Role of Triple Ion Formation in the Acid–Base Reaction between Tropolone and Triethylamine in Acetonitrile

Masashi Hojo,* Hiroshi Hasegawa and Hitoshi Yoneda
Department of Chemistry, Faculty of Science, Kochi University, Kochi 780, Japan

The acceleration of the proton-transfer reaction between tropolone (2-hydroxycyclohepta-2,4,6-trien-1-one) and triethylamine by the addition of various salts in acetonitrile was examined by UV–VIS spectroscopy. The addition of lithium perchlorate to the tropolone–triethylamine solution caused the formation of a cationic 'triple ion', $C_7H_5O_2^-(Li^+)_2$ (λ_{max} = 393 nm): $C_7H_5O_2H{-}NEt_3 + 2\ Li^+ \rightleftharpoons C_7H_5O_2^-(Li^+)_2 + Et_3NH^+$; the 'free' tropolonate ion ($Bu_4NC_7H_5O_2$) gave a band at 414 nm in acetonitrile. The effects of Na^+ on the reaction were much smaller than those of Li^+. Alkaline-earth metal ions ($M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+} and Ba^{2+}) promoted the deprotonation of tropolone by forming the species $C_7H_5O_2^-(M^{2+})$. On the other hand, the addition of Et_4NCl to the tropolone–triethylamine mixture produced the 'free' tropolonate ion (λ_{max} = 414 nm): $C_7H_5O_2H{-}NEt_3 + 2\ Cl^- \rightleftharpoons C_7H_5O_2^- + Et_3NH^+(Cl^-)_2$. The decrease in the amount of $C_7H_5O_2^-$ formed with Et_4NBr or Et_4NI was attributed to a decrease in the formation constants of the anionic 'triple ions' [$Et_3NH^+ + 2\ X^- \rightleftharpoons Et_3NH^+(X^-)_2$]. Thus, 'the salt effects' upon the deprotonation of the weak acid by the amine were explained quantitatively by the 'coordination' reactions and not merely by ion-pair exchange reactions.

Gordon[1] has stated that covalent bonding is believed to be absent in alkali metal–halide and alkaline earth–fluoride ion-pairs. However, Oelkers and Helgeson have suggested[2] the formation of higher ion-aggregates (multiple ion association) from NaCl in supercritical aqueous solutions. In poorly solvating media, such as acetonitrile and acetone, complex formation with weaker ligands can be observed. For instance, alkali metal complexes of the benzoate ion [$M^+(C_6H_5CO_2^-)_2$, M = Li, Na, K],[3] the chloride ion [$Li^+(Cl^-)_n$, n = 1–4],[4] cyclic [*e.g.*, Li^+(cyclam) or Na^+(TMC)][5] and acyclic [M^+(trien), M = Li, Na][6] polyamines have been detected polarographically in acetonitrile.

While some workers may not easily accept that two or more alkali metal ions (especially Li^+) can combine with a single-charged anion (L^-), *i.e.* 'reverse coordination', we have detected the $(Li^+)_2L^-$ species with $CH_3CO_2^-$ and $C_6H_5CO_2^-$,[3] Cl^-,[7] $C_6H_5SO_3^-$, $(PhO)_2PO_2^-$,[8] *etc.* Carboxylate ions have an extraordinarily strong affinity towards Na^+ as well as towards Li^+, and can form the reverse coordinated species of Na^+, $RCO_2^-(Na^+)_2$.[3,9] Such 'weak' bonds can only be revealed in the absence of the strongly solvating powers of water towards the ions. The formation of higher ion-aggregates (triple ions and quadrupoles), through mainly hydrogen-bonding and coordination forces, has been proposed for many 1:1 electrolytes in protophobic aprotic solvents with relatively high permittivities ($20 < \varepsilon_r < 65$) by means of spectrophotometry and conductometry.[4,8,10–15]

In their series of studies in $LiClO_4$–diethyl ether solutions, Pocker and Ciula[16] reported an extremely large enhancement for the deprotonation of tropolone by amine bases (pyridines and anilines) by increasing the concentration of $LiClO_4$. They explained these results by the solvation of the ion-pairs produced in the proton-transfer equilibrium and their interaction with the solvated $LiClO_4$ ion-pairs and higher aggregates. They have suggested two types of solvated lithium ions, $Li(OEt_2)^+$ and $Li(OEt_2)_2^+$.[17] The present work was planned in order to explain properly the above salt effects by the formation of higher ion-aggregates, such as triple ions. Previously, we have succeeded in explaining quantitatively the 'levelling effect' of carboxylic acids in pyridine solution containing $LiClO_4$ and $NaClO_4$ by the formation of $RCO_2^-(M^+)_2$-type species,[18] instead of in terms of simple ion-exchange reactions, *i.e.* eqn. (1) (A^- = conjugate base from an acid) as

$$PyH^+A^- + M^+ClO_4^- \rightleftharpoons PyH^+ClO_4^- + M^+A^- \qquad (1)$$

proposed by Tsuji and Elving.[19]

In the present paper, the effects of various cations (alkali and alkaline-earth metal ions) and anions (halides) on the acid–base reaction of tropolone–triethylamine in acetonitrile have been examined spectrophotometrically. The effects are discussed from the standpoint of 'complex' formation among the species in the solution. The effects of alkali and alkaline-earth metal ions on the 'free' tropolonate ion ($Bu_4NC_7H_5O_2$) were also examined so as to confirm the formation of complexes between the metal ions and the tropolonate ion.

Experimental

Reagents.—Commercially obtained acetonitrile (Nacalai Tesque, specially prepared reagent for spectrophotometry) was used as received. Tropolone ($C_7H_5O_2H$, 2-hydroxycyclohepta-2,4,6-trien-1-one), obtained from Aldrich, and triethylamine, of GR grade from Wako Pure Chemicals, were used without further purification. Tetrabutylammonium tropolonate ($Bu_4NC_7H_5O_2$) was prepared from tetrabutylammonium hydroxide (10% aqueous solution, Wako, GR grade) and the equivalent amount of tropolone in methanol. The produced crystals were dried under vacuum at 50 °C (Found: C, 75.15; H, 11.3; N, 3.9. Calc. for $C_{23}H_{41}NO_2$: C, 75.98; H, 11.36; N, 3.85%).

Apparatus and Procedure.—UV–VIS spectra were measured using a Hitachi double-beam spectrophotometer (model U-2000) in 1.0 and 0.1 cm quartz cuvettes at room temperature. When precipitation occurred, the solution was sonicated for 5 min. The supernatant solution was removed after centrifuging at *ca.* 2500 rpm for 20 min. Tetrabutylammonium tropolonate solutions and tropolone–triethylamine–Et_4NX solutions were prepared in brown-coloured containers.

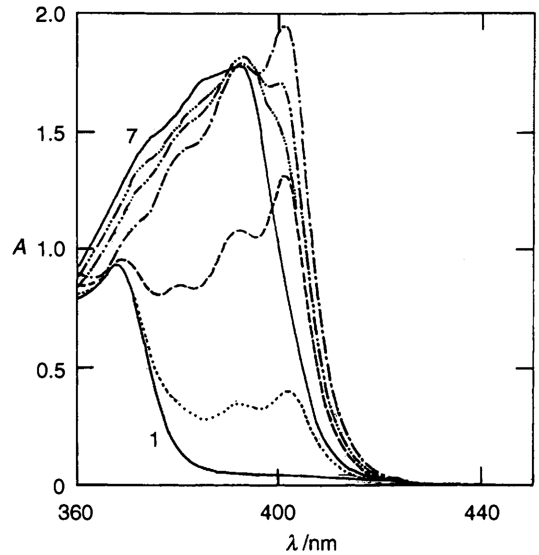

Fig. 1 UV–VIS spectra of tropolone (2.0×10^{-4} mol dm^{-3}) and triethylamine (2.0×10^{-4} mol dm^{-3}) in acetonitrile as a function of $LiClO_4$ concentration (l = 1.0 cm): (———, 1) 0; (- - - -) 2.0×10^{-5}; (– – –) 1.0×10^{-4}; (— · —) 1.0×10^{-3} and 2.0×10^{-3}; (— - - —) 1.0×10^{-2}; (—- - - - —) 2.0×10^{-2}; (———, 7) 1.0×10^{-1} mol dm^{-3} of $LiClO_4$. The ionic strength was maintained at 0.1 mol dm^{-3} with Et_4NClO_4.

Results and Discussion

Effects of Li^+ *and* Na^+ *on the Tropolone–Triethylamine Reaction.*—In acetonitrile, tropolone ($C_7H_5O_2H$) gave UV absorption peaks at 368 (ε/dm^3 cm^{-1} mol^{-1} = 4.5×10^3), 352 (5.7×10^3), 320 (7.2×10^3) and 229 nm (*ca.* 2.2×10^4). Tropolone is a weak acid (pK_a = 6.7)[20] in H_2O; therefore, it does not dissociate in the aprotic solvent. The addition of a large excess of triethylamine ([Et_3N] > 1×10^{-2} mol dm^{-3}) to 2×10^{-4} mol dm^{-3} tropolone caused a new absorption band to appear (λ_{max} = 407 nm), which should be due to the complex formed by proton-transfer from tropolone to the amine. The formation of the species $C_7H_5O_2^-Et_3NH^+NEt_3$ has been postulated on the basis of IR spectra for tropolone and an excess of Et_3N in carbon tetrachloride.[21]

With less than 1×10^{-3} mol dm^{-3} Et_3N, however, the deprotonation of tropolone (2×10^{-4} mol dm^{-3}) barely proceeded, although tropolone and triethylamine might interact with each other by hydrogen-bonding forces. The presence of 0.1 mol dm^{-3} Et_4NClO_4 in the tropolone–triethylamine system had almost no influence on the absorption bands; the increases in the absorbance of the tailing of the specturm of tropolone were only 0.02 and 0.01 at 400 and 414 nm, respectively. In the presence of 2×10^{-4} mol dm^{-3} Et_3N, a peak of an ionized tropolone species appeared at 401 nm (*cf.* Fig. 1) upon addition of $LiClO_4$ (up to 2×10^{-3} mol dm^{-3}) to the 2×10^{-4} mol dm^{-3} tropolone solution [see eqn. (2)]. The absorption peak at 401 nm is different to the peak

$$C_7H_5O_2H\text{-}NEt_3 + Li^+ \rightleftharpoons C_7H_5O_2^-Li^+H^+NEt_3 \quad (2)$$

(λ_{max} = 414 nm) of the 'free' tropolonate ion (*e.g.*, $Bu_4NC_7H_5O_2$) in acetonitrile or the peak (λ_{max} = 407 nm) due to the amine-added tropolone (present in large excess of the amine). The further addition of $LiClO_4$ (> 1×10^{-2} mol dm^{-3}) caused a shift of the absorption peak at 401 to 393 nm. This phenomena suggested the complete protonation of the amine, induced by the formation of the triple ion, $C_7H_5O_2^-(Li^+)_2$ [see eqn. (3)].

$$C_7H_5O_2^-Li^+H^+NEt_3 + Li^+ \rightleftharpoons C_7H_5O_2^-(Li^+)_2 + Et_3NH^+ \quad (3)$$

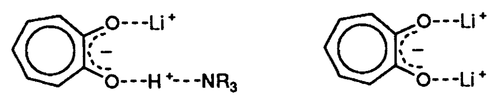

Fig. 2 Proposed structures of $C_7H_5O_2^-Li^+H^+NEt_3$ and $C_7H_5O_2^-(Li^+)_2$

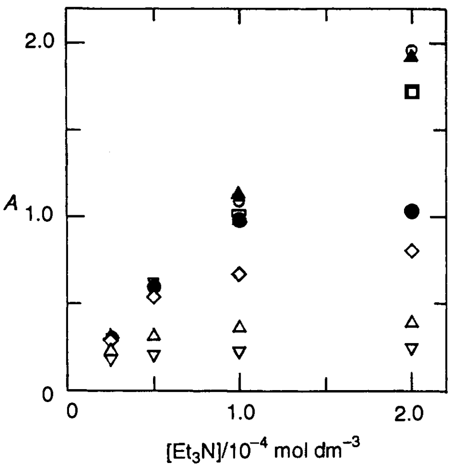

Fig. 3 Absorbance at 401 nm for the mixtures of tropolone (2.0×10^{-4} mol dm^{-3}) and triethylamine (2.5×10^{-5} to 2.0×10^{-4} mol dm^{-3}) in acetonitrile as a function of $LiClO_4$ concentration (l = 1.0 cm): (▽) 1.0×10^{-5}; (△) 2.0×10^{-5}; (◇) 5.0×10^{-5}; (●) 1.0×10^{-4}; (□) 2.0×10^{-4}; (▲) 5.0×10^{-4}; (○) 1.0×10^{-3} mol dm^{-3} of $LiClO_4$

Proposed structures of $C_7H_5O_2^-Li^+H^+NEt_3$ and $C_7H_5O_2^-(Li^+)_2$ are given in Fig. 2. The formation of $C_7H_5O_2^-(Li^+)_2$ in acetonitrile (λ_{max} = 393 nm) has been concluded by the re-dissolution of $C_7H_5O_2^-Li^+$ precipitates *via* the addition of a large excess of $LiClO_4$ (*vide infra*). Polarographic data have suggested that trialkylammonium ions cannot interact with the tropolonate ion ($Bu_4NC_7H_5O_2$) in the presence of 5×10^{-2} mol dm^{-3} $LiClO_4$. Notably, in the absence of triethylamine, the addition of a large excess of $LiClO_4$ to 2×10^{-4} mol dm^{-3} tropolone caused a small increase in the absorbance at 393 nm [formation of $C_7H_5O_2^-(Li^+)$ by the direct reaction between Li^+ and tropolone]; *e.g.*, 0.02 and 0.14 with 1×10^{-2} and 1×10^{-1} mol dm^{-3} $LiClO_4$, respectively.

Pocker and Ciula[16] have deduced the n-value to be 1.5–4 for the equilibrium reaction of the proton-transfer reaction of tropolone with amine bases in diethyl ether [eqn. (4)]. For the

$$HA + B + nLiClO_4 \rightleftharpoons Li^+A^-\cdot(n - m - 1)LiClO_4 + BH^+ClO_4^-\cdot mLiClO_4 \quad (4)$$

proton transfer from p-nitrophenol to imidazole in $LiClO_4$–diethyl ether solutions, Pocker and Ellsworth[22] postulated the presence of species of $Li^+(OEt_2)_x\,^-OC_6H_4NO_2\text{-}p\ Li^+(OEt_2)_x$.

Fig. 3 shows the absorbance at 401 nm ($C_7H_5O_2^-Li^+H^+NEt_3$) as a function of $LiClO_4$ concentration for mixtures of tropolone (2×10^{-4} mol dm^{-3}) and various concentrations of triethylamine. With 1×10^{-4} mol dm^{-3} Et_3N, the absorbance of the peak reached a maximum by the addition of 5×10^{-4} mol dm^{-3} $LiClO_4$; the overall maximum absorbance was obtained using 1×10^{-3} (or 2×10^{-3}) mol dm^{-3} $LiClO_4$ with 2×10^{-4} mol dm^{-3} Et_3N. The absorbance of the maximum at 401 nm increased almost linearly with increasing concentration of triethylamine.

The addition of $NaClO_4$ to the mixture of tropolone and triethylamine (both 2×10^{-4} mol dm^{-3}) gave a peak at 405 nm. However, the intensity of the absorption was much smaller (less than one quarter at the same concentrations of $MClO_4$) than with $LiClO_4$. The absorbance at 405 nm increased linearly with

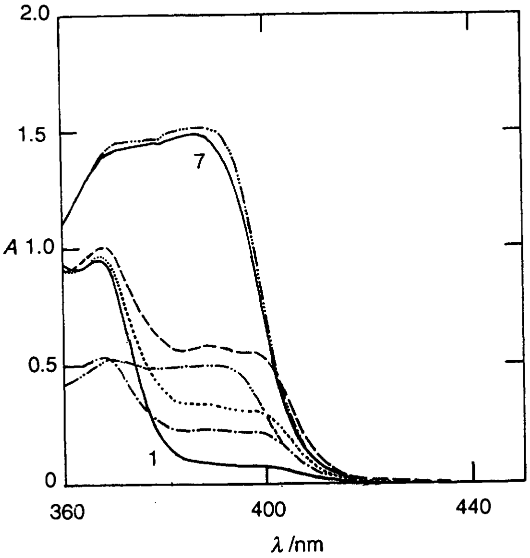

Fig. 4 UV–VIS spectra of tropolone (2.0×10^{-4} mol dm^{-3}) and triethylamine (2.0×10^{-4} mol dm^{-3}) in acetonitrile as a function of $Ca(ClO_4)_2$ concentration (l = 1.0 cm): (———, 1) 0; (- - - -) 1.0×10^{-5}; (— — —) 2.0×10^{-5}; (— · —) 5.0×10^{-5}; (— · · —) 1×10^{-4}; (— · · · —) 2.0×10^{-4}; (———, 7) 1.0×10^{-3} mol dm^{-3} of $Ca(ClO_4)_2$. The ionic strength was maintained at 0.1 mol dm^{-3} with Et_4NClO_4.

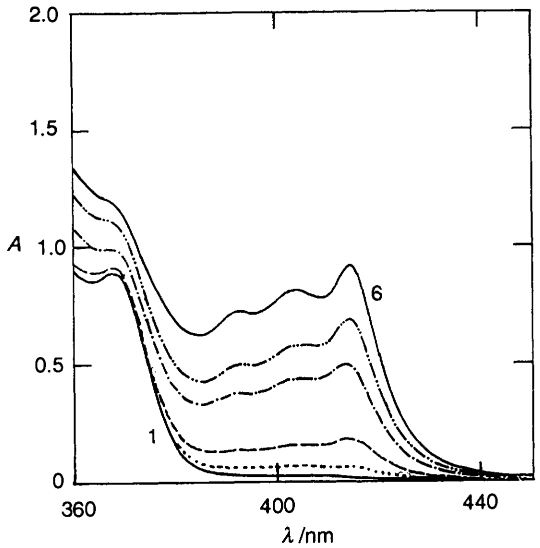

Fig. 5 UV–VIS spectra of tropolone (2.0×10^{-4} mol dm^{-3}) and triethylamine (2.0×10^{-4} mol dm^{-3}) in acetonitrile as a function of Et_4NCl concentration (l = 1.0 cm): (———, 1) 0; (- - - -) 1.0×10^{-3}; (— — —) 1.0×10^{-2}; (— · —) 1.0×10^{-1}; (— - - —) 2.0×10^{-1}; (———, 6) 5.0×10^{-1} mol dm^{-3} of Et_4NCl. The ionic strength was maintained at 0.1 mol dm^{-3} with Et_4NClO_4, except for 0.2 and 0.5 mol dm^{-3} of Et_4NCl.

increasing concentration of Et_3N (5×10^{-5} to 2×10^{-4} mol dm^{-3}) in the presence of 1×10^{-3} mol dm^{-3} $NaClO_4$. This absorption peak may be caused by an intermediate species, such as $C_7H_5O_2^-Na^+H^+NEt_3$.

Effects of Alkaline-earth Metal Ions.—Fig. 4 shows the UV–VIS spectra of the mixture of tropolone (2×10^{-4} mol dm^{-3}) and triethylamine (2×10^{-4} mol dm^{-3}) as a function of $Ca(ClO_4)_2$ concentration. A broad peak around 400 nm appeared upon the addition of a small amount of Ca^{2+}, continuing to increase up to 2×10^{-5} mol dm^{-3} of Ca^{2+}. However, the absorbance decreased upon formation of precipitates of non-charged species [$(C_7H_5O_2^-)_2Ca^{2+}$, *cf.* the final section] in the presence of 5×10^{-5} or 1×10^{-4} mol dm^{-3} Ca^{2+}. The absorbance increased suddenly again, to give a peak around 390 nm, in the presence of 2×10^{-4} mol dm^{-3} of Ca^{2+}. 1 : 1 Coordination complexes of alkaline-earth metal ions with the tropolonate ion have been reported.[23]

Similar phenomena were observed at other triethylamine concentrations. The maximum absorbance was observed at equal Ca^{2+} and Et_3N concentrations (*i.e.*, $[Ca^{2+}] = [Et_3N] = 1.0 \times 10^{-4}$ mol dm^{-3}). On the other hand, the minimum absorbance (by precipitation) was given when the concentration of Ca^{2+} was half that of Et_3N (*i.e.*, $[Et_3N]/[Ca^{2+}]$ = *ca.* 2.0). The above spectrophotometric results can be explained by eqns. (5)–(8). The intermediate species

$$C_7H_5O_2H + Et_3N \rightleftharpoons C_7H_5O_2H\text{-}NEt_3 \qquad (5)$$

$$C_7H_5O_2H\text{-}NEt_3 + \frac{1}{n}Ca^{2+} \rightleftharpoons C_7H_5O_2^-(Ca^{2+})_{\frac{1}{n}}H^+NEt_3 \qquad (6)$$

$$C_7H_5O_2^-(Ca^{2+})_{\frac{1}{n}}H^+NEt_3 + \left(\frac{1}{2}-\frac{1}{n}\right)Ca^{2+} \rightleftharpoons \tfrac{1}{2}(C_7H_5O_2^-)_2Ca^{2+} + Et_3NH^+ \qquad (7)$$

$$\tfrac{1}{2}(C_7H_5O_2^-)_2Ca^{2+} + \tfrac{1}{2}Ca^{2+} \rightleftharpoons C_7H_5O_2^-Ca^{2+} \qquad (8)$$

$C_7H_5O_2^-(Ca^{2+})_{\frac{1}{n}}H^+NEt_3$ in eqns. (6) or (7) was tentatively assigned to the broad absorption around 400 nm.

The addition of $Mg(ClO_4)_2$ to the tropolone–triethylamine mixtures gave results similar to those with $Ca(ClO_4)_2$, except for the much more distinct appearance of the intermediate species (λ_{max} = 399, 388 and 379 nm, absorbances of *ca.* 1.6 at 5×10^{-5} mol dm^{-3} Mg^{2+}), tentatively assigned to $C_7H_5O_2^-(Mg^{2+})_{\frac{1}{n}}H^+NEt_3$. The other difference between Mg^{2+} and Ca^{2+} was that the magnesium ion could react with tropolone in the absence of a base to give $C_7H_5O_2^-Mg^{2+}$, but not the calcium ion in acetonitrile. Some transition metal ions can form coordination compounds directly with tropolone in non-aqueous solutions.[24,25] The direct reaction between 1×10^{-3} mol dm^{-3} $Mg(ClO_4)_2$ and 2×10^{-4} mol dm^{-3} tropolone, which caused the absorbance increase of 0.099 at 392 nm, seemed to affect slightly the absorbance of the tropolone–triethylamine solutions.

In contrast to the Mg^{2+} and Ca^{2+} cases, the addition of Ba^{2+} did not cause an initial increase in the absorbance around 400 nm. However, the precipitation of $(C_7H_5O_2^-)_2Ba^{2+}$ (the non-charged species), with concomitant decrease in tropolone absorbance at 370 nm was initially observed. Then, the re-dissolution of the precipitate by the formation of $C_7H_5O_2^-Ba^{2+}$ (the 1 : 1 complex) was observed with increasing concentration of Ba^{2+}. The effects with Sr^{2+} were similar to those with Ba^{2+}.

Effects of Halide Ions.—As shown above, metal ions affect the tropolone–triethylamine reaction by interacting with the anionic species ($C_7H_5O_2^-$) to form triple cations and cationic complexes, *e.g.* $C_7H_5O_2^-(Li^+)_2$, $C_7H_5O_2^-Mg^{2+}$, *etc.* In contrast, it is predicted that some anions might affect the system by interacting with the cationic species present, *e.g.* the Et_3NH^+ ion [see eqn. (9)]. Fig. 5 shows the effects of Et_4NCl

$$C_7H_5O_2H\text{-}NEt_3 + nX^- \rightleftharpoons C_7H_5O_2^- + Et_3NH^+(X^-)_n \; (n = 1 \text{ or } 2) \qquad (9)$$

on the UV–VIS spectrum of the tropolone–triethylamine mixture. A new absorption band with three peaks (414, 404 and

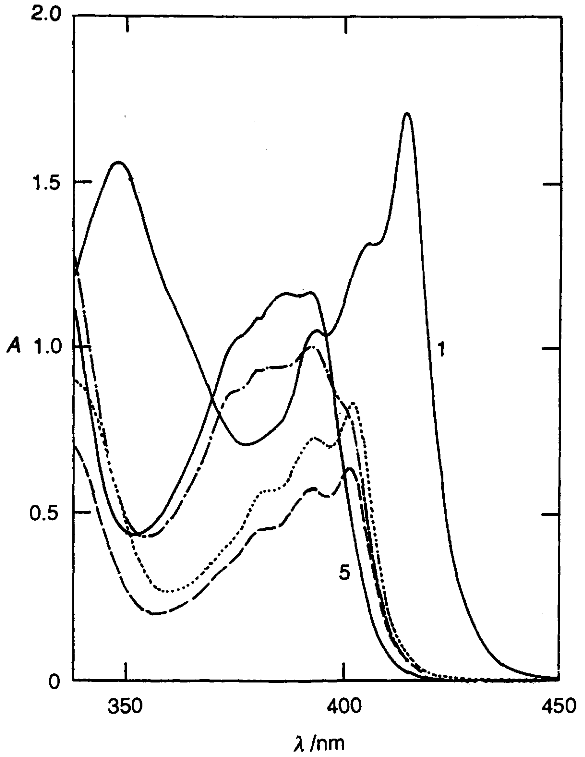

Fig. 6 UV–VIS spectra of 1.21 × 10^{-3} mol dm^{-3} $Bu_4NC_7H_5O_2$ (0.1 cm cuvette) in acetonitrile as a function of $LiClO_4$ concentration: (———, 1) 0; (- - - -) 1.2 × 10^{-3}; (– – –) 2.4 × 10^{-3}; (— · —) 1.2 × 10^{-2}; (———, 5) 1.2 × 10^{-1} mol dm^{-3} of $LiClO_4$

393 nm) appeared on the addition of Et_4NCl. The intensity of the peaks increased with increasing concentration of the salt and their wavelength was completely consistent with that of the 'free' tropolonate ion ($Bu_4N^+C_7H_5O_2^-$, *cf.* Fig. 6). Tetraethylammonium bromide (Et_4NBr) also gave a similar effect to give the 'free' tropolonate ion. However, the effects of the Br^- salt were much smaller than the Cl^- salt. The effects of the iodide ion were smaller still; the absorbance increase at 414 nm with 0.1 mol dm^{-3} Et_4NI was only 0.04 (*cf.* 0.192 and 0.475 for 0.1 mol dm^{-3} Br^- and Cl^-, respectively). We have reported[4] the (overall) formation constants, log K_1 and log K_2 values of $Et_3NH^+(X^-)_n$ (X = Cl, Br and I; n = 1 and 2) at 25 °C in acetonitrile as follows: 5.4 and 7.1 for Cl^-; (3.4) and 5.0 for Br^-; (2.1) and (3.3) for I^-, respectively. The deprotonation of tropolone occurred through the amine and not by direct interaction with the halide ions because the addition of 0.1 mol dm^{-3} Et_4NCl, Br, or I to the 2 × 10^{-4} mol dm^{-3} tropolone solution without Et_3N did not give any tropolonate ions. This is as expected, because triethylamine is a much stronger base than Cl^-, Br^- or I^- according to the pK_a values of their conjugate acids;[26] pK_a = 18.7, 8.9 and 5.5 for Et_3NH^+, HCl and HBr, respectively, in acetonitrile.

The 'free' tropolonate ion was obtained by the addition of halide ions to tropolone–triethylamine, whereas the presence of metal ions produced 'coordinated' tropolonates. We would like to stress that the difference in spectra between these two systems is explained by the complex formation reactions, rather than contact and solvent-separated ion-pairs.

Interaction between the Tropolonate Ion and Alkali or Alkaline-earth Metal Ions.—In acetonitrile, tetrabutylammonium tropolonate ($Bu_4NC_7H_5O_2$) gave three main absorption bands, at 414 (ε/dm^3 cm^{-1} mol^{-1} = 1.6 × 10^4), 348 (1.4 × 10^4) and 250 nm (*ca.* 2 × 10^4). The addition of triethylammonium or tributylammonium perchlorate (Et_3NHClO_4, Bu_3NHClO_4) to the solution caused the tropolonate ion peak at 414 nm to decrease linearly, and this peak completely disappeared when an equivalent amount of the trialkylammonium salt was present according to eqn. (10). The resultant spectra were consistent

$$C_7H_5O_2^- + R_3NH^+ \rightleftharpoons C_7H_5O_2H\text{–}NR_3\ (R = \text{Et or Bu}) \quad (10)$$

with those of tropolone (or tropolone–trietnylamine) for > 300 nm (the trialkylamines gave absorbance at < 300 nm). On the other hand, the addition of ethanol to the tropolonate solution in acetonitrile caused the intensity of the tropolonate bands to decrease and shift hypsochromically. Thus, the tropolonate ion clearly has a strong affinity with acids or hydrogen-bonding donors.

When 1 × 10^{-3} to 1 × 10^{-2} mol dm^{-3} $LiClO_4$ was added to 1 × 10^{-3} mol dm^{-3} $Bu_4NC_7H_5O_2$ acetonitrile solutions, precipitation of $C_7H_5O_2Li$ occurred. The addition of 0.1 mol dm^{-3} $LiClO_4$, however, caused re-dissolution of these precipitates. The absorption spectra of the (supernatant) solutions are shown in Fig. 6. The absorbance of the main peaks decreased with the formation of precipitates. However, in the presence of a large excess of Li^+ (> 1 × 10^{-2} mol dm^{-3}), a new peak at 393 nm appeared; this peak seemed to be identical with that produced by the addition of $LiClO_4$ (> 1 × 10^{-2} mol dm^{-3}) to the tropolone–triethylamine mixture (*vide supra*). Similarly the addition of $NaClO_4$ to a $Bu_4NC_7H_5O_2$ solution also caused a decrease in the absorbance of the tropolonate ion by the formation of precipitates of $C_7H_5O_2Na$. Even in the presence of a large excess of Na^+, the small absorbance around 403–405 nm, based on the 'tropolonate ion', did not increase very much. If a smaller concentration (2 × 10^{-4} mol dm^{-3}) of $Bu_4NC_7H_5O_2$ was chosen, however, the effect of $NaClO_4$ becomes more significant; the absorbance of 403 nm was 0.876 at 0.1 mol dm^{-3} $NaClO_4$. The above results suggested the formation of the triple cation (2:1 complex) from the 1:1 salt precipitate by the addition of a large excess of Li^+ according to eqn. (11).

$$[C_7H_5O_2^-Li^+](\text{ppt.}) + Li^+(\text{soln.}) \rightleftharpoons [C_7H_5O_2^-(Li^+)_2](\text{soln.}) \quad (11)$$

The addition of 5 × 10^{-4} mol dm^{-3} $Ca(ClO_4)_2$ to 1 × 10^{-3} mol dm^{-3} $Bu_4NC_7H_5O_2$ caused precipitation of the uncharged species, $(C_7H_5O_2^-)_2Ca^{2+}$ to occur, and the absorption bands of the tropolonate ion disappeared almost completely. In the presence of 1 × 10^{-3} mol dm^{-3} $Ca(ClO_4)_2$, however, a peak at 391 nm appeared suddenly, possibly caused by formation of the cationic species (the 1:1 complex) according to eqn. (12). Effects

$$[(C_7H_5O_2^-)_2Ca^{2+}](\text{ppt.}) + Ca^{2+}(\text{soln.}) \rightleftharpoons 2\,[C_7H_5O_2^-Ca^{2+}](\text{soln.}) \quad (12)$$

of other alkaline-earth metal ions were explained in a similar way.

The present work on the acid–base reaction between tropolone ($C_7H_5O_2H$) and triethylamine (Et_3N) in acetonitrile can be summarized as follows: (*a*) almost no effect was produced by Et_4NClO_4; (*b*) the effect of $LiClO_4$ was larger than that of $NaClO_4$; the salt effects are due to the formation of triple ions, $C_7H_5O_2^-(M^+)_2$, in the solution; (*c*) alkaline-earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) form 1:1 complex species, $C_7H_5O_2^-M^{2+}$, thereby promoting the deprotonation of tropolone; (*d*) halide ions (Cl^- > Br^- > I^-) can produce the 'free' tropolonate ion ($C_7H_5O_2^-$) by forming triple anions, $Et_3NH^+(X^-)_2$.

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