# Salt Effects on Proton Transfer from Nitrophenols to Amine or Pyridine Bases in Acetonitrile

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The addition of MClO<sub>4</sub> (M<sup>+</sup> = Li<sup>+</sup> and Na<sup>+</sup>) to  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> 2,4-dinitrophenol and the equivalent concentration of  $\gamma$ -picoline (4-methylpyridine) in acetonitrile caused a promoted proton transfer from the phenol to the base to the extent of 62 and 23% for 0.1 mol dm<sup>-3</sup> Li<sup>+</sup> and Na<sup>+</sup>, respectively. Alkaline-earth metal perchlorates (M(ClO<sub>4</sub>)<sub>2</sub>) had larger effects even at low concentrations of  $M^{2+}$ , e.g., the proton-transfer ratio was 90% for  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> Mg(ClO<sub>4</sub>)<sub>2</sub>. The effects of M<sup>2+</sup> decreased with increasing size of the cation: Mg<sup>2+</sup> > Ca<sup>2+</sup> > Sr<sup>2+</sup> > Ba<sup>2+</sup>. With the addition of MClO<sub>4</sub> or M(ClO<sub>4</sub>)<sub>2</sub>, a higher proton transfer ratio was observed for 2,5-dinitrophenol +  $\gamma$ -collidine than for 2,4-dinitrophenol +  $\gamma$ -picoline. The salt effects of MClO<sub>4</sub> or M(ClO<sub>4</sub>)<sub>2</sub> on the acid-base reactions were accounted for by the formation of triple cations or complex species of  $M^+$  or  $M^{2+}$  with the phenolate ions (B represents base):  $(NO_2)_2PhOH-B^+$  $2M^+ \rightleftharpoons (NO_2)_2 PhO^-(M^+)_2 + BH^+;$   $(NO_2)_2 PhOH - B + M^{2+} \rightleftharpoons (NO_2)_2 PhO^-M^{2+} + BH^+.$  The stronger the base, the greater the proton transfer (based on the addition of salts) from the phenols. The effects of  $LiClO_4$ on 2,4,6-trinitrophenol (picric acid) + 2-chloropyridine were very small; however, the effects on the proton transfer from 2- and 4-nitrophenol to triethylamine were very large. The extent of the proton transfer (based on the addition of LiClO<sub>4</sub>) from nitrophenols in the presence of appropriate bases was coincident with the order of the formation constants of ion aggregates (ion pairs and triple ions) for lithium nitrophenolates in acetonitrile:  $2 \rightarrow 4$ ,  $2,5 \rightarrow 2,4 \rightarrow 2,4,6$ . The "free" phenolate ions were produced by the addition of tetraalkylammonium halides ( $R_4N^+X^-$ : R = Et, *n*-Bu;  $X^- = Cl^-$ , Br<sup>-</sup>, I<sup>-</sup>) to the nitrophenols in the presence of bases in acetonitrile:  $(NO_2)_n PhOH-B + 2X^- \rightleftharpoons (NO_2)_n PhO^- + BH^+(X^-)_2$ . The presence of a base was not essential for the deprotonation of picric acid with  $R_4NX$ .

#### Introduction

The alternation between the contact ion pair (CIP) and the solvent separated ion pair (SSIP)<sup>1</sup> in solution may explain the steady-state behavior of electrolytes and the dynamic behavior of ions as transient intermediates. Many investigations<sup>2</sup> have been conducted in an attempt to distinguish SSIP from CIP. Time-resolved spectroscopy<sup>3</sup> seems to be one of the most effective techniques for the observation of ion-pair dynamics.

Nevertheless, we have explained the salt effects on some acid-base reactions in nonaqueous solvents<sup>4-6</sup> in terms of the formation of triple ions, not merely the ion-exchange or the presence of CIP and SSIP. In acetonitrile, the addition of a large excess of different salts to tropolone-triethylamine gave different tropolonate ions.<sup>5</sup> The production of different types of tropolonate ions was explained quantitatively by the following reactions

$$C_7H_5O_2H - NEt_3 + 2LiClO_4 \rightleftharpoons$$

$$C_7H_5O_2^{-}(Li^+)_2 + Et_3NH^+ + 2ClO_4^{-} (1)$$

$$C_7H_5O_2H - NEt_3 + M(ClO_4)_2 \rightleftharpoons$$

$$C_7H_5O_2^-M^{2+} + Et_3NH^+ + 2ClO_4^- (2)$$

$$C_7H_5O_2H - NEt_3 + 2Et_4NX \Longrightarrow$$
  
 $C_7H_5O_2^- + Et_3NH^+(X^-)_2 + 2Et_4N^+$  (3)

where  $M(ClO_4)_2$  stands for alkaline-earth metal perchlorates and Et<sub>4</sub>NX for tetraethylammonium halides (X<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>). The species  $C_7H_5O_2^{-}(Li^+)_2$  and  $C_7H_5O_2^{-}$  are the "reverse-

coordinated" and the "free" tropolonate ions, respectively. The salt effects on the Hammett acidity function with a neutral indicator (*p*-(dimethylamino)azobenzene) in acetonitrile have been elucidated also by the "complex" formation.<sup>6</sup> We have proposed that some "special" salt effects<sup>7</sup> in nucleophilic substitution reactions can be caused by the triple-cation formation ( $RX \rightarrow R^+//X^-$ ,  $R^+//X^- + 2Li^+ \rightarrow R^+ + (Li^+)_2X^-$ ).<sup>8</sup>

The possibility of the formation of higher ion aggregates from uni-univalent salts in higher permittivity media ( $\epsilon_r > 10$ ) has been denied for a long time. Fuoss and Kraus<sup>9</sup> assumed that the triple-ion formation for spherical symmetric ions by the Coulombic interaction does not occur in higher permittivity media ( $\epsilon_r > 23.2$ ). We have proposed<sup>10</sup> by means of spectrophotometry, polarography, and conductometry that in lowsolvating media with higher permittivities ( $20 < \epsilon_r < 65$ ), many 1:1 salts of non-spherical-symmetric ions can form higher ion aggregates through hydrogen bonding and "coordination" forces as well as the Coulombic force. In our systems, tetraalkylammonium ions  $(R_4N^+)$  and the perchlorate ion  $(ClO_4^-)$  are regarded as having no chemical interaction (with any ion) other than the Coulombic interaction in the solution. We have pointed out the rather strong coordination abilities of Li<sup>+</sup> (and Na<sup>+</sup>) in low-solvating media as those of transition metal ions in aqueous solution. We have used the term "triple ions" not only for the species formed through "pure" Coulombic attractions but also for species formed through other interactions.<sup>10</sup>

In the present study, the effects of alkali (Li<sup>+</sup>, Na<sup>+</sup>) and alkaline-earth (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) metal perchlorates on the proton transfer from nitrophenols to amine or pyridine bases in acetonitrile were examined by means of spectrophotometry. Various nitrophenols with the nitro group at the ortho position were examined: 2-nitrophenol, 2,4- and 2,5-dinitrophenols, and

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2,4,6-trinitrophenol. In addition, 4-nitrophenol was examined in order to discuss the difference in the complex-forming ability between the *o*-nitrophenolate ions and the nitrophenolate ions that are not ortho. The effects of tetraalkylammonium halides  $(R_4N^+X^-: R = Et, n-Bu; X^- = Cl^-, Br^-, I^-)$  on the deprotonation of nitrophenols in the presence of bases in acetonitrile were also examined.

Steigman and Lorenz<sup>11</sup> have reported the effects of added quaternary ammonium salts on the acid—base reactions of some nitrophenols in benzene. The research stemmed from an observation by Pearson and Vogelsang.<sup>12</sup> In the present paper, we would like to discuss quantitatively the effects of various salts from the standpoint of the formation of triple ions  $((NO_2)_nPhO^-(M^+)_2$  and  $R_3NH^+(X^-)_2)$  in acetonitrile. The "real" formation constants of higher ion aggregates have been obtained by calculations with our method<sup>10</sup> for lithium and sodium nitrophenolates in several aprotic solvents.<sup>13</sup> The successive formation constants in acetonitrile have been already reported.<sup>14</sup> The 1:1 complex formation  $((NO_2)_nPhO^-M^{2+})$ between alkaline-earth metal ions and nitrophenolate ions will be reported in the final section of the present paper.

#### **Experimental Section**

Commercially obtained acetonitrile (Nacalai Tesque, specially prepared reagent for spectrophotometry) was used as received. Nitrophenols, i.e., 2- and 4-nitrophenols and 2,4- and 2,5dinitrophenols (TCI, GR grade), were used without further purification. Picric acid (2,4,6-trinitrophenol, Wako, GR grade, 15-25% water added) was dried in vacuo at 80 °C. The tetraethylammonium phenolates were prepared by the neutralization in methanol between the phenols and the equivalent amount of Et<sub>4</sub>NOH (Aldrich, 20% aqueous solution). The solutions were evaporated to dryness, adding MeOH, acetone, and diethyl ether successively, under reduced pressure at <50°C. The crystals were washed with diethyl ether and were dried in vacuo at 50-60 °C. Tetraethylammonium 2,4-dinitrophenolate was extremely hygroscopic. In a previous paper<sup>6</sup> are described the preparation and purification methods (or the reagent resources) for LiClO<sub>4</sub>, NaClO<sub>4</sub>, alkaline-earth metal perchlorates, and tetraethylammonium or tetrabutylammonium halides and perchlorates. Other reagents obtained commercially were used as received.

UV-visible spectra were measured using a Hitachi doublebeam spectrophotometer (Model U-2000) in 1.0 and 0.1 cm quartz cuvettes at room temperature.

### **Results and Discussion**

Effects of Alkali and Alkaline-Earth Metal Ions. In acetonitrile, 2,4-dinitrophenol is a very weak acid ( $pK_a = 16.0$ in MeCN and 4.0 in H<sub>2</sub>O).<sup>15</sup> Therefore, it does not dissociate at all in the protophobic aprotic solvent. Figure 1 shows the changes in the UV-visible absorption spectra of 2,4-dinitrophenol (1.0  $\times$  10<sup>-4</sup> mol dm<sup>-3</sup>) with the addition of  $\gamma$ -picoline (4-methylpyridine). The addition of the equivalent amount of the base had almost no effect on the spectrum of the phenol. However, two peaks at 371 and 425 nm appeared, corresponding to the 2,4-dnitrophenolate ion formed upon the addition of a large excess of the base; with 0.1 mol dm<sup>-3</sup>  $\gamma$ -picoline, it was found that ca. 67% of the phenols was converted to the phenolate ions. On the other hand, a  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> tetraethylammonium 2,4-dinitrophenolate solution gave two peaks at 373 and 426 nm (for > 300 nm) with a molar absorption coefficient of  $\log(\epsilon/cm^{-1} \text{ mol}^{-1} dm^3) = ca. 4.2$  (cf. Table 1). The production of the conjugate base  $(A^{-})$  by the addition of a large



**Figure 1.** Changes in the UV-visible absorption spectra of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> 2,4-dinitrophenol with the addition of  $\gamma$ -picoline in acetonitrile: (-) 0; (···)  $1 \times 10^{-4}$ ; (-·-)  $1 \times 10^{-3}$ , (-·-)  $1 \times 10^{-2}$ ; (-··-) 0.1 mol dm<sup>-3</sup>  $\gamma$ -picoline.

TABLE 1: Changes in  $\lambda_{max}$  and Absorbance ofTetraethylammonium Phenolates upon the Addition ofAlkali and Alkaline-Earth Metal Perchlorates [0.1 mol dm<sup>-3</sup>MClO<sub>4</sub> and 0.02 mol dm<sup>-3</sup> M(ClO<sub>4</sub>)<sub>2</sub>] in Acetonitrile

	$\lambda_{max}/nm$ (absorbance)						
$Et_4N^+-(NO_2)_nPhO^-$	none	Li <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
2-nitrophenolate $(2.0 \times 10^{-4} \text{ mol dm}^{-3})$ 4-nitrophenolate $(2.0 \times 10^{-4} \text{ mol dm}^{-3})^b$	450 (1.57) <sup><i>a</i></sup> 430 (0.65)	424 (1.22) 395 (0.20)	440 (1.34) 417 (0.40)				
2,4-dinitrophenolate ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ )	373 (1.50) 426 (1.57)	(0.120) 350 (1.31) 413 (0.98)	361 (1.48) 420 (1.27)	334 (1.23) 410 (0.74)	344 (1.31) 408 (0.81)	352 (1.33) 410 (0.86)	361 (1.49) 410 (0.97)
2,5-dinitrophenolate ( $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ )	487 (1.04) 351 (0.59)	454 (1.16) c	468 (1.20)	453 (1.27)	452 (1.13)	455 (1.11)	457 (1.04)
2,4,6-trinitrophenolate ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ )	375 (~1.8)	344 (1.31) 402 <sup>d</sup> (0.89)	361 (1.40)	323 (1.22) 405 (0.73)	336 (1.34) 400 (0.81)	341 (1.43) 403 (0.87)	343 (1.45) 402 (0.86)

<sup>*a*</sup> Absorbance in 1.0 cm path length, unless otherwise stated. <sup>*b*</sup> Pathlength of 0.1 cm. <sup>*c*</sup> The peak at the lower wavelength disappeared upon the addition of metal ions. <sup>*d*</sup> A second peak appeared upon the addition of metal ions.

excess of a weak base (B) to a weak acid (HA) in aprotic and inert solvents<sup>5,16</sup> has been explained by the formation of the homoconjugate species,  $B_2H^{+,17}$ 

$$HA + 2B \rightleftharpoons A^{-} \cdots B_{2}H^{+}$$
(4)

Interaction between  $A^-$  and  $B_2H^+$  must be much smaller than that between  $A^-$  and  $BH^+$ . It was found that even a large excess of dimethylaniline was too weak of a base to produce a sufficient amount of the 2,4-dinitrophenolate ion from the phenol. On the contrary, triethylamine or  $\gamma$ -collidine (2,4,6-trimethylpyridine) was so strong that the presence of an amount of the amine equivalent to the amount of the phenol produced some of the 2,4-dinitrophenolate ion.

Figure 2 shows the effects of LiClO<sub>4</sub> on the absorption spectra of the mixture of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> 2,4-dinitrophenol and  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>  $\gamma$ -picoline. Upon the addition of LiClO<sub>4</sub> to the mixture solution, two absorption bands at around 350 and 420 nm appeared. In the presence of 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>, the absorbances of the distinct peaks were 0.94 and 0.62 at  $\lambda_{max}$ = 349 and 413 nm, respectively. We need to mention that the wavelength and absorbance values of two peaks of the 2,4-



**Figure 2.** Effects of LiClO<sub>4</sub> on the absorption spectra of the mixture of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> 2,4-dinitrophenol +  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>  $\gamma$ -picoline: (-) 0; (···)  $1.0 \times 10^{-3}$ ; (- -)  $1.0 \times 10^{-2}$ ; (-·-) 0.1; (-··-) 0.2 mol dm<sup>-3</sup> LiClO<sub>4</sub>.



**Figure 3.** Ratio of proton transfer from 2,4-dinitrophenol  $(1.0 \times 10^{-4} \text{ mol dm}^{-3})$  to  $\gamma$ -picoline  $(1.0 \times 10^{-4} \text{ mol dm}^{-3})$  in the presence of alkali metal ions in acetonitrile: (O) LiClO<sub>4</sub>; ( $\bullet$ ) NaClO<sub>4</sub>.

dinitrophenolate ion ([Et<sub>4</sub>N<sup>+</sup>-2,4-(NO<sub>2</sub>)<sub>2</sub>PhO<sup>-</sup>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>) were altered by the addition of LiClO<sub>4</sub>. For instance, the absorbances of the peaks were 1.31 and 0.98 at  $\lambda_{max} = 350$  and 413 nm, respectively, with 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub> (cf. Table 1). The  $\lambda_{max}$  values of the 2,4-dinitrophenol +  $\gamma$ -picoline solution containing LiClO<sub>4</sub> (of higher concentrations) were completely coincident with those of the 2,4-dinitrophenolate ion in the presence of the corresponding concentrations of LiClO<sub>4</sub>. The ratio of the produced phenolate to the original phenol concentration was calculated to be 62–63% by the absorbances at 413 nm for 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>. Figure 3 shows the ratio of the proton transfer from 2,4-dinitrophenol to  $\gamma$ -picoline with various concentrations of Li<sup>+</sup> and Na<sup>+</sup>. The effects of Na<sup>+</sup> were much smaller than those of Li<sup>+</sup>: Li<sup>+</sup>  $\gg$  Na<sup>+</sup>.

Alkaline-earth metal ions ( $M^{2+}$ ) had very large effects on the proton transfer from 2,4-dinitrophenol even at very low concentration of  $M^{2+}$  (Figure 4). Upon the addition of 1 ×  $10^{-4}$  mol dm<sup>-3</sup> Mg(ClO<sub>4</sub>)<sub>2</sub> to the 1.0 ×  $10^{-4}$  mol dm<sup>-3</sup> 2,4dinitrophenol +  $\gamma$ -picoline solution, the proton transfer proceeded up to 80%, for instance. The proton transfer increased linearly with increasing concentration of M(ClO<sub>4</sub>)<sub>2</sub>; this fact suggested the 1:1 interaction between M<sup>2+</sup> and (NO<sub>2</sub>)<sub>2</sub>PhO<sup>-</sup> (vide infra). The effects of alkaline-earth ions decreased with increasing size of the cations: Mg<sup>2+</sup> > Ca<sup>2+</sup> > Sr<sup>2+</sup> > Ba<sup>2+</sup>. In the absence of the base, the deprotonation of 2,4-dinitrophenol that occurred upon by the addition of 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub> and NaClO<sub>4</sub> and 0.05 mol dm<sup>-3</sup> Mg(ClO<sub>4</sub>)<sub>2</sub> was ca. 30, 15, and 20%, respectively. The similar direct reaction<sup>5</sup> between



**Figure 4.** Ratio of proton transfer from 2,4-dinitrophenol  $(1.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$  to  $\gamma$ -picoline  $(1.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$  in the presence of alkaline-earth metal ions in acetonitrile: ( $\Delta$ ) Mg(ClO<sub>4</sub>)<sub>2</sub>; ( $\bigcirc$ ) Ca(ClO<sub>4</sub>)<sub>2</sub>; ( $\bigcirc$ ) Sr(ClO<sub>4</sub>)<sub>2</sub>; ( $\bigcirc$ ) Ba(ClO<sub>4</sub>)<sub>2</sub>.



**Figure 5.** Changes of visible absorption spectra of 2,5-dinitrophenolate ([Et<sub>4</sub>N<sup>+</sup>-2,5-(NO<sub>2</sub>)<sub>2</sub>PhO<sup>-</sup>] =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>) with increasing concentration of Li<sup>+</sup> in acetonitrile: (-) 0; (...)  $1.0 \times 10^{-4}$ ; (---)  $2.0 \times 10^{-4}$ ; (---)  $5 \times 10^{-4}$  and  $1.0 \times 10^{-3}$ ; (----) 0.1; (----) 0.2 mol dm<sup>-3</sup> LiClO<sub>4</sub>.

 $Mg^{2+}$  and an acid, tropolone (C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>H), without bases in acetonitrile has been reported.

A weaker acid, 2,5-dinitrophenol ( $pK_a = 5.2$  in H<sub>2</sub>O),<sup>18</sup> gave phenomena similar to, but more remarkable than, those of 2,4dinitrophenol in acetonitrile. The changes in the UV-visible absorption spectra of the 2,5-dinitrophenolate ion with the addition of LiClO<sub>4</sub> are shown in Figure 5. The free 2,5dinitrophenolate ion ( $[Et_4N^+-2,5-(NO_2)_2PhO^-] = 2.0 \times 10^{-4}$ mol dm<sup>-3</sup>) gave four peaks at ca. 220 nm (absorbance > 2.0), 264 nm (1.75), 351 nm (0.59), and 487 nm (1.04). Upon the addition of a small amount of LiClO<sub>4</sub> ( $2 \times 10^{-4}$  mol dm<sup>-3</sup>), the peak at 351 nm disappeared to give a valley around 370 nm instead; the peaks at 220 and 246 nm showed bathochromic shifts, but the peak at 487 nm showed the hypsochromic shift and the hyperchromic effect. The absorbance of the peak in the spectra of Figure 5 reached its maximum (1.27 at 460 nm) with  $5 \times 10^{-4}$  or  $1 \times 10^{-3}$  mol dm<sup>-3</sup> LiClO<sub>4</sub>. With the further addition of LiClO<sub>4</sub>, the absorbance of the peak decreased gradually with the further hypsochromic shift, e.g., an absorbance of 1.12 occurred at 447 nm for 0.2 mol  $dm^{-4}$  LiClO<sub>4</sub>. While the concentration of LiClO<sub>4</sub> increased from  $1 \times 10^{-4}$  to 0.2 mol dm<sup>-3</sup>, two distinct isosbestic points were observed successively at 482 and 440 nm. The first isosbestic point (482 nm) showed the copresence of the ion pair  $(Li^+A^-)$  and the free phenolate ion (A<sup>-</sup>); the second one (440 nm) suggested



**Figure 6.** Variation of the ratio of proton transfer from 2,5dinitrophenol  $(2.0 \times 10^{-4} \text{ mol dm}^{-3})$  to various bases  $(2.0 \times 10^{-4} \text{ mol dm}^{-3})$  in the presence of LiClO<sub>4</sub>: ( $\Delta$ )  $1.0 \times 10^{-3}$ ; ( $\oplus$ )  $1.0 \times 10^{-2}$ ; ( $\bigcirc$ ) 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>. Bases are dimethylaniline (pK<sub>a</sub> = 4.63 for aniline), pyridine (5.25),  $\gamma$ -picoline (6.02),  $\gamma$ -collidine (6.69), 2-chlorobenzylamine (8~9, predicted), benzylamine (9.33), and triethylamine (10.72).

the formation of the triple cation  $((Li^+)_2A^-)$  by the reaction between  $Li^+A^-$  and  $Li^+$  in the presence of a large excess of  $Li^+$ . Successive isosbestic points have been observed for the reaction between the 2,4-dinitrobenzoate ion and  $Li^+$  in acetonitrile, and the formation of the ion pair and the triple cation have been confirmed.<sup>19</sup> For the present system, the formation constants of the ion pair  $(Li^+ + A^- \rightleftharpoons Li^+A^-, K_1)$  and the triple cation (2  $Li^+ + A^- \rightleftharpoons (Li^+)_2A^-, K_2)$  were estimated to be roughly  $K_1 = 2 \times 10^6$  and  $K_2 = 3 \times 10^7$ , respectively. The interaction between the 2,5-dinitrophenolate ion and Na<sup>+</sup> gave similar successive isosbestic points at 495 and 462 nm; the formation of the ion pair  $(Na^+A^-)$  and the triple cation  $((Na^+)_2A^-)$  was suggested.

Conductometric data of lithium and sodium nitrophenolates in acetonitrile<sup>13</sup> have shown that the formation constants of higher ion aggregates decreased as follows:  $2 - \gg 4 -$ , 2,5 - > $2,4 - \gg 2,4,6$ -nitrophenolate and Li<sup>+</sup>  $\gg$  Na<sup>+</sup>. In THF, the aggregation of lithium phenolates has been investigated by NMR, vapor-pressure osmometry, and conductometry.<sup>20</sup>

The salt effects on the proton transfer from 2,5-dinitrophenol to amine or pyridine bases in acetonitrile were examined. The fact that the association constants (ion pair and triple ions) of lithium 2,5-dinitrophenolate are larger than those of the lithium 2,4-derivative (by conductometry)<sup>13</sup> suggested that the lithium ion would have larger effects on proton transfer from 2,5dinitrophenol than those from 2,4-dinitrophenol. However, experiments gave the opposite result: lithium effects on the 2,5dinitrophenol +  $\gamma$ -picoline (both 2.0  $\times$  10<sup>-4</sup> mol dm<sup>-3</sup>) solution were smaller than those on the 2,4-dinitrophenol +  $\gamma$ -picoline (both  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>) solution. The reason for the contradiction between the prediction and the experimental result may lie in the strength of base for each nitro-substituted phenol. Figure 6 shows the changes in the ratio of proton transfer from 2,5-dinitrophenol to amine and pyridine bases with various basicities in the presence of  $1 \times 10^{-3}$ ,  $1 \times 10^{-2}$ , and 0.1 mol  $dm^{-3}$  LiClO<sub>4</sub>. The proton-transfer ratios of 5, 12, and 31% for 2,5-dinitrophenol +  $\gamma$ -picoline (pK<sub>a</sub> = 6.02 at 20 °C in H<sub>2</sub>O)<sup>21</sup> were indeed smaller than the values of 14, 31, and 62% for the 2,4-dinitrophenol +  $\gamma$ -picoline system (cf. Figure 3) in the presence of  $1 \times 10^{-3}$ ,  $1 \times 10^{-2}$ , and 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>, respectively. With a stronger base,  $\gamma$ -collidine (pKa = 6.69),<sup>22</sup> however, the proton transfer from 2,5-dinitrophenol jumped up to 18, 41, and 74%, respectively. Using an even stronger base, the proton-transfer ratio increased further. On the other hand, one must pay attention to the fact that bases that are too strong may deprotonate from acids in the absence of metal ions, as do

benzylamine  $(pK_a = 9.33)^{21}$  and triethylamine  $(pK_a = 10.72)^{18}$  for 2,5-dinitrophenol in acetonitrile. The most appropriate choice of bases was found to be  $\gamma$ -collidine or 2-chlorobenzylamine  $(pK_a = 8-9, a \text{ predicted value})$  for 2,5-dinitrophenol.

The effects of NaClO<sub>4</sub> on the proton transfer from 2,5dinitrophenol to  $\gamma$ -collidine were as small as those on the proton transfer from 2,4-dinitrophenol to  $\gamma$ -picoline. The effects of alkaline-earth ions (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>) on the 2,5- +  $\gamma$ -collidine system were all larger than those on the 2,4- +  $\gamma$ -picoline system in Figure 4. In the absence of bases, 2,5dinitrophenol was deprotonated up to 37% by 0.05 mol dm<sup>-3</sup> Mg(ClO<sub>4</sub>)<sub>2</sub>, although the effects of Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> were very small. The increases of the 2,5-dinitrophenolate peaks by 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub> and NaClO<sub>4</sub> in the absence of bases were even smaller.

From the above experimental results, it can be concluded that the salt effects of alkali  $(M^+)$  and alkaline-earth  $(M^{2+})$  metal perchlorates on the deprotonation from the dinitrophenols in the presence of a base (B) are caused by the following equations:

$$(NO_2)_2 PhOH - B + n M^+ \rightleftharpoons$$
  
 $(NO_2)_2 PhO^- (M^+)_n + BH^+ \quad (n = 1 \text{ and } 2) \quad (5)$ 

$$(NO_2)_2PhOH-B + M^{2+} \rightleftharpoons (NO_2)_2PhO^-M^{2+} + BH^+$$
 (6)

The metal ions must interact with (or "contact") the phenolate ions tightly; otherwise, the conjugate acid (BH<sup>+</sup>) may be ready to react with the phenolate ions because the phenolate ions are fairly strong bases and may be neutralized back by BH<sup>+</sup> in acetonitrile (cf. the next section).

Sodium ions have a lower ability than lithium ions to form ion pairs and triple ions with the nitrophenolate ions. Alkalineearth ions interact with the nitrophenolate ions to form the 1:1 ion pairs (or the complex species), and the ability decreases with increasing ionic size:  $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ . We would like to stress that tetraethylammonium or tetrabutylammonium perchlorate of 0.1 or 0.2 mol dm<sup>-3</sup> did not affect the deprotonation reactions in acetonitrile.

Although 2,4,6-trinitrophenol (picric acid) is a rather strong acid in aqueous solution ( $pK_a = 0.3$ ),<sup>15</sup> it can barely dissociate in acetonitrile  $(pK_a = 11.0)$ .<sup>15</sup> The data of absorption spectra for tetrabutylammonium picrate in acetonitrile have been reported.<sup>23</sup> As the most appropriate base for this acid, 2-chloropyridine was selected from many weak bases: the base strength decreased, in acetonitrile, as dibenzylamine > tribenzylamine, dimethylaniline > 3-chloropyridine > 2-chloropyridine > 3-cyanopyridine > methyldiphenylamine, diphenylamine > 2,6-dichloropyridine. The effects of Li<sup>+</sup> on the protontransfer reaction of picric acid + 2-chloropyridine (both  $1.0 \times$  $10^{-4}$  mol dm<sup>-3</sup>) were very small: only <20% of picric acids was deprotonated with 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>, while ca. 4% was deprotonated in the absence of LiClO<sub>4</sub>. Sodium ions had almost no effect on the deprotonation of picric acid (8% with even 0.2mol  $dm^{-3}$  NaClO<sub>4</sub>). The minor effects of Li<sup>+</sup> and Na<sup>+</sup> may be connected with the weak (Lewis) basicity of the picrate ion. Conductometric studies<sup>13,24</sup> have shown that lithium and sodium picrates associate only weakly ( $K_a = 9 \times 10^2$  and  $1.6 \times 10^2$ , respectively) and do not form triple ions in acetonitrile, although in benzonitrile the lithium salt associates strongly to form triple ions. The sudden increase in the proton transfer was observed for 0.1 mol dm<sup>-3</sup> Mg<sup>2+</sup>. By contrast, the effects of  $Ba^{2+}$ remained small for the wide concentration range.

The absorption spectrum of 2- or 4-nitrophenol could be completely distinguished from that of the corresponding nitrophenolate ion. The  $pK_a$  values of 2- and 4-nitrophenols are



**Figure 7.** Relationship between  $pK_a$  (in H<sub>2</sub>O) values of phenols and the proton-transfer ratio in the presence of LiClO<sub>4</sub>: ( $\triangle$ ) 1.0 × 10<sup>-3</sup>; ( $\bigcirc$ ) 1.0 × 10<sup>-2</sup>; ( $\bigcirc$ ) 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>. The phenols + appropriate bases are picric acid + 2-chloropyridine (both 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>), 2,4-dinitrophenol +  $\gamma$ -picoline (both 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>), 2,5dinitrophenol + 2-chlorobenzylamine (both 2.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>), and 2-nitrophenol + triethylamine (both 2.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>).

shown to be 7.23 and 7.15 in H<sub>2</sub>O and 22.0 and 20.7 in MeCN, respectively.<sup>15</sup> The  $\lambda_{max}$  (for > 300 nm) and absorbance values of tetraethylammonium nitrophenolates are listed in Table 1. The  $\lambda_{max}$  and  $\epsilon$  values of tetraethylammonium 4-nitrophenolate reported by Kolthoff et al.<sup>15</sup> are somewhat different from the values obtained in the present study.

Triethylamine was used as the base for both nitrophenols. Strictly speaking, triethylamine is not a most effective base for the nitrophenols because the addition of 0.1 mol  $dm^{-3}$  Et<sub>3</sub>N to  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup> nitrophenols resulted in the formation of at most 30% nitrophenolate ions. However, a stronger base, 1,1,3,3-tetramethylguanidine, was too effective: the addition of the equivalent amount of the strong base to the nitrophenols gave >30% nitrophenolate ions ( $\lambda_{max} = 448$  and 430 nm for 2and 4-derivatives, respectively). The addition of  $0.1 \text{ mol dm}^{-3}$ LiClO<sub>4</sub> and NaClO<sub>4</sub> to the mixture of 2-nitrophenol +  $Et_3N$ (both  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) caused the formation of 2-NO<sub>2</sub>- $PhO^{-}(M^{+})_{2}$  at ca. 100 and 44% yields, respectively. However, for 4-nitrophenol, the deprotonation reaction proceeded to a lower extent: 59 and 11% for 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub> and NaClO<sub>4</sub>, respectively. The greater interaction of the 2-nitrophenolate ion with Li<sup>+</sup> or Na<sup>+</sup> should be based on the nitro group at the ortho position.

Figure 7 shows the relationship between the proton-transfer ratio and the  $pK_a$  (in H<sub>2</sub>O) values of 2-, 2,4-, 2,5-, and 2,4,6nitro-substituted phenol solutions containing appropriate bases in the presence of LiClO<sub>4</sub>. The weaker the acid, the greater the deprotonation that occurs by the reaction with Li<sup>+</sup>. The interaction between alkaline-earth metal ions and the 2- or 4-nitrophenolate ion was too strong to be examined fully. Pocker and Ellsworth<sup>25</sup> have studied the salt effects of LiClO<sub>4</sub> on the proton transfer from 2-nitrophenol to imidazole in diethyl ether.

Formation of Free Nitrophenolate Ions by the Addition of R<sub>4</sub>NX. As shown in previous section, reacting with the phenolate ions in acetonitrile, alkali (M<sup>+</sup>) and alkaline-earth (M<sup>2+</sup>) metal ions caused proton transfer from nitrophenols to amine or pyridine bases. The absorption spectra of the produced species,  $(NO_2)_nPhO^-(M^+)_2$  or  $(NO_2)_nPhO^-(M^{2+})$ , showed remarkable hypsochromic shifts from those of the free phenolate ions  $(Et_4N^+-(NO_2)_nPhO^-)$ . In the present section, the effects of tetraalkylammonium halides  $(R_4N^+X^-: R = Et, n-Bu; X =$  $Cl^-, Br^-, I^-)$  are discussed.

Figure 8 shows the changes in the UV-visible absorption spectra of 2,5-dinitrophenol and 2-chlorobenzylamine (both 2.0  $\times 10^{-4}$  mol dm<sup>-3</sup>) with the addition of Et<sub>4</sub>NCl. Upon the



**Figure 8.** Production of free 2,5-dinitrophenolate ions by the addition of various concentrations of Et<sub>4</sub>NCl to  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup> 2,5-dinitrophenol +  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup> 2-chlorobenzylamine in acetonitrile: (-) 0; (···)  $1.0 \times 10^{-3}$ ; (---)  $1.0 \times 10^{-2}$ ; (-·-) 0.1; (-··-) 0.2; (-··-) 0.3 mol dm<sup>-3</sup> Et<sub>4</sub>NCl.

addition of a small amount of Et<sub>4</sub>NCl, an absorption band appeared at 487 nm, and the intensity of the band increased with increasing concentration of Et<sub>4</sub>NCl. The wavelength of the peak was completely coincident with that of the free 2,5-dinitrophenolate ion (Et<sub>4</sub>N<sup>+</sup>-2,5-(NO<sub>2</sub>)<sub>2</sub>PhO<sup>-</sup>). In the presence of 0.5 mol dm<sup>-3</sup> Et<sub>4</sub>NCl, 100% of the 2,5-dinitrophenolate ions was produced; the wavelengths and the absorbances of other peaks of the produced species also coincided beautifully with that of 2.0 × 10<sup>-4</sup> mol dm<sup>-3</sup> Et<sub>4</sub>N<sup>+</sup>-2,5-(NO<sub>2</sub>)<sub>2</sub>PhO<sup>-</sup>. The above observation can be explained by the following equation

2,5-(NO<sub>2</sub>)<sub>2</sub>PhOH−B + 2Cl<sup>-</sup> 
$$\rightleftharpoons$$
  
2,5-(NO<sub>2</sub>)<sub>2</sub>PhO<sup>-</sup> + BH<sup>+</sup>(Cl<sup>-</sup>)<sub>2</sub> (7)

where B is the base 2-chlorobenzylamine. When the base was altered to a weaker one,  $\gamma$ -collidine, the yield of the free phenolate ion decreased substantially (cf. Table 2).

The formation of the free phenolate ion should not be caused by the change in the ionic strength because the addition of 0.5 mol  $dm^{-3}$  Et<sub>4</sub>NClO<sub>4</sub> to 2,5-dinitrophenol + 2-chlorobenzylamine (both  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>) caused only a small increase  $(\sim 10\%)$  in the absorbance at 487 nm. In the absence of bases, ca. 5% of the phenolates was produced by the addition of 0.1mol dm<sup>-3</sup> Et<sub>4</sub>NCl to  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup> 2,5-dinitrophenol: this fact might suggest that the Et<sub>4</sub>NCl reagent contained no strong base (such as Et<sub>4</sub>NOH) as an impurity. Neither did the Et<sub>4</sub>NCl reagent contain any acid, such as Et<sub>3</sub>NHCl, because the absorbance of 487 nm was not decreased by the addition of a large excess of the Et<sub>4</sub>NCl to a Et<sub>4</sub>N<sup>+</sup>-2,5-(NO<sub>2</sub>)<sub>3</sub>PhO<sup>-</sup> solution, while the 2.5-dinitrophenolate ion can be quantitatively neutralized (into the phenol) by the equivalent amount of Et<sub>3</sub>NHClO<sub>4</sub>. Another Et<sub>4</sub>NCl reagent caused the disappearance of the phenolate peaks; this reagent was not used anymore in the experiment.

Although the effects of Et<sub>4</sub>NBr were smaller than those of Et<sub>4</sub>NCl, the free 2,5-dinitrophenolate ion was definitely produced in a similar way. However, the effects of Et<sub>4</sub>NI were not fully comprehended, since ca. 15% of 2,5-dinitrophenolate ions was produced by the addition of 0.1 mol dm<sup>-3</sup> Et<sub>4</sub>NI to the phenol in both the presence and the absence of  $\gamma$ -collidine.

TABLE 2: Production of Free Phenolate Ion by the Addition of Tetraalkylammonium halide<sup>*a*</sup> (0.1 mol dm<sup>-3</sup>) to the Mixtures<sup>*b*</sup> of Phenols and Amine or Pyridine Bases in Acetonitrile

	yie	n)	
phenols + bases	Cl-	Br <sup>-</sup>	I-
2-nitrophenol			
$+ E t_3 N$	23.1 (448)	13.7 (447)	
4-nitrophenol			
$+ Et_3N$	58.4 (429)	55.2 (430)	32.1 (429)
2,4-dinitrophenol			
+ $\gamma$ -picoline <sup>d</sup>	24.0 (426)	18.9 (426)	32.6 (426)
2,5-dinitrophenol			
$+ \gamma$ -collidine	12.0 (487)	9.0 (487)	е
+ 2-chlorobenzylamine	63.3 (487)	41.7 (487)	
2,4,6-trinitrophenol			
+ 2-chloropyridine	100 (375)	87 (375)	66 (365)
+ none	100 (375)	81 (375)	58 (366)

<sup>*a*</sup> Et<sub>4</sub>NX, except for 2,4,6-trinitrophenol (*n*-Bu<sub>4</sub>NX). <sup>*b*</sup> [(NO<sub>2</sub>)<sub>*n*</sub>PhOH] = [base] =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, except that [2,4-dinitrophenol] = [ $\gamma$ -picoline] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> and [2,4,6-trinitrophenol] = [2-chloropyridine] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>. <sup>*c*</sup> The ratio of the peak absorbance of the produced species to that of Et<sub>4</sub>N<sup>+</sup>(NO<sub>2</sub>)<sub>*n*</sub>PhO<sup>-</sup> (cf. Table 1), except the ratio of absorbance at 400 nm for 2,4,6-trinitrophenol. <sup>*d*</sup> The other peak appeared at 370 nm. <sup>*e*</sup> See text.



**Figure 9.** Changes in the UV-visible absorption spectra (in 0.1 cm cuvettes) of the 2,4-dinitrophenolate ion ( $[Et_4N^+-2,4-(NO_2)_2PhO^-] = 1.0 \times 10^{-3}$  mol dm<sup>-3</sup>) with the addition of Sr(ClO<sub>4</sub>)<sub>2</sub> in acetonitrile: (1) 0; (2) 2.0 × 10<sup>-4</sup>; (3) 5.0 × 10<sup>-4</sup>; (4) 1.0 × 10<sup>-3</sup>; (5) 2.0 × 10<sup>-3</sup>; (5) 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup> Sr(ClO<sub>4</sub>)<sub>2</sub>. The ionic strength was kept at 0.1 with Et<sub>4</sub>NClO<sub>4</sub>.

The formation of the free picrate ion was observed to result from the addition of *n*-Bu<sub>4</sub>NCl to picric acid + 2-chloropyridine (both  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>). A concentration of *n*-Bu<sub>4</sub>NCl as low as  $1 \times 10^{-4}$  mol dm<sup>-3</sup> caused a 30% conversion of picric acid to the picrate ion, and at 0.1 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NCl, the conversion was 100%. The copresence of 2-chloropyridine was not significant for this stronger acid. The effects of *n*-Bu<sub>4</sub>NBr and *n*-Bu<sub>4</sub>NI were much smaller than those of *n*-Bu<sub>4</sub>NCl (Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>), especially at low halide concentrations. The free phenolate ions were also produced by the addition of tetraethylammonium halides to 2- and 4-nitrophenols (cf. Table 2).

Strong Interaction between Nitrophenolate Ions with Alkaline-Earth Metal Ions. The demonstration by spectrophotometry (and conductometry)<sup>13</sup> of the presence of reversecoordinated species  $[(NO_2)_nPhO^-(M^+)_2]$  of alkali metal ions with the nitrophenolate ions in acetonitrile has been described in the first section. In the present section, strong interactions between the nitrophenolate ions and alkaline-earth metal ions are reported.

Figure 9 shows the changes in the UV-visible spectra of the 2,4-dinitrophenolate ion ( $[Et_4N^+-2,4-(NO_2)_2PhO^-] = 1.0 \times 10^{-3}$  mol dm<sup>-3</sup>) with the addition of Sr(ClO<sub>4</sub>)<sub>2</sub> in acetonitrile. In the presence of  $0.5 \times 10^{-3}$  mol dm<sup>-3</sup> Sr<sup>2+</sup>, a white precipitate

formed, and the absorption bands of the phenolate ion almost disappeared. However, by the addition of the equivalent amount  $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$  of Sr<sup>2+</sup> to the phenolate ion, new bands at lower wavelengths appeared, with redissolution of the precipitates. The absorbance of a peak of the phenolate increased with increasing concentration of Sr<sup>2+</sup>. The absorbance at 350 nm reached a constant value at >1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup> Sr(ClO<sub>4</sub>)<sub>2</sub>. The above phenomena are explained by eqs 8 and 9. The formation and redissolution of precipitates were also

$$(NO_2)_2 PhO^- + \frac{1}{2}Sr^{2+} \rightarrow \frac{1}{2}((NO_2)_2 PhO^-)_2 Sr^{2+} \downarrow (8)$$

$$1/_{2}((NO_{2})_{2}PhO^{-})_{2}Sr^{2+} \downarrow + 1/_{2}Sr^{2+} \rightarrow (NO_{2})_{2}PhO^{-}Sr^{2+} \uparrow (9)$$

observed at the half-equivalent amount and an excess of  $Ba^{2+}$ , respectively. However, precipitates were not formed by the addition of  $Mg(ClO_4)_2$  and  $Ca(ClO_4)_2$ , although large hypso-chromic shifts were observed.

For the interaction between the picrate ion ( $[Et_4N^+Pic^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) and Ba<sup>2+</sup>, a precipitate formed at 0.5 × 10<sup>-3</sup> mol dm<sup>-3</sup> Ba<sup>2+</sup> in acetonitrile. The absorbance (of the supernatant solution) decreased and, again, began to increase at 2 × 10<sup>-3</sup> mol dm<sup>-3</sup> Ba(ClO<sub>4</sub>)<sub>2</sub>; absorbance at ca. 345 nm reached a constant value at 5 × 10<sup>-2</sup> mol dm<sup>-3</sup> Ba<sup>2+</sup>. The successive formation of a sparingly soluble species, (Pic<sup>-</sup>)<sub>2</sub>Ba<sup>2+</sup>, and a soluble species, Pic<sup>-</sup>Ba<sup>2+</sup>, do account for the phenomena. Other alkaline-earth metal ions did not form precipitates; however, the absorbance of the picrate decreased slightly at the half-equivalent amount of M<sup>2+</sup> and then increased in the presence of an excess of M<sup>2+</sup>.

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