Cation, Solvent, and Substituent Effects on the Optical Spectra of Alkali Metal Salts of Arylthiolate Anions

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The optical spectra of the alkali metal salts of arylthiolate anions have been studied in the two aprotic solvents, tetrahydrofuran (THF) and dimethylformamide (DMF). In the former solvent the position of the absorption maxima depends on the size of the counter cations, even at low temperatures (−72 to −76 °C); nearly linear relationships were observed between the inverse of the alkali metal radius (r_c) and the wave number of the transition ($\tilde{\nu}_{max}$) for both room and low temperatures. The intercepts for the extrapolation of both lines for $1/r_c \rightarrow 0$ agree with the $\tilde{\nu}_{max}$ of the ion pairs observed in DMF at room temperature, and the absorption maxima for this solvent are independent of the size of the counter cations. Thus, the existence of contact ion pairs in THF over the temperature range investigated and that of the solvent-separated ion pairs in DMF at room temperature were revealed. In the latter solvent, however, a hypsochromic shift was observed on lowering the temperature. The substituent effect of arylthiolate anions and the solvent effect of dimethoxyethane and dioxane on the absorption maxima are also discussed. From an inspection of optical spectral data it has been suggested that negative charge of arylthiolate anions is localized mainly on the sulfur atom.

Since the first suggestion by Weinstein that the equilibrium between contact (or intimate) and solvent-separated ion pairs may be established in solutions of low dielectric constant¹⁾ and the further development of this idea by Grunwald,²⁾ there have been extensive investigations of ion pairs in solutions.³⁾ Direct evidence for the existence of two distinct types of ion pairs was first demonstrated by optical spectra on cooling a THF solution of alkali metal salts of fluorenyl anions (carbanions)⁴⁾ and, though not simultaneously, by ESR studies of alkali metal naphthalenides (radical anions).⁵⁾

In this paper the cation, solvent, and substituent effects on the optical spectra of alkali metal salts of arylthiolate anions is reported. The optical spectra of ion pairs other than carbanions have been studied with the alkali metal salts of phenols and enols⁶⁾ and with tetraalkylammonium iodides,⁷⁾ but there is no information about the thiolate anions which have a negative charge on the sulfur atom. The phenylthiolate anion is said to be a stronger nucleophile than the corresponding isoelectronic phenoxide ion,⁸⁾ and interesting results have been reported in other reactions of thiolate anions to double and triple bonds and also to carbonyl groups.⁹,¹⁰⁾ Nucleophilic substitutions with these anions are also interesting; the rate increases in dipolar aprotic solvents (*e.g.*, DMF)¹¹⁾ and electron transfer from the *n*-butylthiolate anion to oxygen in solutions is accelerated in the order methanol$<$THF$<$dimethoxyethane (DME)$<$DMF and is also affected by counter cations ($Na^+<K^+<Rb^+<Cs^+$).¹²⁾ These results can be explained by an increase in reactivity caused by changes in the strength of the thiolate anion-counter cation binding.

Thus, it is interesting to investigate the optical spectra of the solutions of alkali metal salts of arylthiolate anions; the effects of the size of the counter cation, solvent, and of the introduction of substituents at the *para*-position on the absorption spectra give some information about the nature of thiolate anions, *i.e.*, the stronger nucleophilic character of thiolate anions can be revealed by an inspection of spectral data.

Experimental

Diphenyl disulfide, acquired commercially, was recrystallized three times from ethanol. Di-*p*-chlorophenyl-, di-*p*-methylphenyl-, di-*p*-methoxyphenyl-, and di-*p*-*t*-butylphenyl disulfide were synthesized from the oxidation of the corresponding thiols and recrystallized three times from ethanol.

Alkali metal salts of arylthiolate anions were prepared from the reduction of the corresponding symmetric aryl disulfides with an appropriate alkali metal in THF,

$$\text{RS–SR} + \text{alkali metal} \xrightarrow{\text{in THF}} \text{RS}^-, \text{M}^+ + \text{RS}\cdot$$

$$\text{RS}\cdot + \text{alkali metal} \longrightarrow \text{RS}^-, \text{M}^+$$

$$\text{RS}\cdot + \text{RS}\cdot \longrightarrow \text{RS–SR}$$

The purification of solvents and the reduction of the disulfides with alkali metals in the solvents were carried out on a high vacuum line using a technique described in Ref. 3b.

Solutions of thiolate anions in solvents other than THF were usually prepared from the corresponding THF solution by removing the THF under vacuum and distilling the appropriate solvent onto the dry salt.

Electronic spectra were recorded with a Cary 14-UV spectrophotometer, using 0.2 cm quartz optical vacuum cells with some measurements made with a 0.18 cm spacer. Concentrations of thiolate anions could be varied by transferring a part of the sample to an adjacent glass ampoule and by distilling the solvent back by cooling the cell. Using this technique, concentrations were adjusted to give optical densities of 0 to 2. A quartz dewar with optical windows was used for the low temperature measurements and precooled methanol with liquid nitrogen was chosen as the cooling liquid. Dry nitrogen gas was blown onto the optical windows to prevent the formation of a frost covering. The temperature of methanol was recorded with a copper-constantan thermocouple located in the vicinity of the cell.

The concentrations of the sodium salt of phenylthiolate anion in THF were determined by the titration of thiolate anions with silver nitrate using a dithizone as an indicator or by electron transfer from thiolate anions to chloranil in THF forming chloranil radical anions having a known molar extinction coefficient,¹³⁾ and then, by estimating the molar extinction coefficient of the sodium salt of phenylthiolate anion.

Results

The alkali metal salts of thiolate anions were found to be stable in both THF and DMF over the temperature range investigated (25 to −76 °C) and the optical spectra exhibited sharp absorption bands at 280 nm in THF and at 308 nm in DMF at room temperature. The decimal extinction coefficient of the sodium salt of phenylthiolate anion in THF was found to be about 10^4 l/mol·cm. However, the spectrum of the cesium salt of phenylthiolate anion in THF showed a rather broad band.

Optical Spectra in THF. The position of the absorption maxima (λ_{max}) in THF depended upon the size of the counter cation, temperature, and structure of the thiolate anions. However, it was found that a 100-fold dilution of a *ca.* 10^{-3} mol/l solution did not alter the position; the independence of the position of the absorption maximum on the concentration excludes the possibility of an association of ion pairs under the conditions of the experiment (the concentrations were usually about 10^{-4} mol/l). The position of the absorption maxima of the phenylthiolate anion in THF was shifted toward longer wavelengths when the radius of the counter cations increased and the same phenomenon was observed even at low temperature (−72 to −76 °C); nearly linear relationships were observed between the inverse of the counter cation radius ($1/r_c$) and the wave number of the transition ($\tilde{\nu}_{max}$) for both room and low temperatures, as depicted in Fig. 1 (see also Table 1). It is interesting to note that the alkali metal salts of phenylthiolate anions in THF exhibit a single sharp absorption band regardless of the temperature, and at intermediate temperatures the two isolated bands were not observed and no shoulder appeared.

The effect of *para*-substituents of the alkali metal salts of arylthiolate anions on the λ_{max} in THF is shown in Table 2, and Fig. 2 shows a plot of the wave number against the Brown-Okamoto substituent constants.

TABLE 1. DEPENDENCE OF λ_{max} ON THE RADIUS OF THE COUNTER CATION (r_c) FOR ALKALI THIOLATE SALTS IN THF AND DMF AT ROOM AND LOW TEMPERATURES

Counter cation	r_c Å	λ_{max}, nm			
		in THF		in DMF	
		20 °C	low temp.(°C)	20 °C	low temp.(°C)
Li^+	0.60	285	287(−72)	308	303(−63)
Na^+	0.96	292	295(−75)	307	303(−43)
K^+	1.33	296	298(−76)	308	303(−62)
Cs^+	1.66	299		308	303(−60)

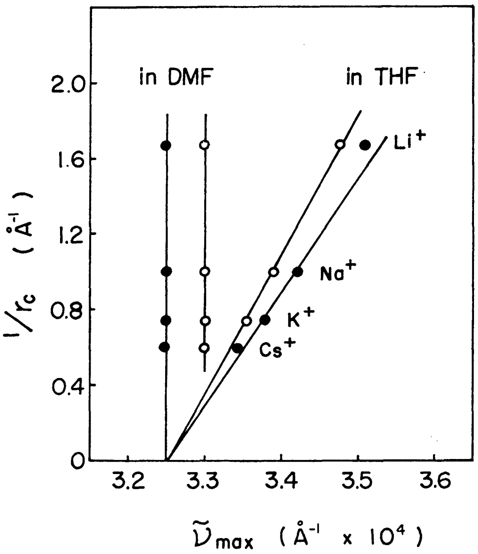


Fig. 1. Relationships between the inverse of the counter cation radius ($1/r_c$) of alkali metal salts of phenylthiolate anions and the wave number of the transition ($\tilde{\nu}_{max}$) in THF and DMF. Black and open circles represent the values obtained in room and low temperatures, respectively.

Optical Spectra in DMF. The λ_{max} observed at both room and low temperatures are assembled in Table 1 and depicted in Fig. 1 together with the data in THF. The position of the absorption maximum was not affected by the counter cation (308 nm) and agreed with the extrapolated wave number of both lines obtained in THF for $1/r_c \rightarrow 0$. On lowering the temperature to *ca.* −70 °C a hypsochromic shift was observed (303 nm).

TABLE 2. SUBSTITUENT EFFECTS OF SODIUM ARYLTHIOLATE ANIONS ON λ_{max} IN THF AT 20 °C

Substituent	CH_3O–	CH_3–	*t*-C_4H_9–	H–	Cl–
λ_{max}(nm)	279	290	292	292	297

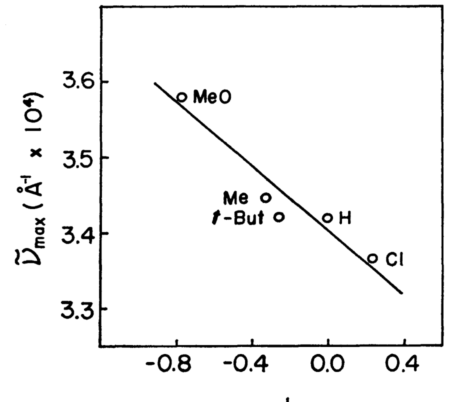


Fig. 2. Relationship between $\tilde{\nu}_{max}$ of sodium arylthiolate anions in THF at room temperature and Brown-Okamoto's substituent constant in the Hammett equation (σ^+).

Optical spectra in other solvents, dimethoxyethane (DME) and dioxane, were also measured. These salts were also found to be stable in the solvents. The λ_{max} are given in Table 3.

TABLE 3. SOLVENT EFFECTS OF PHENYLTHIOLATE SALTS ON λ_{max}(nm) AT 20 °C

	Dioxane	THF	DME	DMF
$C_6H_5S^-$, Li^+		285	286	308
$C_6H_5S^-$, Na^+	279	292	292	307

Discussion

The sharp absorption bands observed in THF depended upon both the counter cation and the temperature; even at low temperatures (−72 to −76 °C) the position of the absorption maximum was shifted toward longer wavelengths with increasing size of the counter cation and a nearly linear relationship is observed between the inverse of the counter cation radius r_c and $\tilde{\nu}_{max}$ (Fig. 1). A similar bathochromic shift for increasing size of the counter cation has been found for alkali metal salts of fluorenyl anions,[14] phenoxide ions,[6] and ketyl radical anions.[15] The independence of λ_{max} on the concentration has been observed for the sodium salt of phenylthiolate anion in THF. Thus, the shift in THF can be explained as a result of the formation of contact ion pairs, and the cause of the shift has been explained[4] as a perturbation of the molecular energy levels by the positive field of the cation, and a perturbation depends on the electrostatic interaction energy. The excited state is less stable due to the counter cation than the ground state, since in the ground state of an ion pair, the cation is located so as to form the smallest dipole, and a redistribution of charge occurs upon excitation, but as expected from the Franck-Condon principle, the cation has no time to readjust its position. Thus, the smaller the cation the larger the transition energy.[14]

As has been described above the relations for THF depicted in Fig. 1 strongly suggest that the alkali metal salts of phenylthiolate anions in THF exist as contact ion pairs and on lowering the temperature these may interact strongly with the surrounding THF molecules to form on its periphery a slight rigid coordination shell. Such an interaction is expected to be exothermic; the counter cations in contact ion pairs may interact more strongly with THF molecules on lowering the temperature. Although the alkali metal salts of phenylthiolate anions in THF at low temperature may still be classified as tight ion pairs, the strong interaction of THF with counter cations apparently results in a dispersion of positive charge (external solvation) and thus in a slight increase in the average interionic distance between the metal cation and thiolate anion, causing the bathochromic shift.

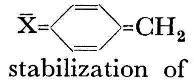
The process which is responsible for the shift of the position of the absorption maxima is reversible with temperature, but no new isolated band or shoulder appeared at intermediate temperatures, indicating that no discrete types of ion pairs such as contact and solvent-separated ion pairs were present in THF over the temperature range investigated. However, sodium fluorenyl salt in the same solvent exists as discrete types of ion pairs at intermediate temperatures (−30 °C).[14] This is probably attributable to a difference in the nucleophilic characters of carbanions and thiolate anions. The interionic interaction between anions and counter cations may be strengthened by the localization of the negative charge. This appears to be the case for our thiolate anions, since bathochromic shifts with counter cations are observed in THF even on lowering the temperature. Furthermore, this may be supported by the fact that the sodium phenoxide ion and the sodium benzyl carbanion, isoelectronic anions of the thiolate anion, have absorption bands at 303[6] and 355[16] nm, respectively. On the other hand, the λ_{max} of the thiolate anions appears at 285 to 290 nm depending on the counter cation, solvent, and substituent, indicating that the localization of the negative charge on the sulfur atom of thiolate anion could be greater than that on the carbon atom of carbanions.

The intercept $\tilde{\nu}^{\circ}_{max}$ obtained on extrapolation of both lines plotted for THF as $1/r_c \rightarrow 0$ agrees with the wave number of the ion pairs observed in DMF at room temperature and no bathochromic shift with counter cation is observed at all in DMF. Thus, it may be safely stated that the entity observed in DMF is solvent-separated ion pairs or solvated free ions, even at room temperature (no difference has been reported in the positions of the absorption maxima of the solvent-separated ion pair and free ion[14]), since the position of the absorption maxima of the ion pairs in DMF at low temperature was not subject to the influence of counter cation (308 nm) (the fraction of free thiolate anions in the investigated solutions should be less than a few percent on the basis of the data reported for solutions containing alkali metal salts of carbanions and radical anions (*e.g.*, Ref. 14). The interionic interaction between a thiolate anion and a counter cation may be weakened by the DMF molecules separating both ions; the anion in the solvent-separated ion pairs is not subject to the influence of the counter cation. A similar observation was made on some alkali metal salts of phenols and enols in DMF.[6] The hypsochromic shift observed on lowering the temperature in DMF (308 to 303 nm) is quite interesting. Two causes could account for such a hypsochromic shift. (1) The negative charge of the thiolate anions may localize on the sulfur atom and hence such anions may exist as a dipolar molecules and be stabilized by an interaction with DMF molecules in the ground state. However, in an excited state, such solvating DMF molecules cannot be rearranged as expected from the Franck-Condon principle giving rise to orientational strain,[17] and thus stablilizing ion pairs. Therefore, thiolate anions in DMF are stabilized on lowering the temperature in the ground state and, on the contrary, the excited state is destabilized, and a hypsochromic shift is expected. (2) It is apparent that thiolate anions in DMF are solvent-separated ion pairs, even at room temperature. On lowering the temperature, however, the strength of the interaction of the DMF separating an ion pair with both the counter cation and the thiolate anion (for more detail, see the discussion of the solvent effect) may increase; *i.e.*, the average interionic distance between the metal cation and the thiolate anion may decrease on lowering the temperature, causing the hypsochromic shift.

As shown in Table 3, the positions of the absorption maxima of the lithium and sodium salts of phenylthiolate anions in the four aprotic solvents shifted toward longer wavelengths; the ease of solvation to the counter cation can be evaluated from the extent of the shift of the position of the absorption maxima, thus, dioxane<

THF<DME<DMF. This order is essentially the same as in the case of the formation of the solvent-separated ion pairs of the alkali metal salts of fluorenyl anions[14] except for DMF (in that study no DMF was used), and is also consistent with the order reported for electron transfer from sodium *n*-butylthiolate anions in solutions to oxygen which was described in the introduction,[12] indicating that the case of electron transfer depends upon the solvation state of the ion pair. Dioxane appears to be a poor solvating agent for alkali cations in view of the reported data on the shift of the absorption spectra of some ion pairs with changing solvents[14] and the position occupied by THF in this order is reasonable. A comparison of the solvating ability of DMF with that of DME can be made for the proton hyperfine coupling constants of alkali metal salts of fluorenone radical anion;[20] DMF yields free ions while DME produces contact ion pairs. Thus, the order obtained here seems, on the whole, plausible. At first sight, the behavior of DME for the lithium salt of phenylthiolate anion may appear strange, since fluorenyl lithium undoubtedly forms a solvent-separated ion pair, even at room temperature. Since the negative charge on thiolate anions is localized mainly on the sulfur atom, arylthiolate anions exist as tight ion pairs even in DME.

It is well known that DMF is a polarizable powerful base like dimethyl sulfoxide and hexamethylphosphoric triamide and the negative charge on the DMF is localized on a bare oxygen atom (the nucleophilicity is centered on this oxygen atom[18]) and DMF possesses a positively-charged nitrogen atom (this is conceivable from NMR data). DMF has a higher dielectric constant (36.7 at 25 °C) than THF (7.4 at 25 °C), but it is obvious that the solvating properties of the solvent rather than its dielectric constant are of prime importance;[19] thus the DMF yields solvent-separated ion pairs by utilizing both sites, one negatively- and the other positively-charged.

As can be seen from Table 2 and Fig. 2, the effects of substituents are reflected on the position of the absorption maxima. As has been described above, the negative charge of the thiolate anions is localized mainly on the sulfur atom, and thus, conjugation between the negative charge located on the sulfur atom and the phenyl ring is not so large. This is also obvious realized from the fact that pK_a of hydrogen sulfide (7.5) roughly equals that of phenylthiol (6.5). In oxide homologues, pK_a of water is 15.8 and that of phenol is 10, thus the oxide anions are stabilized by conjugation with the phenyl ring.[9] Therefore, no substituent effect on the position of the absorption maxima can be expected in the ground state. In general, in $\pi \rightarrow \pi^*$ transitions of odd alternant benzyl-type aromatic hydrocarbons, the excited state is stabilized by conjugation with the substituent, causing a bathochromic shift, *i.e.*, the contribution of the structure  (I) to the excited state produces the stabilization of the excited state (an inductive substituent effect results in only a slight bathochromic shift).[21] This appears to be the case for the substituent effects observed in the optical spectra of sodium metal salts of arylthiolate anions. The greater the localization of the negative charge on the sulfur atom in the ground state, the larger the contribution of structure (I) in the excited state should be, thus a larger bathochromic shift is expected than those caused by the effects of the counter cation and the solvent.

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