^{1}H and ^{13}C NMR Detection of the Carbocations or Zwitterions from Rhodamine B Base, a Fluoran-Based Black Color Former, Trityl Benzoate, and Methoxy-Substituted Trityl Chlorides in the Presence of Alkali Metal or Alkaline Earth Metal Perchlorates in Acetonitrile Solution

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The cleavage of C–O bonds in two fluoran-based dyes by the addition of alkali metal ($M^{+} = Li^{+}, Na^{+}$) and alkaline earth metal ($M^{2+} = Mg^{2+}, Ba^{2+}$) perchlorates in acetonitrile solution was examined by means of UV-visible absorption and ^{1}H and ^{13}C NMR spectroscopy at room temperature. Although the ^{1}H NMR signals of the xanthene part of Rhodamine B base (3′,6′-bis(diethylamino)fluoran) were shifted toward lower fields, those of the isobenzofuran (or the benzoate) part were not shifted much upon the addition of M^{+} and M^{2+}. The appearance of ^{13}C signals at 163.6 and 162.4 ppm (vs TMS) in the presence of Li^{+} and Ba^{2+}, respectively, confirmed the formation of the zwitterions from Rhodamine B base. The assignments of the ^{1}H and ^{13}C signals were performed by the HMBC method. The colored zwitterion of a practical black color former, 2′-anilino-6′-dibutylamino-3′-methylspiro[3*H*-isobenzofuran-1, 9′-(9*H*)xanthene]-3-one, was produced by the addition of M^{+} and M^{2+}. The ^{13}C NMR signals at 162.2 and 159.8 ppm in the presence of 2.0 mol dm^{-3} $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$, respectively, gave conclusive evidence of the formation of the sp^{2}-hybrid carbon center for the black color former. The interaction between the metal ions and the zwitterions from the fluoran-based dyes decreased as $Mg^{2+} > Ba^{2+} > Li^{+} > Na^{+}$. The 1 : 1 complex formation constants with the metal ions for both dyes were evaluated based on the UV-visible absorption data. The smaller formation constants of the black color former, compared with those of Rhodamine B base, indicate some more difficulty in the cleavage of the γ-lactone ring, which is probably based on the asymmetric structure of the compound, i.e, only a single dibutylamono-group at the 3′- and 6′-positions. The evidence for the formation of both the trityl cation and the benzoate ion was obtained by the ^{1}H NMR signals from trityl benzoate in the presence of $Mg(ClO_4)_2$ in CD_3CN containing a small amount of CF_3SO_3D. The C–Cl bond cleavage of 4-methoxy, 4,4′-dimethoxy, and 4,4′,4″-trimethoxytrityl chlorides, through the chemical interaction between Ba^{2+} and Cl^{-} in acetonitrile soluition, was justified by our ^{13}C NMR results.

Fluoran leuco dyes have been widely used as heat- and pressure-sensitive recording or copying materials. The colors are developed by the interaction between the color former and developers, such as active clay, phenols, and zinc salicylates.[1] The application of other metallic ions (Al^{3+}, Cd^{2+}, Ca^{2+}, and Sr^{2+}) was likewise supposed to improve the fade resistance and give a similar intensity.[2] The cleavage of the γ-lactone ring, that is, the formation of zwitterions, is the cause of the deep colors.[3] Kortum and Vogel[4] 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. They showed that the cleavage of the γ-lactone may be caused by a polarizing effect of the cations on the surface of the metal halide crystal lattice. Based on the ^{13}C NMR, X-ray, and crystallographic data, Rihs and Weis[5] concluded the open carboxylate structures for the complexes of Crystal Violet lactone and a fluoran-derivative with Zn^{2+} or Cd^{2+}, which were prepared in acetone solution.

Hojo et al.[6] have definitely demonstrated by means of electrochemical and spectroscopic technics that alkali metal (M^{+}) and alkaline earth metal ion (M^{2+}) can take part directly in chemical reactions in solution. The formation of stable carbocations from 4-methoxy-substituted trityl chlorides ($(4\text{-}MeOC_6H_4)_nPh_{3-n}CCl$), through the interaction between Cl^{-} and M^{+} or M^{2+}, has been observed by ^{1}H NMR.[7] It may be true that little attention has been paid to such “minor” interactions. Gordon[8] has stated that covalent bonding is believed to be absent in alkali metal-halide and alkaline earth-fluoride ion pairs. However, if carbocations are stabilized in the presence of alkali metal and alkaline earth metal ions, the solvolysis re-

Rhodamine B base

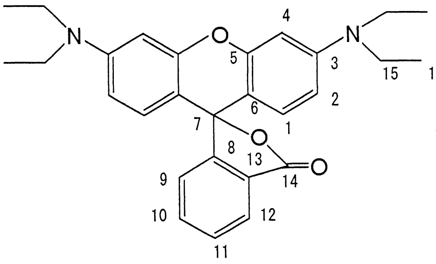

Chart 1.

A Fluoran-Based Black Color Former

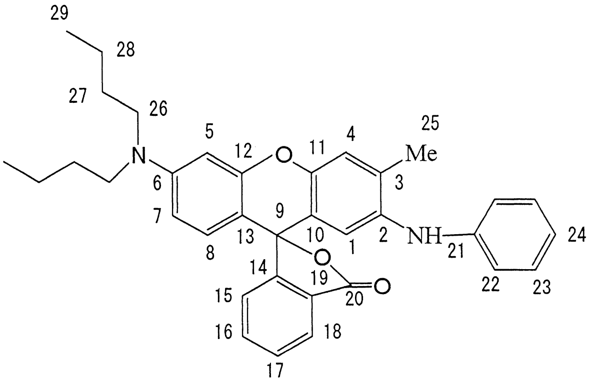

Chart 2.

action rates in S_N1 should be enhanced. This hypothesis has been verified by exponential increases in the S_N1 solvolysis rates of aliphatic halides in the presence of concentrated metal ions.[9] Hojo et al.[10] have proposed that "isolated" water molecules (H–O–H), which are converted from bulk water by concentrated salts, may behave just like "dihydrogen ether" ([R]H–O–H[R]). The Raman spectra[10,11] of concentrated salt solutions have supported the idea of a "dihydrogen ether." It must be possible that a very small but direct "chemical" interaction between M^+ or M^{2+} and simple anions, such as halide and carboxylate ions, occurs even in aqueous or organic-aqueous solutions if they are in the "dihydrogen ether" conditions. In kinetic studies, we have a merit to be able to amplify a minor increase in the concentration of an intermediate species, which can never be detected in the equilibrium sense, into an observable large increase in the reaction rate.

In a previous study,[12] the cleavage of the γ-lactone ring of Rhodamine B base and Crystal Violet lactone in the presence of M^+ or M^{2+} in acetonitrile was examined by means of UV-visible spectroscopy. The color changes of sulfonephthaleins, such as Phenol Red and Bromothymol Blue, were also attributed to cleavage of the γ-sultone rings through a direct interaction between M^+ or M^{2+} and the benzensulfonate ion (function) of the sulfonephthaleins in acetonitrile.[13]

In the present paper, we report on the ^{1}H and ^{13}C NMR spectroscopic evidence of a γ-lactone cleavage of Rhodamine B base (Chart 1) in the presence of alkali metal and alkaline earth metal perchlorates in acetonitrile. The dark color development from a practical fluoran-based black color former (Chart 2) in the presence of the metal ions in acetonitrile solution was examined by means of UV-visible and ^{13}C NMR spectroscopy. Yanagita et al.[14] have performed ^{13}C NMR and electronic absorption spectroscopic studies on the equilibrium between the colorless lactone and the colored zwitterion forms of the black color former in phenols. Several fluoran lueco dyes were newly synthesized, and the color developments have been observed not only in hydrogen-bond donor solvents, but also in alkaline media for fluorans having an –NH-phenyl group.[15] The valence XPS and UV-visible absorption spectra were analyzed using MO calculations for triphenylmethane and fluoran dyes, including Crystal Violet lactone, Rhodamine B base, and the black color former.[16] The crystal and molecular structures of several fluoran-based color formers were determined by single-crystal X-ray diffraction analysis.[17]

The main purposes of the present study were, firstly, a further confirmation of the direct chemical interaction with alkali metal and alkaline earth metal ions in solution and, secondly, to propose alkaline earth metal perchlorates as new candidates of color developers for the fluoran-based black color former in an aprotic solvent. ^{1}H NMR evidence is provided concerning the complete dissociation or separation of the trityl cation from trityl benzoate by the addition of $Mg(ClO_4)_2$ in the co-existence of a small amount of a "strong" acid. In this connection, further studies on the formation of 4-methoxy-, 4,4′-dimethoxy-, and 4,4′,4″-methoxytrityl cations from the trityl chlorides in acetonitrile were performed using the ^{13}C NMR method.

Experimental

Rhodamine B base (3′,6′-bis(diethylamino)fluoran) was purchased from Aldrich. The preparation method of the fluoran-based black color former, 2′-anilino-6′-dibutylamino-3′-methyl-spiro[3*H*-isobenzofuran-1,9′-(9*H*)xanthene]-3-one, was described in a previous paper.[14] Trityl (TCI, GR grade), 4-methoxytrityl (Aldrich, 97%), 4,4′-dimethoxytrityl (Aldrich, 95%), and 4,4′,4″-trimethoxytrityl chlorides (Aldrich, tech. grade), and trityl benzoate (Aldrich) were used without further purification. Methanesulfonic (Wako, GR grade) and trifluoromethanesulfonic acids (Wako or TCI, GR grade), and CF_3SO_3D (Aldrich, 98 atom% D) were used. Anhydrous salts of $LiClO_4$ from Wako of GR grade, $NaClO_4$, $Mg(ClO_4)_2$, and $Ba(ClO_4)_2$ from Aldrich were used as received. Acetonitrile, CH_3CN (Wako, GR grade) and CD_3CN (Aldrich, 99.6 atom% D) were used as UV-visible and NMR spectroscopic solvents, respectively.

^{1}H and ^{13}C NMR measurements were carried out at room temperature with JEOL FT-NMR spectrometers (Model JNM-LA400 and Model ECP500), and a Bruker AMX400. The signals were assigned by two-dimentional (2D) NMR technics, such as HMBC (heteronuclear multiple bond correlation) and others.[14,15] UV-visible spectra were measured using a Hitachi double-beam spectrophtometer (Model U-2000) in a 1.0 cm quartz cuvette at room temperature.

Results and Discussion

Effects of Alkali Metal and Alkaline Earth Metal Ions on the γ-Lactone Ring-Opening of Rhodamine B Base and a Black Color Former. Figure 1 shows the ^{1}H NMR spectral changes of 3.0×10^{-3} mol dm^{-3} Rhodamine B base (cf. Chart 1) with increasing concentration of $LiClO_4$ in CD_3CN at room

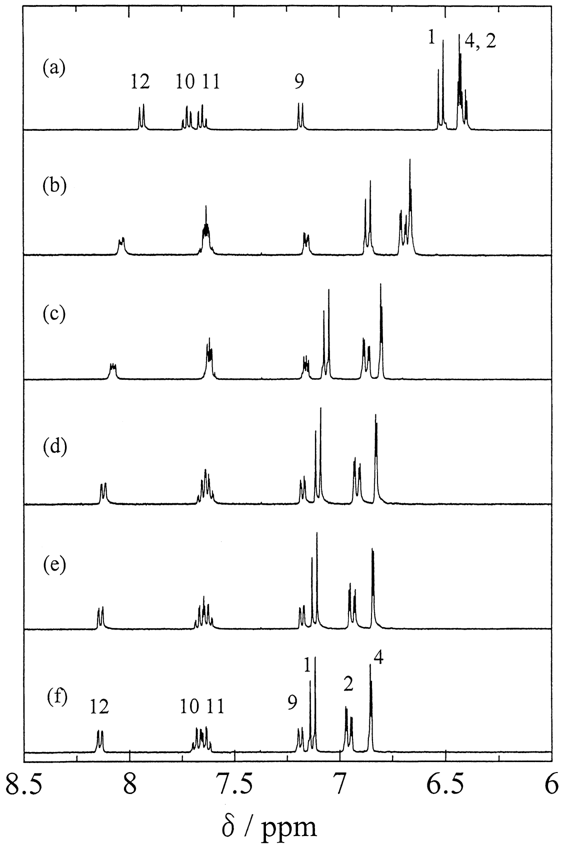

Fig. 1. The ^{1}H NMR spectra of 3.0×10^{-3} mol dm^{-3} Rhodamine B base with increasing concentration of $LiClO_4$ in CD_3CN at room temperature: (a) 0; (b) 0.01; (c) 0.1; (d) 0.2; (e) 0.5; (f) 1.0 mol dm^{-3} $LiClO_4$.

temperature. The proton signals on the xanthene part in Rhodamine B base shifted to lower magnetic fields, while those on the isobenzofuran (or benzoate) part remained at the original value, except for that at the 12-position. Upon the addition of only 0.01 mol dm^{-3} $LiClO_4$, large spectral shifts were observed. With 0.5 mol dm^{-3} $LiClO_4$ and more, the chemical shifts reached constant values, e.g., $\delta = 6.84$ for the 4-position of Rhodamine B base (cf. Fig. 2). The effects of $NaClO_4$ were much smaller than those of $LiClO_4$, although the δ value at the 4-position approached the maximum value at 1.0 mol dm^{-3} $NaClO_4$. Barium perchlorate, even at a much lower concentration, 0.01 mol dm^{-3}, caused almost the ultimate shift. A nonmetallic salt, Et_4NClO_4, caused almost no effects on the ^{1}H NMR signals. However, the spectrum of Rhodamine B base was deformed upon the addition of $Mg(ClO_4)_2$ in CD_3CN, although many signals shifted toward low fields with increasing concentration of the metal perchlorate. The addition of an acid, CF_3SO_3D, also caused complexity in the spectrum. Hydrogen ions (H^+ and D^+) and Mg^{2+} could interact not only with the carboxylate-*O* atom (COO^-), but also with the diethylamino-*N* atom (Et_2N-) of Rhodamine B base. The poly-protonated species, RH_2^{2+} and RH_3^{3+}, as well as RH^+ of Rhodamine B in an acidic aqueous solution were observed.[18] Hojo et al.[19] have reported a strong interaction between Mg^{2+} and *N*-atoms of "Methyl Yellow," *p*-(dimethylamino)azobenzene, in acetonitrile.

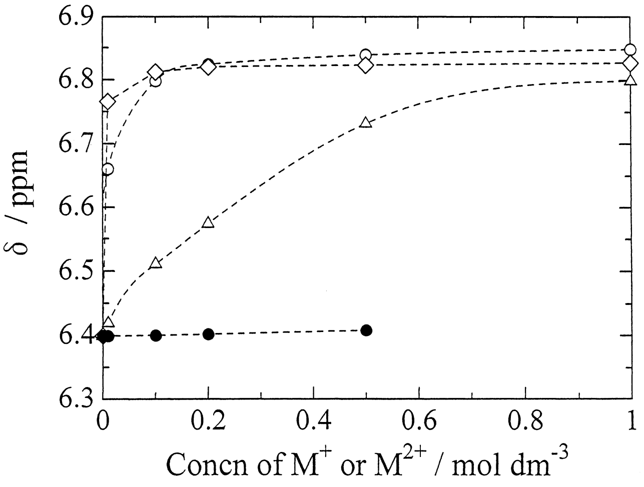

Fig. 2. Changes in the chemical shift of Rhodamine B base (at the 4-position, cf. Chart 1) in the presence of metal perchlorates in CD_3CN: (○) $LiClO_4$; (△) $NaClO_4$; (◇) $Ba(ClO_4)_2$; (●) Et_4NClO_4.

The color changes of Rhodamine B base from no color to a deep pink-red upon the addition of alkali metal ($M^+ = Li^+$, Na^+) and alkaline earth metal ions ($M^{2+} = Mg^{2+}$, Ba^{2+}) had been examined by UV-visible absorption spectroscopy at a lower concentration of Rodamine B base (2.0×10^{-4} mol dm^{-3}).[12] The color change has been attributed to the γ-lactone opening through a direct interaction between the metal ions and the benzoate ion (function) in acetonitrle solution. The formation constants between the Rhodamine B base zwitterion ($RB^{\pm}$) and the metal ions were evaluated using previous data:[12] $\log K = 3.0$, 1.9, and 0.5 for Ba^{2+}, Li^+, and Na^+, respectively, assuming 1 : 1 interaction, as follows:

$$RB + M^+ \text{ (or } M^{2+}) \rightleftharpoons RB^{\pm}M^+ \text{ (or } M^{2+}). \tag{1}$$

For evaluating the formation constants, the absorbances around 545 nm in the presence of different concentrations of the metal ions were utilized; the molar absorptivity of the $RB^{\pm}M^+$ (or M^{2+}) was $\varepsilon = 1.1 \times 10^5$ cm^{-1} mol^{-1} dm^3. The analytical method described in a previous paper[20] was applied with some modifications. The interaction between $RB^{\pm}$ and Mg^{2+} was too large to evaluate the formation constant with $> 1 \times 10^{-4}$ mol dm^{-3} $Mg(ClO_4)_2$; the formation of $Mg^{2+}(RB^{\pm})_2$ was suspected in the presence of lower Mg^{2+} concentrations.

The shifts in the δ values of ^{1}H NMR toward lower fields with increasing concentrations of the metal ions are in good accordance with the increase in the color intensity[12] from Rhodamine B base. We have demonstrated that the formation of the trityl cations in the presence of M^+ or M^{2+} causes remarkable low field shifts in the δ value of ^{1}H NMR.[7] The formation of the zwitterion or the carbocation center from Rhodamine B base was strongly suggested by the shifts in the δ value with increasing the concentration of M^+ or M^{2+} in acetonitrile. The following ^{13}C NMR data directly demonstrates the opening of the γ-lactone ring of Rhodamine B.

Figure 3 shows the ^{13}C NMR spectra of Rhodamine B base in the presence of $LiClO_4$ in CD_3CN. In the absence of metal ions, the signal of C-7 combined with the carboxylate *O*-atom

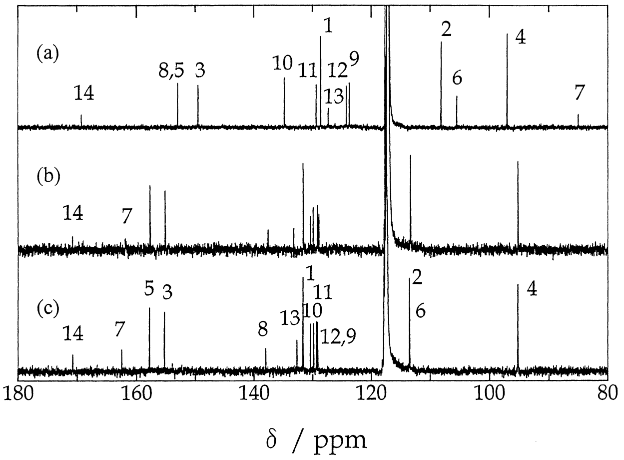

Fig. 3. The ^{13}C NMR spectra of 0.01 mol dm^{-3} Rhodamine B base in CD_3CN in the presence of $LiClO_4$: (a) 0; (b) 0.1; (c) 1.0 mol dm^{-3} $LiClO_4$.

Table 1. The Chemical Shift Values$^{a)}$ of ^{13}C NMR Signals of Rhodamine B Base in the Presence of $Ba(ClO_4)_2$ in CD_3CN at Room Temperature

Carbon no.	$\delta^{b)}$	$\delta^{c)}$	Carbon no.	$\delta^{b)}$	$\delta^{c)}$
1	132.2	128.8	9	129.8	123.9
2	114.3	108.3	10	131.1	135.0
3	155.8	149.7	11	130.6	129.6
4	95.9	97.2	12	130.0	124.5
5	158.2	153.2$^{d)}$	13	133.1	127.5
6	114.0	105.7	14	174.3	169.4
7	162.4	85.2	15	45.9	44.2
8	138.2	153.2$^{d)}$	16	12.3	11.8

a) Vs TMS. b) In the presence of 1.0 mol dm^{-3} $Ba(ClO_4)_2$ for 0.04 mol dm^{-3} Rhodamine B base. c) In the absence of the salt. d) The both signals at nos. 5 and 8 positions were overlapped each other. Also in $CDCl_3$, the signals were found to be overlapped (153.26 and 153.38 ppm).

appeared at 85.2 ppm (vs TMS). However, the signal shifted to 163.6 ppm ($\Delta\delta = +78.4$) in the presence of 1.0 mol dm^{-3} $LiClO_4$. Even at 0.1 mol dm^{-3} $LiClO_4$, a new peak at around 163 ppm of C-7 could be observed. The great low-field shift in the ^{13}C NMR signal of C-7 indicates the formation of the carbocation (sp^2) center, or the opening of the γ-lactone ring. In the presence of 1.0 mol dm^{-3} $Ba(ClO_4)_2$, the C-7 signal appeared at 162.4 ppm ($\Delta\delta = +77.2$); the chemical-shift values of signals in the absence and presence of $Ba(ClO_4)_2$ are listed in Table 1. We would like to mention that no precipitation was observed in a mixed solution of Rhodamine B base and metal perchlorates.

The γ-lactone ring of a fluoran-based black color former (Chart 2) was also cleaved by the alkali metal and alkaline earth metal ions in an acetonitrile solution. Figure 4 shows the effects of $Mg(ClO_4)_2$ on the UV-visible absorption spectra of the black color former (5.0×10^{-5} mol dm^{-3}) in CH_3CN at room temperature. Without the Mg^{2+} ion, the black color former gave no absorption at $>$ 370 nm. Upon the addition on an equivalent amount of Mg^{2+}, the no color solution turned to be a dark color. The color intensity increased with increasing concentration of Mg^{2+}, and reached its maximum value at 0.1 mol dm^{-3} Mg^{2+}. The absorbances at λ_{max} were 1.34, 0.91, and 1.05 at 310, 450, and 576 nm, respectively. The absorptivity of 2.1×10^4 at 576 nm was larger than any value observed in a variety of acidic media.[14] An isosbestic point was given at 293 nm in CH_3CN. The effects of Ba^{2+} were smaller than those of Mg^{2+}; at 1.0 mol dm^{-3} $Ba(ClO_4)_2$, the peak absorbances seemed to reach barely their maximum values: abs = 1.25, 0.86, and 0.97 at 305, around 453, and 570 nm. The isosbestic point was also observed at 291 nm for Ba^{2+}. The effects of alkali metal ions were definitely smaller than those of the alkaline earth metal ions (cf. Fig. 5). The 1:1 formation constants between the metal ions and the zwitterion from the black color former in CH_3CN were evaluated as follows: log K = 3.3, 0.4, and -0.5 for Mg^{2+}, Ba^{2+}, and Li^+, respectively. As described

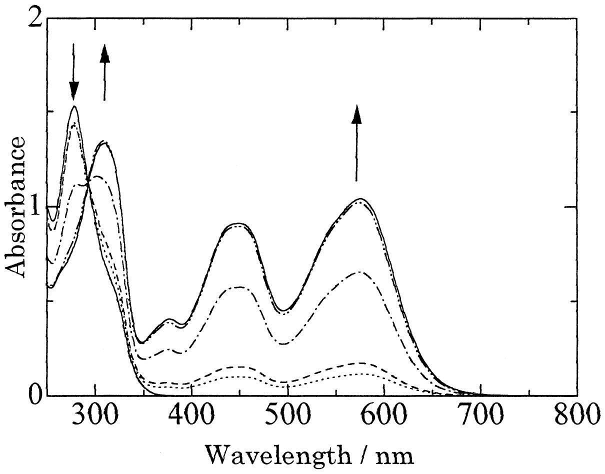

Fig. 4. Effects of $Mg(ClO_4)_2$ on the UV-visible absorption spectrum (path-length: 1.0 cm) of the black color former (5.0×10^{-5} mol dm^{-3}) in CH_3CN; (———) 0; (- - - - -) 5.0×10^{-5}; (— — —) 1.0×10^{-4}; (— - —) 1.0×10^{-3}; (— - - - —) 0.01; (———) 0.1 mol dm^{-3} $Mg(ClO_4)_2$.

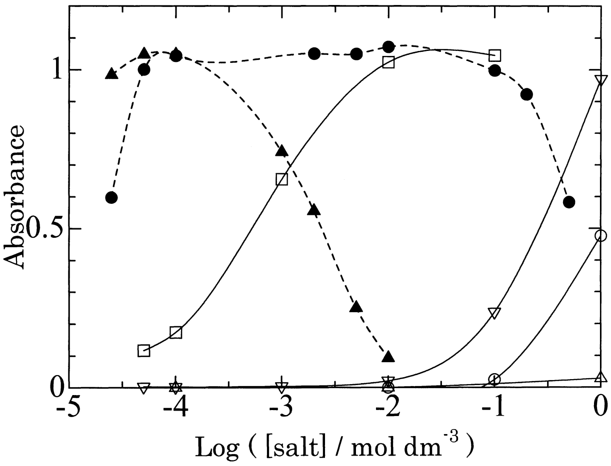

Fig. 5. Changes in absorbance at λ_{max} (ca. 570–585 nm) of 5.0×10^{-5} mol dm^{-3} black color former with increasing concentration of various salts and acids in CH_3CN: (○) $LiClO_4$; (△) $NaClO_4$; (□) $Mg(ClO_4)_2$; (▽) $Ba(ClO_4)_2$; (●) CH_3SO_3H; (▲) CF_3SO_3H.

above, much larger formation constants with the corresponding metal ions were given for Rhodamine B base. The asymmetric structure, i.e., only a single dialkylamino-group at 3- and 6-positions of the black color former (cf. Charts 1 and 2), should cause a difficulty in cleaving the γ-lactone ring.

The effects of rather strong acids on the black color former in CH_3CN were also examined. Upon the addition of 1.0×10^{-4} mol dm^{-3} methanesulfonic acid to 5.0×10^{-5} mol dm^{-3} of the color former, the peak intensities reached their maxima: abs = 1.29, 0.88, and 1.04 at 309, around 448, and 585 nm, displaying an isosbestic point at ca. 293 nm. The absorption spectra were almost identical in the presence of a range of 1.0×10^{-3}–0.01 mol dm^{-3} methanesulfonic acid. However, in the presence of 0.1 mol dm^{-3} and more of the acid, the absorbances of the two peaks decreased; at 0.5 mol dm^{-3}, the peaks disappeared to be shoulders and, instead, a new band appeared between the (previous) two peaks; the new band consisted of three peaks at 467, 497, and 535 nm. Further, a stronger acid, trifluoromethanesulfonic acid, CF_3SO_3H, caused the black color to turn into a red color with much lower concentrations of the acid. At the 1.0×10^{-2} mol dm^{-3} acid, the peak of the black color species disappeared, and the absorbances of the new triple peaks of the red color species approached their maximum values: abs = 1.05, 1.32, and 0.97 at 470, 496, and 530 nm, respectively. Remarkable isosbestic points were given at 455 and 543 nm in the presence of 5.0×10^{-5}–0.01 mol dm^{-3} acid.

The red color should have been caused by monoprotonation to the anilino-*N* group of the black color species, although the dialkylamino-*N* is a stronger base than the anilino-*N* in the usual case. A MO calculation showed that the electron density on *N*-atom at the 2-position (-0.200) is smaller than that at the 6-position (-0.243) for the zwitterion form, whereas the opposite situation holds for the original lactone form. Electronic spectrum studies of the derivative compounds also support our speculation. Monoprotonation to the dialkylamino group of Rhodamine B in acetonitrile caused a red color species: an absorption band with three peaks at ca. 460, 493 nm, and ca. 530 nm. The acidities of CH_3SO_3H and CF_3SO_3H are not very strong in an aprotic solvent, acetonitrile, because of its poor solvation ability;[21] the pK_a values were reported to be 8.36 and 2.60 for CH_3SO_3H and CF_3SO_3H, respectively.[22,23]

By the way, the addition of 1×10^{-3} mol dm^{-3} Et_4NOH or Me_4NOH to the black color former of 5.0×10^{-5} mol dm^{-3} in CH_3CN caused the solution to become pale yellow, giving a broad peak at around 420 nm, although the yellow solution returned to almost colorless in the presence of $> 1 \times 10^{-2}$ mol dm^{-3} of the strong alkalis. The color development should have been caused by the anion which is produced by deprotonation of the –NH group.[15] A weaker base, 1,1,3,3-tetramethylguanidine, at least, up to 0.1 mol dm^{-3}, caused no change in the absorption spectrum of the black color former.

Figure 6 shows the ^{13}C NMR spectra of a 0.04 mol dm^{-3} black color former in the presence of $Ba(ClO_4)_2$ in CD_3CN. The signal at 83.9 ppm of C-9 was shifted to 159.8 ppm in the presence of 2.0 mol dm^{-3} $Ba(ClO_4)_2$. A broad signal appeared at a slightly higher field, ca. 157.5 ppm, with 1.0 mol dm^{-3} $Ba(ClO_4)_2$. In the presence of 2.0 mol dm^{-3} $LiClO_4$, an incomplete peak seemed to be observed at ca. 158.5 ppm, whereas a definite signal appeared at 162.2 ppm in the presence of 1.0 mol dm^{-3} $Mg(ClO_4)_2$; however, the signal of C-20 became rather obscure in this case.

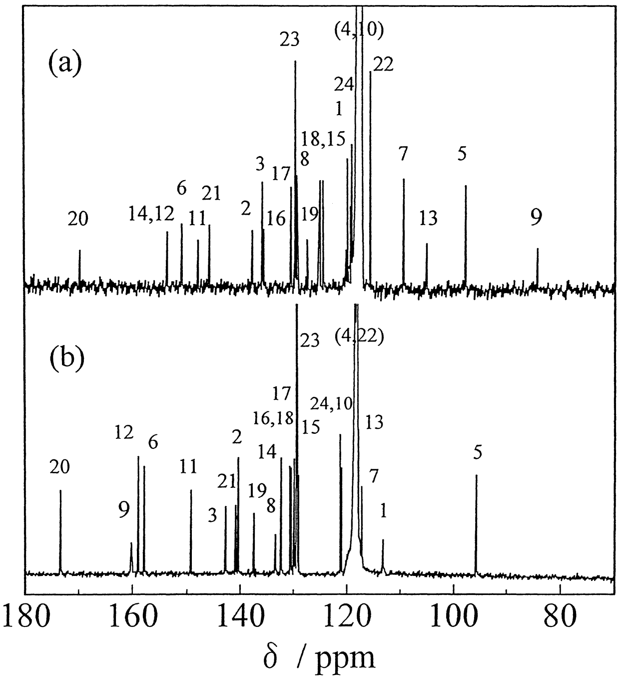

Fig. 6. The ^{13}C NMR spectra of the black color former (0.04 mol dm^{-3}, cf. Chart 2) in the absence and the presence of $Ba(ClO_4)_2$ in CD_3CN: (a) no salt; (b) in the presence of 2.0 mol dm^{-3} $Ba(ClO_4)_2$.

Yanagita et al.[14] have observed the ^{13}C signal of C-9 of the black color former at 162.7 ppm in a normal color developer, phenol-d_6. However, upon increasing the temperature (from 40 to 140 °C), i.e., with the incompleted cleavage of the γ-lactone ring, the ^{13}C NMR signal of the carbocation center shifted remarkably toward higher fields, while the signal of C-14 shifted toward a lower field. Similar phenomena have also been reported for a chloro-derivative of a black color former, 2′-(*o*-chlroanilino)-6′-dibutylamino-3′-methylfluoran, in phenol-d_6.[24] Therefore, the peaks at slightly higher magnetic fields than $\delta = 162$ ppm should be caused mainly by an incomplete cleavage of the γ-lactone ring. Another reason may account for the variable values in the chemical shifts for the ring-opened C-9: the stronger interaction between the metal ions and the carboxylate ion (function) within the fluoran compound would cause a higher field shift. In the ^{13}C signal of C-20, also, the metal cation–O$^-$ interaction may cause different chemical shifts: 170.7 and 173.2 ppm for 1.0 mol dm^{-3} $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$, respectively. Similar arguments also seem to be valid for the effects of Li^+ and Ba^{2+} on Rhodamine B base.

Trityl Benzoate and Methoxy-Substituted Trityl Chlorides. A direct interaction between the metal ions and the benzoate ion was examined by ^{1}H NMR spectroscopy. We have demonsrtrated that the alkali metal ions in acetonitrile could have direct interactions with benzoate ions by means of polarography[25] and UV-visible absorption spectroscopy.[20] The C–O bond of trityl benzoate could never be cleaved by the addition of just M^+ or M^{2+} in acetonitrile. However, in the co-

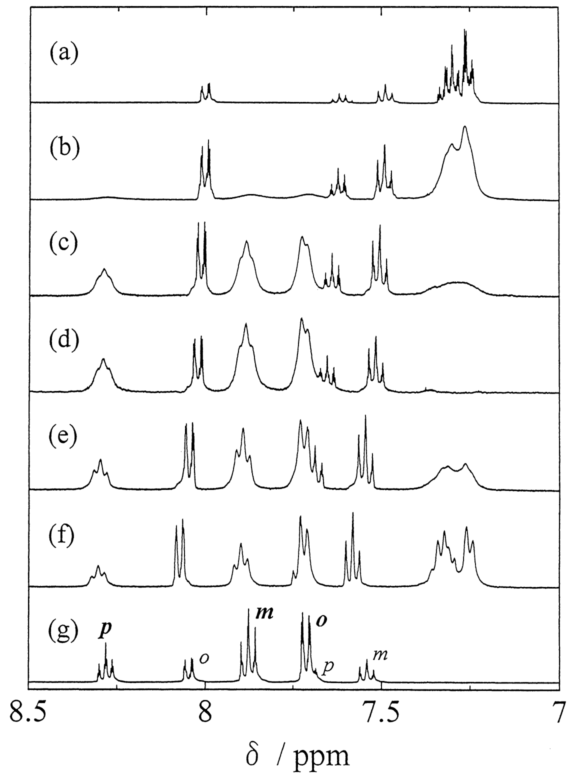

Fig. 7. Changes of ^{1}H NMR spectra of 2.7×10^{-3} mol dm^{-3} trityl benzoate with increasing concentration of $Mg(ClO_4)_2$ in the presence of 2.7×10^{-3} mol dm^{-3} CF_3SO_3D in CD_3CN: (a) no acid; (b) no metal ion; (c) 0.01; (d) 0.1; (e) 0.5; (f) 1.0 mol dm^{-3} $Mg(ClO_4)_2$; (g) 0.5 mol dm^{-3} CF_3SO_3D. The bold signals show the positions on the trityl ion, and the others on the benzoate.

existence of a small amount of CF_3SO_3D, it has been found by means of UV-visible absorption spectroscopy that the magnesium ion has the ability to cleave the C–O bond to produce the trityl ion.[12] In the present study, the formation of not only the trityl ion, but also the benzoate ion from trityl benzoate, was observed by ^{1}H NMR, as follows.

Trityl benzoate in CD_3CN gave signals of the trityl compound (at around 7.3 ppm) and small signals of benzoic acid in the absence of strong acids or metal ions; the signals of benzoic acid developed upon the addition of an equivalence amount of CF_3SO_3D, but still almost no signals of the trityl ion appeared (cf. Fig. 7). However, by the addition of 0.01 mol dm^{-3} $Mg(ClO_4)_2$, broad, but definite, ^{1}H NMR signals of the trityl ions were produced. At 0.1 mol dm^{-3} $Mg(ClO_4)_2$, the signals of Ph_3C^+ developed further at the expense of those of trityl benzoate (Ph_3CX). Strange to say, however, with 0.5 mol dm^{-3} $Mg(ClO_4)_2$, the signals of a trityl compound appeared again, although the signals of Ph_3C^+ were displayed more sharply. Here, the formation of Ph_3COH, based on the reaction between Ph_3C^+ and H_2O introduced with added $Mg(ClO_4)_2$ (hydrated water as the impurity), may be suspected. It goes without saying that, in the presence of 0.5 mol dm^{-3} CF_3SO_3D, trityl benzoate was converted into the trityl ion and benzoic acid, completely. The ^{1}H NMR results, mentioned above, confirm that the magnesium ion can cleave the C–O bond of trityl benzoate with the assistance of a small amount of a "strong" acid in acetonitrile. The mechanism for the cleavage of the C–O bond of trityl benzoate in the co-existence of H^+ and Mg^{2+} has been provided in the previous paper.[12]

In this connection, the formation of trityl ions from methoxy-trityl chlorides, based on the interaction between Ba^{2+} and Cl^- in acetonitrile, was examined by ^{13}C NMR. In the previous paper, Hojo et al.[7] have reported that the ^{1}H NMR signals of 4-methoxytrityl chlorides were greatly shifted toward lower fields by the addition of the perchlorate salts of alkali metal (Li^+, Na^+) and alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). It has been found that barium perchlorate is the most effective salt among them because of the precipitation of the mixed anion salt, $BaCl(ClO_4)$, from acetonitrile solution,[26] as follows where n = 1–3:

$$\begin{aligned}&(4\text{-}MeOC_6H_4)_nPh_{3-n}CCl + Ba(ClO_4)_2\\&\rightarrow (4\text{-}MeOC_6H_4)_nPh_{3-n}C^+ClO_4^-\\&+ BaCl(ClO_4)\downarrow \text{(precipitation)}.\end{aligned} \tag{2}$$

The above reaction has been utilized for a new preparation method of methoxy-substituted trityl perchlorates from the corresponding chlorides in acetonitrile,[7] instead of using perchloric acid or $AgClO_4$.[27]

Figure 8 shows the ^{13}C NMR spectra (of the supernatant solution) of 4-methoxytrityl, 4,4′-dimethoxytrityl, and 4,4′,4″-trimethoxytrityl chlorides in the presence of 1.0 mol dm^{-3} $Ba(ClO_4)_2$ in CD_3CN at room temperature. The signals around 200 ppm indicate the formation of the methoxy-substituted trityl cations: 200.8, 196.9, and 194.0 ppm for 4-methoxytrityl, 4,4′-dimethoxytrityl, and 4,4′,4″-trimethoxytrityl ions, respectively. These values seem to be quite reasonable, based on the values of unsubstituted-trityl[28] and 4,4′,4″-trimethoxytrityl ions[29] (δ = 212 and 193.2 ppm, respectively) in the conc. H_2SO_4 solvent. The assignments of other carbon atoms were performed, following the literature data.[28,29] The chemical shift values of the signals are listed in Table 2. As for unsubstituted-trityl chloride, in the presence of the alkali metal and alkaline earth metal ions in acetonitrile solution, the trityl ion was not able to be observed by the NMR method, while the UV-visible absorption spectra[12] gave evidence of the formation of the trityl ion (ca. 25 and 40% yields, respectively) from 1.0×10^{-3} mol dm^{-3} trityl chloride and bromide in the presence of 1.0 mol dm^{-3} $Ba(ClO_4)_2$. UV-visible spectroscopy makes it possible to observe the formation of the trityl ion, even at lower concentrations, because of its large absorptivity of 4.0×10^4 cm^{-1} mol^{-1} dm^3 at 403 nm. However, a strong interaction between R_3C^+ and the mother compound, R_3CX, causes line-broadening in NMR signals, which must make it difficult to observe the formation of the trityl ions at lower yields (< 50%), even if the absolute concentration of the trityl ion is high enough for the NMR observation. As for the stabilities of the carbocations, a methoxy group brings great stability to the trityl ion.[7,12,30]

The present study demonstrates that a strong interaction can operate between the metal ions (alkali metal and alkaline earth metal ions) and anions to produce stable carbocations or zwitterions in solution when ions are not strongly solvated. We believe that some features in concentrated salt effects on S_N1-

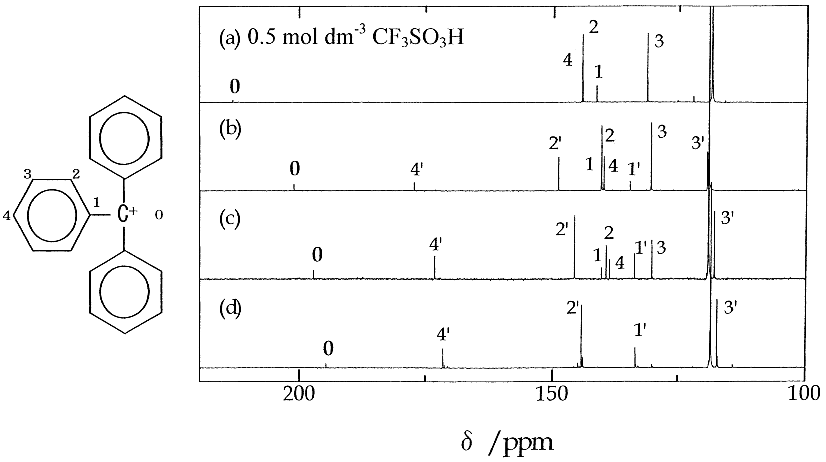

Fig. 8. Effects of 1.0 mol dm^{-3} Ba(ClO$_4$)$_2$ on the ^{13}C NMR spectra of 0.01 mol dm^{-3} trityl chlorides in CD$_3$CN: (a) trityl chloride with 0.5 mol dm^{-3} CF$_3$SO$_3$H and no salt; (b) 4-methoxytrityl chloride; (c) 4,4′-dimethoxytrityl chloride; (d) 4,4′,4″-trimethoxytrityl chloride. The primed numbers represent the positions on the methyoxy-substituted phenyl groups.

Table 2. The Chemical Shift Values[a)] of ^{13}C NMR Signals of Trityl Chlorides and the Trityl Cations in CD$_3$CN at Room Temperature

	C-0	C-1	C-1′[b)]	C-2	C-2′[b)]	C-3	C-3′[b)]	C-4	C-4′[b)]
Ph$_3$CCl	82.8	146.2	—	130.5	—	129.0	—	128.1	—
Ph$_3$C$^+$ [c)]	213.1	141.3	—	144.1	—	131.2	—	144.1	—
(4-MeOC$_6$H$_4$)Ph$_2$C$^+$ [d)]	200.8	140.3	134.5	140.2	148.8	130.3	119.2	139.7	177.1
(4-MeOC$_6$H$_4$)$_2$PhC$^+$ [d)]	196.9	140.1	133.6	139.2	145.6	130.1	117.7	138.5	173.0
(4-MeOC$_6$H$_4$)$_3$C$^+$ [d)]	194.0	—	133.1	—	143.9	—	117.0	—	171.1

a) Vs TMS. b) The primed numbers represent the positions on the methoxy-substituted pheny groups. c) In the presence of 0.5 mol dm^{-3} CF$_3$SO$_3$H for 0.01 mol dm^{-3} trityl chloride. d) In the presence of 1.0 mol dm^{-3} Ba(ClO$_4$)$_2$ for 0.01 mol dm^{-3} trityl chlorides.

type solvolysis rates for RX (organic halides) are certainly caused by direct interactions between the X$^-$ ion and the metal ions (M$^+$, M^{2+}) in aqueous organic solutions; in these solutions, the water structure through hydrogen bonging is distorted by organic solvents as well as by concentrated salts. Raman spectroscopic evidence for the increased distortion of water structure (i.e., the conversion of bulk water into "dihydrogen ether")[10,11] by the addition of organic solvents, such as acetonitrile, will be reported later.

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