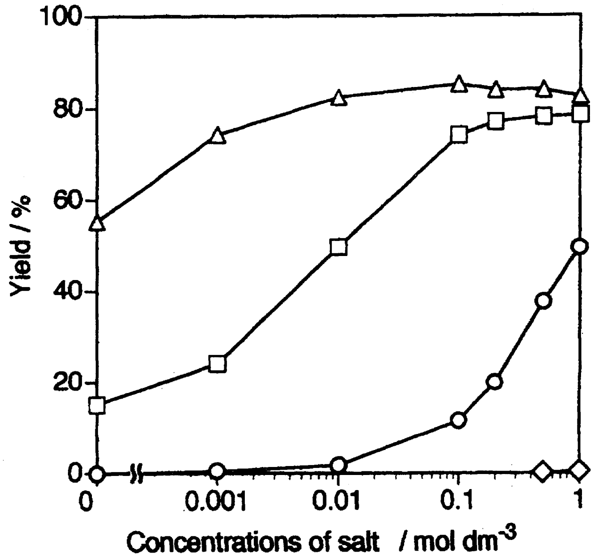


Fig. 6. The production yields of trityl cations by the addition of $LiClO_4$ to non-substituted, 4-, 4,4′-, and 4,4′, 4″-methoxytrityl chlorides in acetonitrile: (◇) trityl chloride (1.0×10^{-3} mol dm^{-3}), (○) 4-methoxytrityl chloride (5.0×10^{-4} mol dm^{-3}); (□) 4,4′-dimethoxytrityl chloride (5.0×10^{-4} mol dm^{-3}); (△) 4,4′,4″-trimethoxytrityl chloride (2.0×10^{-4} mol dm^{-3}).

The formation of trityl cations was observed by means of ^{1}H NMR; also, the formation of trityl cations upon the addition of $NaClO_4$ or $Ba(ClO_4)_2$ was applied to a simple preparation of methoxy-substituted trityl perchlorates, $(4\text{-}MeOC_6H_4)_nPh_{3-n}CClO_4$ (n=1—3).[25a] With the higher concentrations of RX (ca. 0.03 mol dm^{-3}) in acetonitrile, we obtained precipitates between X^- and alkali metal and alkaline-earth metal perchlorates (except for Li^+ and Mg^{2+}). The precipitates of NaCl and $BaCl^+$ (ClO_4^-) (tentatively assigned) were characterized by a component analysis (e.g.,

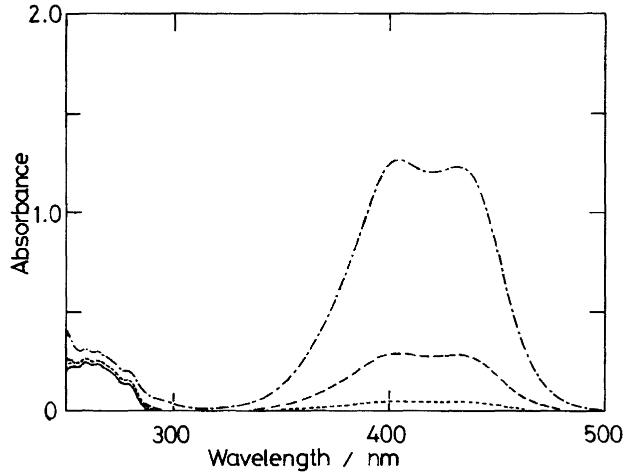


Fig. 7. Changes in UV-visible absorption spectra (l=1.0 cm) of 2.0×10^{-4} mol dm^{-3} triphenylmethyl benzoate with increasing concentration of $LiClO_4$ in acetonitrile containing 1.0×10^{-3} mol dm^{-3} CH_3SO_3H: (—) 0; (····) 0.1; (- - -) 0.2; (–·–) 0.5 mol dm^{-3} $LiClO_4$.

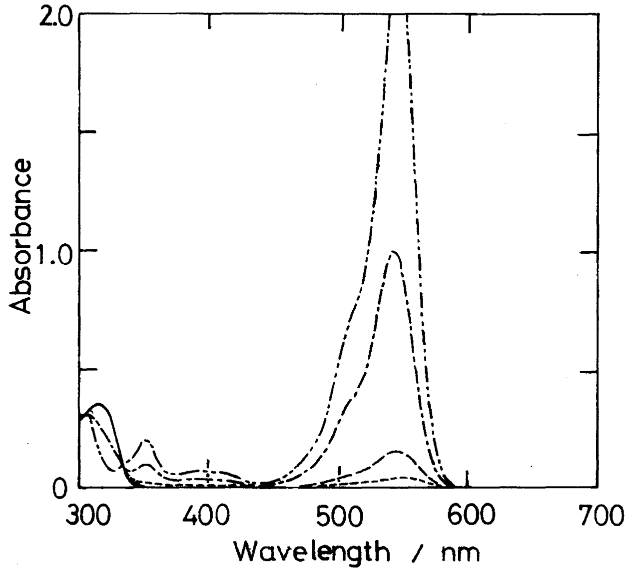
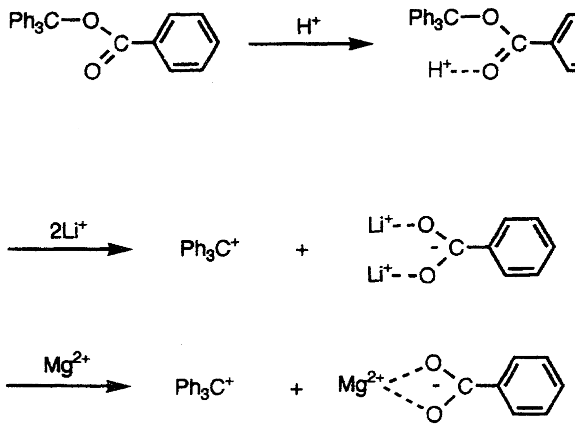


Fig. 8. Changes in UV-visible absorption spectra (l = 0.1 cm) of 2.0×10^{-4} mol dm^{-3} Rhodamine with increasing concentration of $LiClO_4$ in acetonitrile: (—) 0; (····) 1.0×10^{-4}; (- - -) 1.0×10^{-3}; (–·–) 1.0×10^{-2}; (–··–) 0.1 mol dm^{-3} $LiClO_4$.

$[Ba^{2+}]:[Cl^-]:[ClO_4^-]=1:1:1$), IR, X-ray powder method, and thermal analysis.[25b)] In the present systems, the curious order of alkali metal and alkaline-earth metal ions in the effects on the formation yields of the trityl cations may have been caused by both the coordination and precipitation reaction abilities. Incidentally, it is known that trityl perchlorate can be prepared from trityl chloride and $AgClO_4$ in nitrobenzene upon precipitation by benzene addition.[26)]

On the other hand, the addition of $LiClO_4$ or $Mg(ClO_4)_2$ to 2.0×10^{-4} mol dm^{-3} trityl benzoate ($Ph_3COOCPh$) did not give the trityl cation. However, the addition of methanesulfonic acid (CH_3SO_3H) to 2.0×10^{-4} mol dm^{-3} trityl benzoate caused the formation of the trityl cation in acetonitrile: the yields of Ph_3C^+ were 0.0, 0.13, and 5.9% at 1.0×10^{-3}, 1.0×10^{-2}, and 0.1 mol dm^{-3} CH_3SO_3H, respectively. Figure 7 shows the formation of the Ph_3C^+ ion in acetonitrile upon the addition of $LiClO_4$ to 2.0×10^{-4} mol dm^{-3} $Ph_3COOCPh$ in the co-presence of 1.0×10^{-3} mol dm^{-3} CH_3SO_3H. The two peaks at around 403 and 431.5 nm were characteristic of the trityl cation (cf., the first section). The yields of the trityl cation were 0.58, 3.6, and 15.9% for 0.1, 0.2, and 0.5 mol dm^{-3} $LiClO_4$, respectively. The higher yields were obtained by the co-presence of higher concentrations of methanesulfonic acid: 42.6 and 82.0% at 1.0×10^{-2} and 0.1 mol dm^{-3} CH_3SO_3H, respectively, with 0.5 mol dm^{-3} $LiClO_4$ (cf. Table 3). The addition of 0.1—0.5 mol dm^{-3} $Mg(ClO_4)_2$ to 2.0×10^{-4} mol dm^{-3} $Ph_3COOCPh$ in the presence of 1.0×10^{-2} mol dm^{-3} CH_3SO_3H gave a constant yield of 87—89%. As shown in Scheme 1, at first, the acid (or H^+) may attack the carbonyl group in the compound; then, the partially activated (or ionized) benzoate would react with Li^+ or Mg^{2+} to form the trityl cation. A strong interaction between $PhCOO^-$ and Li^+ or Na^+ has been established;[3,5)] the formation constant of a soluble species, $PhCOO^-(Li^+)_2$, has been reported to be $K=$ ca. 1×10^9 in acetonitrile.[3)] The interaction between $PhCOO^-$ and Mg^{2+} should be larger than that between $PhCOO^-$ and Li^+ in acetonitrile, since higher yields of Ph_3C^+ were obtained with $Mg(ClO_4)_2$ than $LiClO_4$. In the final section of the present paper, direct evidence will be provided for strong chemical interactions between benzoate ions and alkaline-earth metal ions in acetonitrile.



Scheme 1.

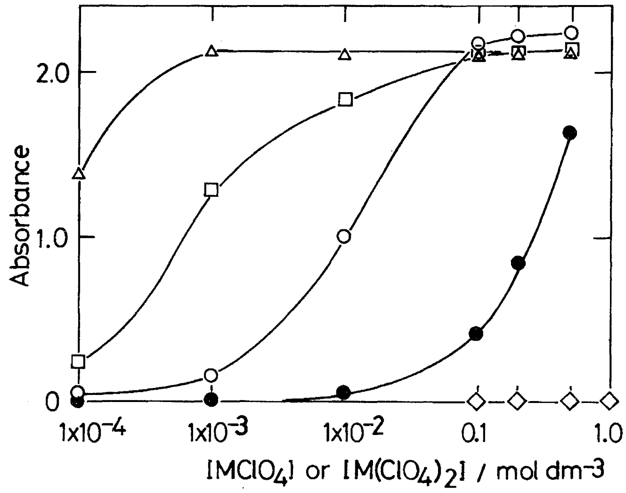


Fig. 9. Changes in absorbance ($l=0.1$ cm) of λ_{max} of 2.0×10^{-4} mol dm^{-3} Rhodamine with changing concentration of alkali metal and alkaline-earth metal perchlorates: (○) $LiClO_4$; (●) $NaClO_4$; (△) $Mg(ClO_4)_2$; (□) $Ba(ClO_4)_2$; (◇) Et_4NClO_4.

Rhodamine and Crystal Violet Lactone. In the previous section, it was shown that the formation of triarylmethyl cations from RX (X = Cl, Br, and the benzoate) was caused by an interaction between X^- and M^+ or M^{2+}. In the present section, we would like to demonstrate that the interactions between X^- and M^+ or M^{2+} are strong enough to cleave intramolecular covalent bondings (C–O bonds) of some γ-lactones, i.e., Rhodamine (or Rhodamine B base) and Crystal Violet lactone.

Table 3. The Yield of the Trityl Cation from 2.0×10^{-4} mol dm^{-3} Trityl Benzoate with the Addition of $LiClO_4$ and $Mg(ClO_4)_2$ in the Co-Presence of CH_3SO_3H in Acetonitrile

$[CH_3SO_3H]$/mol dm^{-3}	0	1.0×10^{-3}	1.0×10^{-2}	0.1
No salt	0%	ca. 0%	0.13%	5.9%
$[LiClO_4]=0.1$ mol dm^{-3}	0%	0.58%	9.8%	42.8%
$[LiClO_4]=0.2$ mol dm^{-3}	0%	3.6%	21.4%	60.5%
$[LiClO_4]=0.5$ mol dm^{-3}	0%	15.9%	42.6%	82.0%
$[Mg(ClO_4)_2]=0.1$ mol dm^{-3}	0%		87.6%	
$[Mg(ClO_4)_2]=0.2$ mol dm^{-3}	0%		88.8%	
$[Mg(ClO_4)_2]=0.5$ mol dm^{-3}	0%		86.6%	

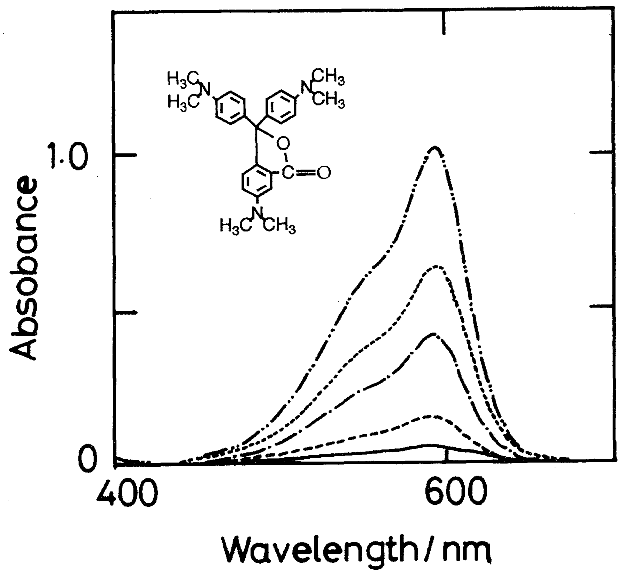


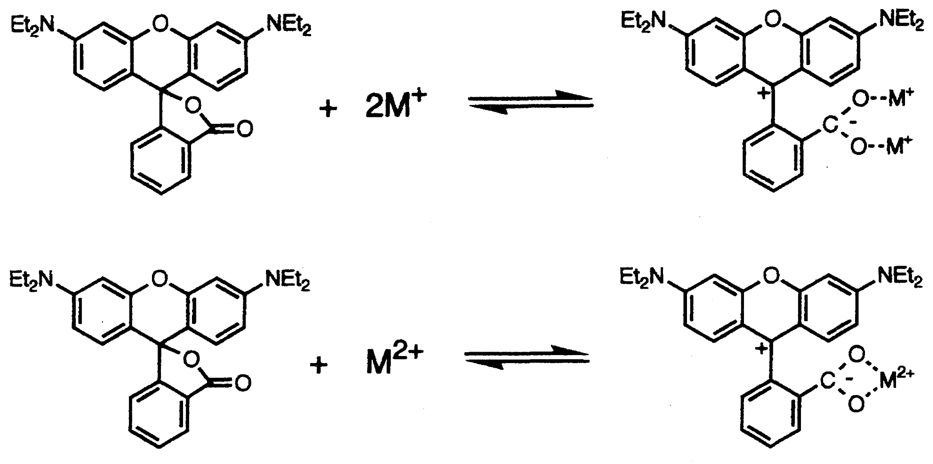
Fig. 10. Changes in UV-visible absorption spectra ($l = 0.1$ cm) of 2.0×10^{-4} mol dm^{-3} Crystal Violet lactone with the addition of $Mg(ClO_4)_2$ in acetonitrile: (—) 1.0×10^{-2}; (- - -) 0.1; (–•–) 0.2; (••••) 0.3; (–••–) 0.5 mol dm^{-3} $Mg(ClO_4)_2$.

Figure 8 shows the changes of UV-visible absorption spectra of 2.0×10^{-4} mol dm^{-3} Rhodamine (or Rhodamine B base: HCl free) upon the addition of $LiClO_4$ in acetonitrile. Without $LiClO_4$, Rhodamine gave almost no absorption band in the visible region: an absorbance of ca. 0.005 (with $l = 0.1$ cm) at $\lambda = 544$ nm. However, upon the addition of a small amount of $LiClO_4$, the solution turned red color with fluorescence. The absorbance at around 543 nm increased with increasing concentration of $LiClO_4$, up to ca. 2.2 (at 0.1—0.5 mol dm^{-3} $LiClO_4$). Other metal ions also caused a red color with fluorescence: $NaClO_4$ 543 nm; $Mg(ClO_4)_2$ 549 nm; $Ba(ClO_4)_2$ 547 nm at 0.1 mol dm^{-3} salt concentration. Figure 9 shows the changes in absorbances at λ_{max} of Rhodamine with a variety of concentrations of salts. The effects of Et_4NClO_4 on 2.0×10^{-4} mol dm^{-3} Rhodamine–MeCN solution were very small: 1.0 mol dm^{-3} Et_4NClO_4 caused a peak absorbance of 0.075 (with $l = 1.0$ cm) around 540 nm. Remette and Sandell[27)] have reported the formation of a zwitterion R^{+-} ($\varepsilon = 1.1\times10^5$, $\lambda = 553$ nm) from Rhodamine B in 1.0 mol dm^{-3} KCl aqueous solution.

In acetonitrile, the addition of CH_3SO_3H to 2.0×10^{-4} mol dm^{-3} Rhodamine caused an increase in a peak at 555 nm (1.0×10^{-4}—1.0×10^{-2} mol dm^{-3} CH_3SO_3H), a successive decrease of the peak (0.1—0.2 mol dm^{-3} CH_3SO_3H) and the appearance of a new peak at 493 nm; the latter peak showed the formation of $RH_2{}^{2+}$, referring to the literature.[27)] A stronger acid, CF_3SO_3H, at lower concentrations, gave a similar behavior with Rhodamine. The addition of a strong base, 1,1,3,3-tetramethylguanidine (0.1—2.0 mol dm^{-3}), did not change the absorption spectra (at least for 350—800 nm) of Rhodamine in acetonitrile, indicating no interaction between the γ-lactone and the base. The red color with fluorescence (even pink color because of the strong fluorescence) of Rhodamine in the presence of the metal perchlorates can be explained by the formation of a zwitterion (R^+–COO^-), which should have been caused by an interaction between the metal ions (M^+ or M^{2+}) and the intramolecule carboxylate (C–COO^- from the γ-lactone) of Rhodamine (cf. Scheme 2). For the present system, the effects of M^+ and M^{2+} were found to be in the normal order ($Na^+ < Li^+ < Ba^{2+} < Mg^{2+}$), probably because a precipitation reaction of the large zwitterion is not apt to occur, even with Na^+ or Ba^{2+}.

Small amounts of water would always be brought into acetonitrile solutions upon the addition of "dried" salts. However, we think that the amount of water brought by "dried" salts must be too small to cause a cleavage of the γ-lactone ring of Rhodamine, judging from the fact that the formation of the zwitterion (red color with fluorescence) remained at a very low level, even at ca. 1 vol% contents of H_2O in acetonitrile. Hinckley et al.[28)] have reported the solvatochromism and thermochromism of Rhodamine solutions.

The γ-lactone ring of Crystal Violet lactone in acetonitrile was cleaved by the addition of $Mg(ClO_4)_2$ to give a strong violet color, whereas, $LiClO_4$, $NaClO_4$, or $Ba(ClO_4)_2$ had no (or very small) effects in solution. Figure 10 shows the changes in the spectra of 2.0×10^{-4} mol dm^{-3} Crystal Violet lactone in the presence of various concentrations of



Scheme 2.

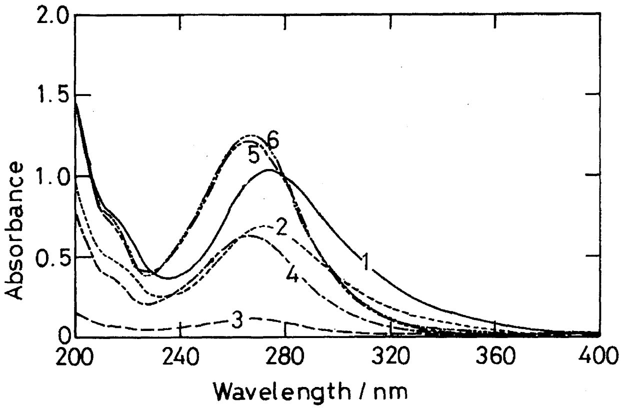


Fig. 11. Changes in UV absorption spectra ($l = 0.1$ cm) of *p*-nitrobenzoate ($[Et_4N^+p\text{-}NO_2C_6H_4COO^-] = 1.0\times10^{-3}$ mol dm^{-3}) with the addition of $Ca(ClO_4)_2$ in acetonitrile: (1) 0; (2) 2.0×10^{-4}; (3) 5.0×10^{-4}; (4) 1.0×10^{-3}; (5) 2.0×10^{-3}; (6) 5.0×10^{-2} mol dm^{-3} $Ca(ClO_4)_2$. Et_4NClO_4 was added to keep the ionic strength to be 0.1, except for 0 and 5.0×10^{-2} mol dm^{-3} of $Ca(ClO_4)_2$.

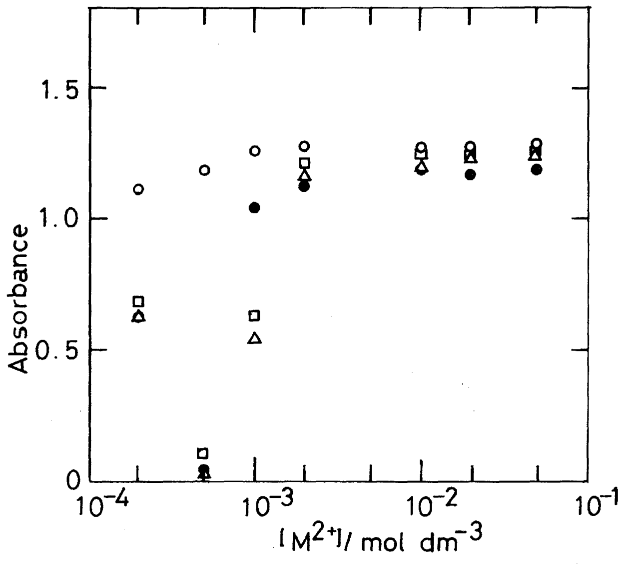
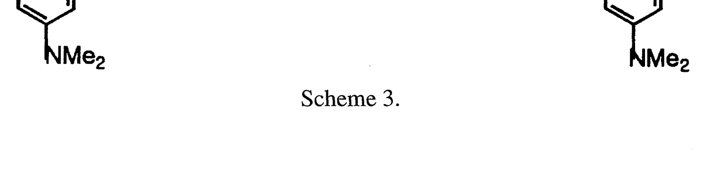


Fig. 12. The change of absorbance ($l = 0.1$ cm) at λ_{max} of *p*-nitrobenzoate ($[Et_4N^+p\text{-}NO_2C_6H_4COO^-] = 1.0\times10^{-3}$ mol dm^{-3}) with the addition of $M(ClO_4)_2$ in acetonitrile at a constant ionic strength ($\mu = 0.1$, except for 5.0×10^{-2} mol dm^{-3} $M(ClO_4)_2$); (○) Mg^{2+}; (△) Ca^{2+}; (□) Sr^{2+}; (●) Ba^{2+}.

$Mg(ClO_4)_2$. While the absorbance of the peak at 270 nm decreased, the absorbance at 598 nm increased linearly with increasing concentration of $Mg(ClO_4)_2$. The magnesium ion has a large "ionic potential" value, and therefore a larger coordination ability than the other ions. It goes without saying that the addition of a strong base, 1,1,3,3-tetramethylguanidine, to a Crystal Violet lactone–MeCN solution caused no violet color. On the other hand, the addition of CH_3SO_3H to a 2.0×10^{-4} mol dm^{-3} Crystal Violet lactone–MeCN solution caused a pale-violet color. The absorbance of the peak at ca. 600 nm reached its maximum value (at most 0.06 with $l = 0.1$ cm) at 2.0×10^{-4} mol CH_3SO_3H, and then decreased with further addition of CH_3SO_3H. A weaker acid, CF_3COOH, gave a maximum absorbance of 0.08 ($l = 0.1$ cm) at 1.0×10^{-3} mol dm^{-3} CF_3COOH. The peak at around 270 nm almost disappeared with 0.1 mol dm^{-3} CF_3COOH. We could not explain the reason why the violet color disappeared at higher acid concentrations, even though the γ-lactone ring of Crystal Violet lactone should be cleaved by stronger acids. Rhodamine may differ much from crystal violet lactone due to its xanthene structure. Mckinley et al.[29] determined the stabilities of aryl carbocations by NMR, while discussing the difference between 9-aryl-9-xanthenyl and trityl cations. The above results with Rhodamine and Crystal Violet lactone suggested that the γ-lactone rings can be cleaved by a strong interaction between carboxylate (ion) and M^+ or M^{2+} (cf. Schemes 2 and 3). Kortum and Vogel[30] have reported that, on surfaces of alkali halides and alkaline-earth metal sulfates, the γ-lactone of Malachite Green-*o*-carboxylic acid is cleaved to give a zwitterion. In our systems, however, the reactions occurred in bulk solution and not on the surfaces of solid salts or of glass vessels. Very recently,[31] the valence X-ray photoelectron spectra of UV-visible absorption spectra of several leuco dyes (DEAMAF, Crystal Violet lactone, Rhodamine B base) were compared with the MO calculation results.

Strong Interactions between Benzoate Ions and M^{2+}. Figure 11 shows the UV-visible absorption spectra of 1.0×10^{-3} mol dm^{-3} *p*-nitrobenzoate ion ($Et_4N^+p\text{-}NO_2C_6H_4COO^-$) in the presence of various concentrations of $Ca(ClO_4)_2$ in acetonitrile. The absorbance of a peak at 274 nm decreased with increasing concentration of Ca^{2+}, forming white precipitates. The absorbance at around 270 nm reached its minimum at 5.0×10^{-4} mol dm^{-3} Ca^{2+}; however, at 1.0×10^{-3} mol dm^{-3} Ca^{2+}, the precipitates were redissolved to give a peak at 267 nm, in spite of increasing concentration of the common ion. The absorbance of the peak increased with further addition of Ca^{2+}. The changes in the absorbances of the peaks are shown in Fig. 12. Strontium



Scheme 3.

and barium ions exhibited results similar to those of Ca^{2+}. The precipitation and successive re-dissolution of precipitates with increasing concentration of alkaline-earth metal ions (M^{2+}) at a constant ionic strength can be explained as follows:

$$2\,p\text{-}NO_2C_6H_4COO^- + M^{2+} \rightleftarrows (p\text{-}NO_2C_6H_4COO^-)_2M^{2+}\downarrow \quad (3)$$

$$(p\text{-}NO_2C_6H_4COO^-)_2M^{2+} + M^{2+} \rightleftarrows 2\,p\text{-}NO_2C_6H_4COO^-M^{2+}\uparrow \quad (4)$$

Similar reactions should be expected with Mg^{2+}, even with the precipitation of $(p\text{-}NO_2C_6H_4COO^-)_2\ Mg^{2+}$ did not occur: the Mg^{2+} ion may be coordinated strongly by four oxygen atoms.

The interaction between the non-substituted benzoate ion ($[Et_4N^+PhCOO^-] = 5.0\times10^{-3}\ mol\ dm^{-3}$) and alkaline-earth metal ions was also examined. The peak absorbances at around 220—230 nm were monitored to give a behavior similar to that of *p*-nitrobenzoate. These results indicated that the 1 : 1 complex formation abilities between the benzoate ions and alkaline-earth metal ions were strong enough to cause a re-dissolution of precipitates of the no-charged salts in acetonitrile. Similar interactions with M^{2+} in the same solvent have been reported for nitrophenolate ions and the tropolonate ion.[10]

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