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Chemical Interaction between the Chloride Ion and Alkali Metal or Alkaline Earth Metal Cations as an Effective Motive Force for the Formation of Carbocations from Trityl Chlorides in Acetonitrile

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Introduction

In a previous study,[1] the formation of stable carbocations from trityl and methoxy-substituted trityl halides in the presence of alkali metal (M^+) or alkaline earth metal (M^{2+}) ions in acetonitrile solution was observed by means of UV−vis spectroscopy (Scheme 1). The γ-lactone rings of Rhodamine B and Crystal Violet lactone in the solvent were also cleaved by the addition of M^+ or M^{2+}. The color changes in the sulfonaphthaleins, such as Thymol Blue and Bromothymol Blue,[2] were attributed to the cleavage of the γ-sultone rings in the presence of M^+ or M^{2+}.

In the present paper, we report on observation by ^1H NMR of the formation of stable carbocations from 4-methoxy-substituted trityl chlorides ($(4\text{-}MeOC_6H_4)_nPh_{3-n}CCl$) at higher concentrations, i.e., a preparative level, in the presence of alkali metal and alkaline earth metal perchlorates in acetonitrile at 25 °C. The carbocations are isolated as perchlorate salts from acetonitrile solutions. Metal precipitates formed in the solution are characterized by chemical and instrumental analyses, and a novel salt, $BaCl^+ClO_4^-$, is proposed. Also, if carbocations are stabilized in the presence of alkali metal and alkaline earth metal ions, solvolysis reaction rates in S_N1 should be promoted. This hypothesis has been verified by the exponential increases in S_N1 solvolysis rates of aliphatic halides in the presence of metal salts.[3] We have proposed that "isolated" water molecules (HOH), which are converted from bulk waters by concentrated salts, may behave just like "ethers" (ROR). The main purpose of the present study is to definitively demonstrate that alkali metal and alkaline earth metal ions can take part directly in the chemical reactions in solution.

The NMR spectra of triarylmethyl cations have been reported by Moodie et al.[4] The conformational equilibria in trityl cations have been established by ^{19}F NMR studies.[5] The reversible reaction of trityl tetrafluoroborate with water in acetonitrile has been studied using NMR line broadening.[6] McKinley et al.[7] have determined the stabilities of trityl substituents by means of NMR.

Results and Discussion

Observation of Carbocations by ^{1}H NMR. In dried acetonitrile, 4-methoxytrityl chloride, $(4\text{-}MeOC_6H_4)Ph_2CCl$, dissociated very slightly autonomously; an apparent dissociation constant has been evaluated as $K_d = 3.4 \times 10^{-9}$ by UV−vis spectroscopy.[1] However, upon the addition of $LiClO_4$, an acetonitrile solution of 5.0×10^{-4} mol dm^{-3} $(4\text{-}MeOC_6H_4)Ph_2CCl$ turns bright yellow, giving the two absorption bands around 390 and 470 nm of the trityl cation.

Figure 1 shows the ^1H NMR spectra of 0.032 mol dm^{-3} $(4\text{-}MeOC_6H_4)Ph_2CCl$ with or without alkali metal and alkaline earth metal perchlorates in CD_3CN at 25 °C. In the absence of the salts, the signals of the trityl chloride in CD_3CN were observed at $\delta < 7.4$ ppm.[8] The $(4\text{-}MeOC_6H_4)Ph_2C^+$ cation produced by the addition of CF_3SO_3D to the chloride in CD_3CN gave signals at much lower magnetic fields, i.e., $\delta \geq 7.4$ ppm. Upon the addition of an excessive amount of $LiClO_4$ to 0.032 mol dm^{-3} $(4\text{-}MeOC_6H_4)Ph_2CCl$, the signals at ca. 7.35 ppm changed to merely a broad peak at 7.468 ppm. At a lower concentration (5×10^{-4} mol dm^{-3}) of the trityl choride, the trityl cation of a 49.3% yield has been produced by the addition of 1.0 mol dm^{-3} $LiClO_4$.[1] Sodium perchlorate was much more effective than $LiClO_4$; the NMR signal peaks were observed at magnetic fields similar to those of the trityl cation. Unexpectedly, the effects of $Mg(ClO_4)_2$ were very incomplete, although not so much as $LiClO_4$. However, the addition of 0.05 mol dm^{-3} $Ba(ClO_4)_2$ to 0.032 mol dm^{-3} $(4\text{-}MeOC_6H_4)Ph_2CCl$ caused the almost complete formation of the $(4\text{-}MeOC_6H_4)Ph_2C^+$ cation. The effects of $Sr(ClO_4)_2$ or $Ca(ClO_4)_2$ were definitely smaller than those of $Ba(ClO_4)_2$. It should be noted that precipitates were formed by the addition of all of the salts, except for $LiClO_4$ and $Mg(ClO_4)_2$; therefore, for the NMR samples, the supernatant solutions were taken after they had been left standing for 20−30 min.

The formation of the trityl cation from 4-methoxytrityl chloride at a higher concentration upon the addition of $Ba(ClO_4)_2$ in acetonitrile can be expressed by eq 1. The

$$(4\text{-}MeOC_6H_4)Ph_2CCl + Ba(ClO_4)_2 \rightleftharpoons (4\text{-}MeOC_6H_4)Ph_2C^+ClO_4^- + BaCl^+ClO_4^-\ (\text{ppt}) \quad (1)$$

identification of the species $BCl^+ClO_4^-$ will be discussed elsewhere. To a great extent, the complete ionzation of 4-methoxytrityl chloride in the presence of $Ba(ClO_4)_2$ might be due to the insoluble species (out of the system) in acetonitrile. The effects of calcium and strontium perchlorates must be based on a similar mechanism. As mentioned above, the precipitation did not occur for $Mg(ClO_4)_2$, which resulted in the incomplete formation of the trityl cations by Mg^{2+} despite its (expected) stronger interaction with Cl^-. In addition, the precipitation of NaCl upon the addition of $NaClO_4$ should have brought

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[1] Hojo, M.; Hasegawa, H.; Tsurui, H.; Kawamura, K.; Minami, S.; Mizibe, A.; *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1619.

[2] Hojo, M.; Ueda, T.; Kawamura, K. Unpublished results.

[3] Manege, L. C.; Ueda, T.; Hojo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 589. Manege, L. C.; Ueda, T.; Hojo, M.; Fujio, M. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1961.

[4] Moodie, R. B.; Connor, T. M.; Stewart, R. *Can. J. Chem.* **1959**, *37*, 1402.

[5] Colter, A. K.; Schuster, I. I.; Kurland, R. J. *J. Am. Chem. Soc.* **1965**, *87*, 2278.

[6] Brauman, J. I.; Archie, W. C., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 5981.

[7] McKinley, S. V.; Rakshys, J. W., Jr.; Young, A. E.; Freedman, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 4715.

[8] Compare the NMR spectrum in $CDCl_3$: *The Aldrich Library of ^{13}C and ^1H FT-NMR Spectra*; Vol. 1(2); 190A.

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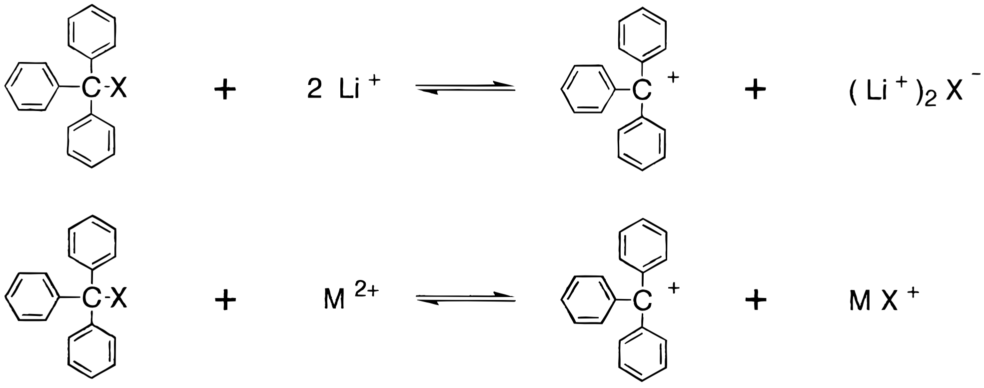
Scheme 1



about the greater effects of $NaClO_4$ compared to those of $LiClO_4$, which caused no precipitation. The effects of $NaClO_4$ were in fact greater than those of $Mg(ClO_4)_2$. We think that factors responsible for breaking the C−Cl (or $C^+{-}Cl^-$) bond are the chemical interactions between Cl^- and metal ions (such as Li^+Cl^-, $(Li^+)_2Cl^-$, $BaCl^+$, etc.), as well as the Coulombic interaction between them in the protophobic aprotic solvent of a higher permittivity (ϵ_r = ca. 36).[1] The precipitation reactions should contribute greatly to the remarkable dissociation of the trityl chloride. The effects of $NaClO_4$ and $Ba(ClO_4)_2$ will be discussed in further detail below.

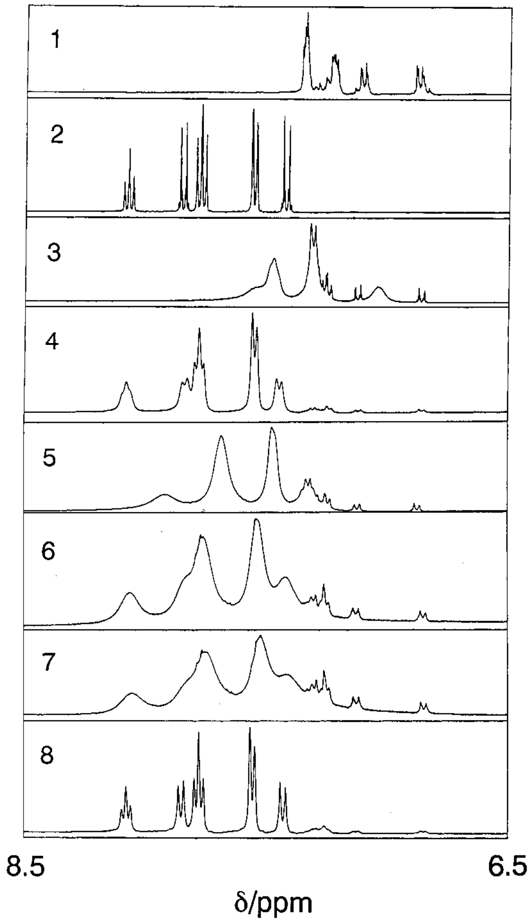


Figure 1. ^1H NMR (400 MHz) spectra of 0.032 mol dm^{-3} 4-methoxytrityl chloride in the presence of various perchlorate salts in CD_3CN at 25 °C: (1) no salt, (2) ca. 0.1 mol dm^{-3} CF_3SO_3D, (3) 1.0 mol dm^{-3} $LiClO_4$, (4) 1.0 mol dm^{-3} $NaClO_4$, (5) 1.0 mol dm^{-3} $Mg(ClO_4)_2$, (6) 0.1 mol dm^{-3} $Ca(ClO_4)_2$, (7) 0.05 mol dm^{-3} $Sr(ClO_4)_2$, and (8) 0.05 mol dm^{-3} $Ba(ClO_4)_2$. TMS is the internal reference for the chemical shift.

Figure 2 shows the effects of increasing $NaClO_4$ concentration on the NMR spectra of 4-methoxytrityl chloride in acetonitrile. By the addition of 0.1 mol dm^{-3} $NaClO_4$, three broad peaks appeared at much lower magnetic fields than the original signals of $(4\text{-}MeOC_6H_4)Ph_2CCl$. At 0.5 mol dm^{-3} $NaClO_4$, the peaks became sharp signals, and ultimately, in the presence of 1.0 mol dm^{-3} $NaClO_4$, the chemical shift values of the signals were almost consistent with those of the 4-methoxytrityl cation produced by the addition of CF_3SO_3D.

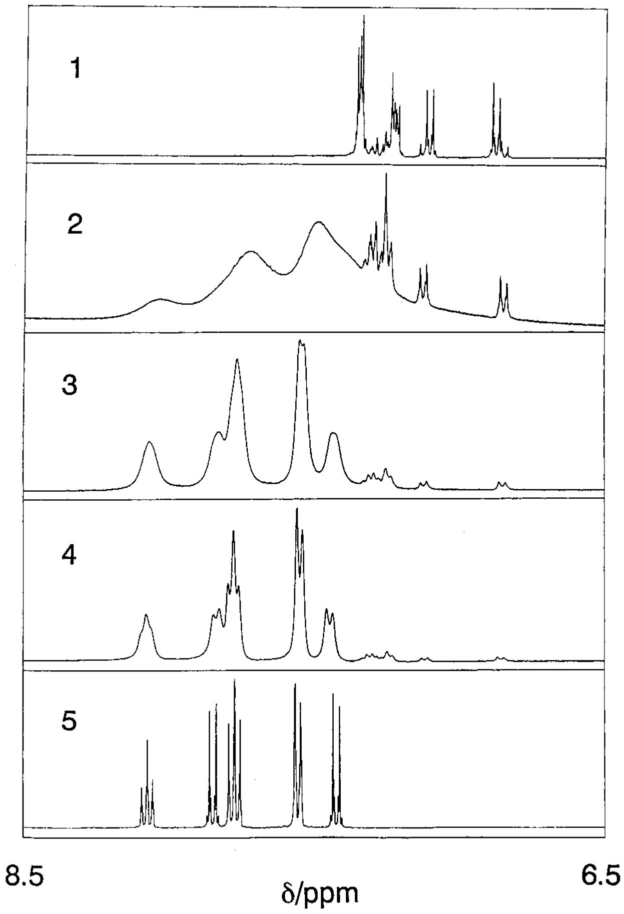


Figure 2. Effects of increasing concentration of $NaClO_4$ on the ^1H NMR spectra of 0.032 mol dm^{-3} 4-methoxytrityl chloride: (1) 0, (2) 0.1, (3) 0.5, and (4) 1.0 mol dm^{-3} $NaClO_4$; (5) 0.1 mol dm^{-3} CF_3SO_3D.

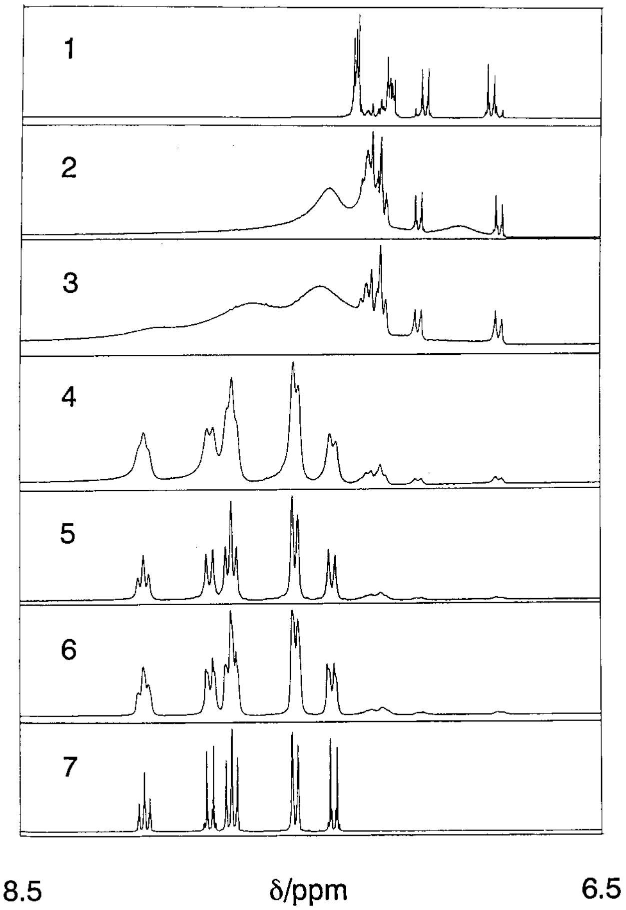


Figure 3. Effects of increasing concentration of $Ba(ClO_4)_2$ on the ^1H NMR spectra of 0.032 mol dm^{-3} 4-methoxytrityl chloride: (1) 0, (2) 0.001, (3) 0.01, (4) 0.02, (5) 0.05, and (6) 0.1 mol dm^{-3} $Ba(ClO_4)_2$; (7) 0.1 mol dm^{-3} CF_3SO_3D.

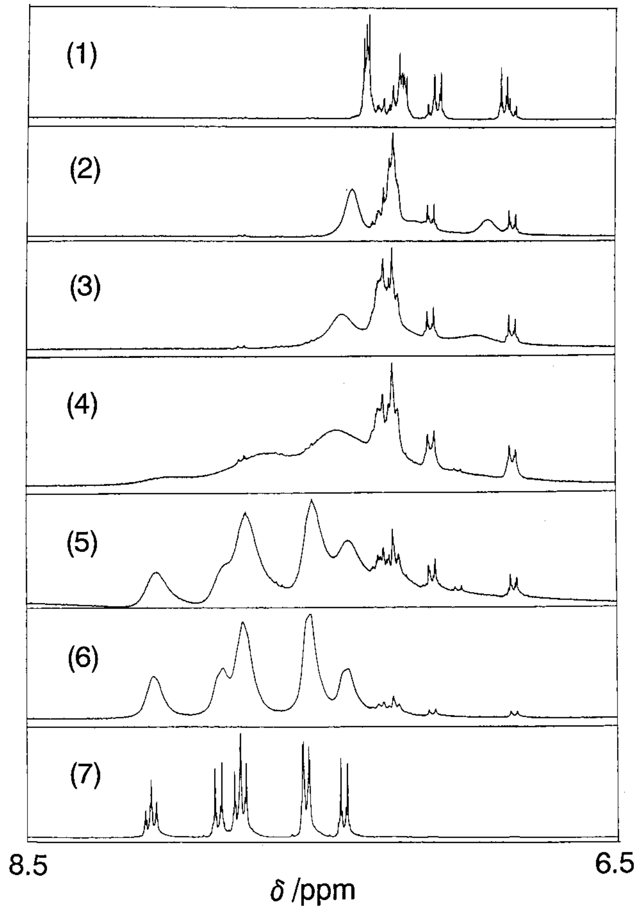


Figure 4. ^1H NMR spectra of mixtures of $(4\text{-}MeOC_6H_4)Ph_2$-Cl and $(4\text{-}MeOC_6H_4)Ph_2CClO_4$ in CD_3CN at ~21.5 °C: (1) 0%, (2) 10%, (3) 20%, (4) 50%, (5) 80%, (6) 90%, and (7) 100% of the perchlorate. The total concentration of the two compounds is 0.03 mol dm^{-3}.

Figure 3 shows the effects of $Ba(ClO_4)_2$ in a wide concentration range, 1×10^{-3} to 0.1 mol dm^{-3}, on the NMR spectra of 4-methoxytrityl chloride. Even at 1×10^{-3} mol dm^{-3} $Ba(ClO_4)_2$, a broad peak was observed at $\delta = 7.438$ ppm; these effects are close to those caused by 1.0 mol dm^{-3} $LiClO_4$ in Figure 1. The presence of 0.05 mol dm^{-3} $Ba(ClO_4)_2$ resulted in a complete dissociation of 0.03 mol dm^{-3} $(4\text{-}MeOC_6H_4)Ph_2CCl$, whereas that of 0.02 mol dm^{-3} $Ba(ClO_4)_2$ caused insufficient effects. The precipitation was observed in the CD_3CN solutions of $Ba(ClO_4)_2$ at every concentration. Note that the solubilities of $Ba(ClO_4)_2$ (without hydrated water) in CD_3CN and CH_3CN were substantially high (~2 mol dm^{-3}) at room temperature.

Our conductometric data of 4-methoxytrityl chloride in acetonitrile[9] have suggested a very high tendency to form higher ion aggregates, such as $Cl^+(Cl^-)_2$, $(C^+)_2Cl^-$, and $(C^+)_2(Cl^-)_2$, among the 4-methoxytrityl cation (C^+) and Cl^-. That is, the carbocation seems to have the high potential to form ion aggregates with Cl^-, an active anion, in the higher permittivity media. We think it possible that the trityl cations produced upon the addition of the metal ions may interact with the mother compound, 4-methoxytrityl chloride, to form a higher aggregate, $C^+{-}Cl^-\cdots C^+$. The formation of the species $C^+{-}Cl^-\cdots C^+$ at a sufficiently high concentration could be the cause of line broadening in the ^1H NMR spectra. The remaining trityl chloride (out of equilibrium?) might give sharp peaks as well. Figure 4 shows the NMR spectra of the mixtures in various ratios of $(4\text{-}MeOC_6H_4)Ph_2CClO_4$ and $(4\text{-}MeOC_6H_4)Ph_2CCl$. The interaction between the carbocation and the trityl chloride caused line broadening, even with 90% of the perchlorate. The formation yields of the carbocation in Figures 1−3 can be estimated by referring to Figure 4. Incidentally, the 1:1 mixture between 4,4′-dimethoxytrityl perchlorate and the corresponding chloride gave slightly broadened peaks of $\delta \leq 7.7$.

The ionization of 4,4′-dimethoxytrityl chloride[10] in acetonitrile was promoted by a smaller amount of the metal perchlorates. The addition of 0.1 mol dm^{-3} $NaClO_4$ caused the complete dissociation from 0.03 mol dm^{-3} $(4\text{-}MeOC_6H_4)_2PhCCl$ (Figure 5). It is natural that a slight excess of an equivalent amount of $Ba(ClO_4)_2$ would be essential for the complete dissociation of the trityl chloride. The ^1H NMR spectra of 0.027 mol dm^{-3} 4,4′,4″-trimethoxytrityl chloride in CD_3CN at 25 °C indicated that even $LiClO_4$ or $Mg(ClO_4)_2$ at 0.1 mol dm^{-3} caused the complete dissociation of $(4\text{-}MeOC_6H_4)_3CCl$. The cation effects on the ionization of the trityl chlorides increased as $Li^+ < Mg^{2+} < Na^+ < Ca^{2+} < Sr^{2+} < Ba^{2+}$. The precipitation reactions of the cations, excluding Li^+ and Mg^{2+}, in acetonitrile are regarded as the chemical reac-

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(9) Hojo, M.; Hamada, H. Unpublished results.

(10) *The Aldrich Library of ^{13}C and ^1H FT-NMR Spectra*; Vol. 1(2); 190B.

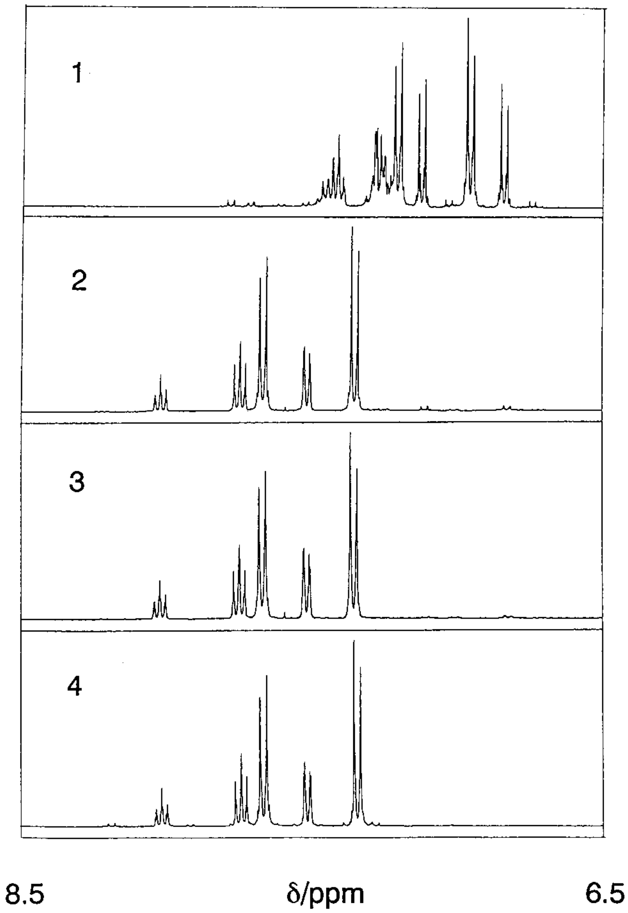

Figure 5. ^{1}H NMR spectra of 0.030 mol dm^{-3} 4,4′-dimethoxytrityl chloride in the presence of salts or a strong acid in CD$_3$CN at 25 °C: (1) no salt, (2) 0.1 mol dm^{-3} NaClO$_4$, (3) 0.05 mol dm^{-3} Ba(ClO$_4$)$_2$, and (4) 0.1 mol dm^{-3} CF$_3$SO$_3$D.

tions that greatly promote the ionization of the trityl chlorides. Our ^{1}H NMR data verified that the stabilitiy of carbocations in the presence of alkali metal or alkaline earth metal ions increased as 4-methoxy- < 4,4′-dimethoxy- < 4,4′,4″-trimethoxytrityl derivative.

In contrast, the direct observation by ^{1}H NMR of the carbocation (Ph$_3$C$^+$) from the nonsubstituted trityl chloride upon the addition of the metal perchlorates was not successful, although UV−vis absorption spectra have shown the formation of Ph$_3$C$^+$, e.g., at a yield of 25.8% with 1.0 mol dm^{-3} Ba(ClO$_4$)$_2$, from 1 × 10^{-3} mol dm^{-3} Ph$_3$CCl.[1] Evidence of the trityl cation formation at a higher concentration was given by the substantial progress of a conventional reaction,[11] namely, the preparation of tropylium perchlorate with hydride abstraction from cycloheptatriene by the trityl ion:

$$C_7H_8 + Ph_3C^+(ClO_4^-) \rightarrow C_7H_7^+(ClO_4^-) + Ph_3CH \quad (2)$$

The preparation of tropylium perchlorate was successfully completed; the procedure and the results are as follows. Mixing of 0.036 mol dm^{-3} Ph$_3$CCl and 0.05 mol dm^{-3} Ba(ClO$_4$)$_2$ in acetonitrile (a total of 50 mL) caused a bright yellow solution, which indicated the formation of Ph$_3$C$^+$. The yellow solution was left for 1 day at room temperature after an addition of 0.185 mL C$_7$H$_8$; the yellow color gradually turned more pale. The solution was evaporated, and the remaining dry solid mixture was washed with diethyl ether to remove Ph$_3$CH and other substances. Soxhlet extractions with dichloromethane were continued for several days. The ^{1}H NMR spectra of isolated C$_7$H$_7$ClO$_4$ and commercially obtained C$_7$H$_7$BF$_4$ in CD$_3$CN each gave a single peak (characteristic for C$_7$H$_7^+$) at 9.257 and 9.287 ppm, respectively. The elemental analyses of the isolated C$_7$H$_7$ClO$_4$ were as follows: found C, 43.79; H, 3.66; calcd for C$_7$H$_7$O$_4$Cl C, 44.12; H, 3.70. Other metal perchlorates caused the production of C$_7$H$_7$ClO$_4$ at lower yields (Li$^+$ < Na$^+$ < Ba^{2+}) when the solid mixtures were checked before the Soxhlet extraction by NMR and UV spectroscopy (217 and 273.5 nm).[11]

A Simple Preparation of Methoxy-Substituted Trityl Perchlorates. Common methods of preparing trityl perchlorate have been developed[12] that utilize HClO$_4$ or AgClO$_4$. For the present study, we propose a simple preparation method for 4-methoxytrityl perchlorate as follows. A solution of barium perchlorate (1.68 g) in MeCN (50 mL) was added to a solution of 1.0 g of (4-MeOC$_6$H$_4$)Ph$_2$CCl in MeCN (50 mL), with formation of a white precipitate. The filtered solution was evaporated at <50 °C to dryness, followed by extractions with CHCl$_3$. A red-brownish colored powder of (4-MeOC$_6$H$_4$)Ph$_2$CClO$_4$ (a yield of 79.6%) was obtained after the solvent evaporated. The ^{1}H NMR spectrum of the compound in CD$_3$CN confirmed a complete formation of (4-MeOC$_6$H$_4$)Ph$_2$C$^+$-ClO$_4^-$. (Found: C, 64.51; H, 4.66. Calcd for C$_{20}$H$_{17}$O$_5$Cl: C, 64.43, H, 4.60.) A similar procedure using 1.0 mol dm^{-3} NaClO$_4$ caused the production of (4-MeOC$_6$H$_4$)Ph$_2$CClO$_4$ (a yield of ca. 84%), accompanied by a minor amount of the original chloride, according to the NMR spectra. (Found: C, 65.42; H, 4.72.) Washing with diethyl ether was effective for removing the chloride.

The addition of 0.05 mol dm^{-3} Ba(ClO$_4$)$_2$ and 0.1 mol dm^{-3} NaClO$_4$ to 0.03 mol dm^{-3} 4,4′-dimethoxytrityl chloride produced (4-MeOC$_6$H$_4$)$_2$PhCClO$_4$ (found to be pure by NMR) with the yields of 76.8% and 90.8%, respectively. (Found: C, 62.37; H, 4.77. Calcd for C$_{21}$H$_{19}$O$_6$Cl: C, 62.81; H, 4.80.) In both cases, yields with NaClO$_4$ were higher than those with Ba(ClO$_4$)$_2$, because the extraction by CHCl$_3$ was more easily done in the case of the dried solid mixture containing NaClO$_4$ than it was in the case of the somewhat oily mixture of Ba(ClO$_4$)$_2$.

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(11) Dauben, H. J., Jr.; Gadecki, F. A.; Harmon, K. M.; Pearson, D. L. *J. Am. Chem. Soc.* **1957**, *79*, 4557. Harwood, L. M.; Moody, C. J. *Experimental Organic Chemistry, Principles and Practice*; Blackwell: London, 1989; p 704.

(12) Dauben, H. J., Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.