772. *Solvation of Ions. Part IV.*[1] *The Electronic Absorption Spectra of Some Group VI Anions and their Conjugate Acids in Protic and Dipolar Aprotic Solvents.*

By A. J. Parker and D. Brody.

The electronic absorption spectra of sodium *p*-nitrophenoxide and methyl *p*-nitrophenyl ether, of their sulphur and selenium analogues, and of *p*-nitrophenol, in a number of protic, dipolar aprotic, and mixed solvents, have been measured. The blue shift of up to 5500 cm.$^{-1}$, observed in the absorption of anions in protic solvents, is due to a general hydrogen-bonding effect rather than to a specific interaction involving a stoicheiometric hydrogen-bonded species.

SOLVENTS produce shifts in the position of absorption maxima by changing the energy difference between ground and excited state. The Franck–Condon principle demands that solvent molecules do not reorientate themselves about an excited state during an electronic transition,[2,3] but polar solvents may rearrange their π-electrons according to the requirements of their environment during an electronic transition. Thus mutual polarization between an excited state and the solvent may produce an excited state which is more solvated than the ground state, provided that the solvent molecules are orientated favourably before the transition.[2,4] This would be the case if the excited state had a dipole moment which was orientated in the same way as, but was greater than, the dipole moment of the ground state; or if specific interactions such as hydrogen bonding became stronger in the excited state than in the ground state, because of the altered charge distribution in the excited molecule.

The effect of protic and dipolar aprotic solvent mixtures on the energies of electronic transitions of anions shows whether the " hydrogen-bonding solvation effect " [5] for anions in protic solvents is a general solvent effect or a specific interaction.[6-8] A specific interaction between an anion (X^-) and a protic solvent (ROH), in mixtures of ROH and aprotic solvents, produces two absorption bands corresponding to X^- and the stoicheiometric bonded species [$X^- \cdots HOR$]. Since X^- and [$X^- \cdots HOR$] are in equilibrium, the intensities of their absorption bands will vary as the concentration of ROH changes. The concept of a specific interaction between anion and protic solvent, in mixtures of protic with dipolar aprotic solvents, has been supported by the work of Cavell and Speed.[8]

A general solvent effect allows only one species, whose absorption maximum shifts progressively in proportion to the increase in concentration of protic solvent.[7] Miller and Parker [9] discussed the effect of protic solvents on the rates of some replacement

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[1] Part III, Parker, *J.*, 1961, 4398.
[2] Bayliss and McCrae, *J. Phys. Chem.*, 1954, **58**, 1002.
[3] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.
[4] Pimentel, *J. Amer. Chem. Soc.*, 1957, **79**, 3323.
[5] Parker, *Quart. Rev.*, 1962, **16**, 163.
[6] Bayliss and Brackenridge, *J. Amer. Chem. Soc.*, 1955, **77**, 3959.
[7] Brealey and Kasha, *J. Amer. Chem. Soc.*, 1955, **77**, 4462.
[8] Cavell and Speed, *J.*, 1961, 226.
[9] Miller and Parker, *J. Amer. Chem. Soc.*, 1961, **83**, 117.

reactions, in terms of a general electrostatic anion–dipole interaction. This involved an unspecified number of solvent molecules and was very strong when the positive portion of the solvent dipole was on hydrogen. However, this physical [6] interaction is of the same type, but much weaker, when the positive portion of the solvent is on an atom other than hydrogen.

This paper examines the effect of both specific and general interactions on the electronic absorption spectra of sodium *p*-nitrophenoxide and methyl *p*-nitrophenyl ether, their sulphur and selenium analogues, and *p*-nitrophenol, in a number of protic, dipolar aprotic, and mixed solvents. Although some of the spectra have been measured previously,[10-12] all measurements have been repeated in order to obtain a uniform set of results.

The compounds are denoted by ArMH, ArM^-, and ArMMe, respectively, throughout this paper. Ar is *p*-nitrophenyl and M is oxygen, sulphur, or selenium. The property studied is the position of the absorption maximum, $\nu_{max.}$. This is said to undergo a red shift if it moves to lower frequencies and a blue shift if displaced to higher frequencies by change of solvent. The shifts are relative to some standard in which, as far as is possible, all solute–solvent interactions, except those being considered, are the same as those for the solute under investigation.

RESULTS AND DISCUSSION

The Nature of the Electronic Transition.—There was no correlation between the very small changes in $\nu_{max.}$ of ArMMe and the dielectric constant, refractive index, or dipole moment of the polar solvents, water, *N*-methylformamide, dimethylformamide, and dimethyl sulphoxide, despite large variations in these properties within this group of solvents.[5] The absorption bands for ArMMe do, however, show a red shift, with increasing polarity of the solvent, from cyclohexane through carbon tetrachloride and acetonitrile to dimethyl sulphoxide and formamide (Table 1). This indicates that the excited state has a larger dipole moment than the ground state.[2]

TABLE 1.

Positions of $\nu_{max.}$ (cm.$^{-1}$) in the ultraviolet spectrum of *p*-nitroanisole (ArOMe), methyl *p*-nitrophenyl sulphide (ArSMe) and selenide (ArSeMe) in solvents shown.

Solvent	ArOMe	ArSMe	ArSeMe	Solvent	ArOMe	ArSMe	ArSeMe
Cyclohexane	33,800	—	—	H_2O	31,600	28,600	27,800
CCl_4	33,400	30,000	—	MeOH	32,700	29,400	28,600
MeCN	32,500	29,200	—	$H\cdot CO\cdot NH_2$	31,200	28,200	—
Me_2CO	—	—	28,400	$H\cdot CO\cdot NHMe$	32,100	28,700	27,800
$H\cdot CO\cdot NMe_2$	31,600	28,700	27,800	$H_2O–Ac\cdot NMe_2$ *	31,500	28,600	—
$Ac\cdot NMe_2$	31,800	28,600	27,800	$H_2O–Ac\cdot NMe_2$ †	31,300	—	—
Me_2SO	31,600	—	—	$MeOH–Ac\cdot NMe_2$ ‡	—	29,000	—

* Mole fraction H_2O, 0·56. † Mole fraction H_2O, 0·88. ‡ Mole fraction MeOH, 0·60.

TABLE 2.

Effect of polarizability [14] of X on $\nu_{max.}$ (cm.$^{-1}$) for ArX (Ar = *p*-nitrophenyl) in solvents.

Solvent	X: H	F	Cl	Br	I	OMe	SMe	SeMe	O^-	S^-	Se^-
Gas [13]	41,800	40,800	39,800	39,200	37,900	—	—	—	—	—	—
n-Heptane [13]	39,500	39,100	37,900	37,200	34,800	34,000	—	—	—	—	—
CCl_4	38,600 [10]	—	—	—	—	33,400	30,000	—	—	—	—
EtOH	38,500 [10]	—	—	—	—	32,800	29,500	28,600	24,800	23,700	22,600
$Ac\cdot NMe_2$	—	—	—	—	—	31,800	28,600	27,800	23,000	19,800	18,300

There is a red shift for all compounds ArMMe and ArM^- as the polarizability of M increases and the electronegativity of M decreases. Similar behaviour has been observed

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[10] Dearden and Forbes, *Canad. J. Chem.*, 1960, **38**, 896.
[11] Mangini and Passerini, *J.*, 1952, 1168.
[12] Parker, *Acta Chem. Scand.*, 1962, **16**, 855.

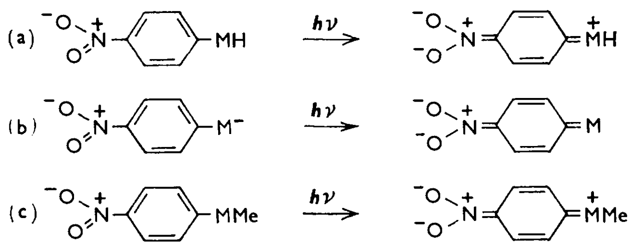
in the spectra of the *p*-halogenonitrobenzenes,[13] and the values of $\nu_{\text{max.}}$ shown in Table 2 can be accounted for qualitatively by the orders of polarizability: [14]

$$\text{SeR} > \text{SR} > \text{OR};\quad \text{Se}^- > \text{S}^- > \text{O}^-;\quad \text{Se}^- > \text{SeR};\quad \text{OR} > \text{F} > \text{H};\quad \text{SR} > \text{Cl}.$$

All the compounds ArMMe, ArM^-, and ArOH have broad absorption bands of half-band width 3000—5000 cm.$^{-1}$, which are of the shape shown in Fig. 2. The intensities are also quite similar, *i.e.*, log ε is 4·0—4·3 in all solvents, so it is likely that the same type of transition is being studied in each case.

These observations support [2,3] the assumption that the first absorption bands for ArMMe,[11] ArM^-, and ArOH correspond to a $\pi^{10} \longrightarrow \pi^{10*}$ transition of the ArM chromophore, modified by the nature of M, the solvent, and the species fulfilling the valency requirements of M.

Transitions of this type (*e.g.*, for *p*-halogenonitrobenzenes [13]) are sometimes represented in terms of valence-bond structures. Although the structures which follow can be no more than a plausible speculation, they do show the likely changes in charge density at the M atom during a $\pi^{10} \longrightarrow \pi^{10*}$ transition and will be used to discuss the interactions between solvent and the aromatic compound in the vicinity of M during an electronic transition.



Hydrogen-bonding Interactions with Ground and Excited States.—Dearden and Forbes [10] have discussed some of the effects of intermolecular hydrogen bonding on electronic spectra of anilines, phenols, and anisoles. The shifts are small and are often obscured by other solvent–solute interactions.[15] Much larger solvent effects, which can be unambiguously attributed to differences in the hydrogen-bonding interactions of the ground and the excited state with the solvents, are observed in the position of $\nu_{\text{max.}}$ of ArM^- in protic solvents relative to aprotic solvents.

The variety of interactions [2] between the solvent and ArMH or ArM^- makes it difficult to evaluate directly any one interaction, such as hydrogen bonding. We have used the appropriate ArMMe compounds as reference standards. Effects due to solvation of the *p*-nitrophenyl portion of the molecule [2,10,16] are assumed to be similar in ArMH, ArM^-, and ArMMe. Hydrogen-bond acceptance by ArMMe does not appear to be significant. Two observations suggest this. The $\nu_{\text{max.}}$ of *p*-nitroanisole in water and in a series of amides of very different hydrogen-bond donating power [5] are similar (Table 1). Secondly, the difference, $\Delta\nu_{\text{max.}}$, between *p*-nitroanisole and methyl *p*-nitrophenyl sulphide is the same in methanol (protic solvent) as in dimethylacetamide (aprotic solvent) despite the fact that sulphur in sulphides is a much weaker acceptor than oxygen in ethers.[17,18] Thus, by comparing shifts relative to those of ArMMe, the effect of hydrogen-bond acceptance by ArM^- and hydrogen-bond donation by ArMH can be separated from effects due to other solvent–solute interactions.

[13] Schubert, Craven, and Steadly, *J. Amer. Chem. Soc.*, 1959, **81**, 2695.

[14] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, (*a*) p. 122, (*b*) p. 77.

[15] Nagakura and Baba, *J. Amer. Chem. Soc.*, 1952, **74**, 5693.

[16] Hammond and Modic, *J. Amer. Chem. Soc.*, 1953, **75**, 1385.

[17] Pimentel and McClellan, " The Hydrogen Bond," Freeman and Co., San Francisco, 1960.

[18] Tarbell and Harnish, *Chem. Rev.*, 1951, **49**, 2.

Values of $\nu_{max.}$ for *p*-nitrophenol and ArM$^-$ in a number of solvents are recorded, and are compared with the values for the appropriate ArMMe compounds in Tables 3 and 4. The results can be explained if it is realised that, when the excited state becomes more solvated than the ground state with change of solvent, a red shift is observed but that, when the ground state becomes more solvated than the excited state, a blue shift is observed.[2,4]

TABLE 3.

Solvent shifts in $\nu_{max.}$ (cm.$^{-1}$) of *p*-nitrophenol (ArOH) relative to *p*-nitroanisole (ArOMe).

Solvent	Cyclohexane	0·005M-Ac·NMe$_2$ *	0·30M-Ac·NMe$_2$ *	1·5M-Ac·NMe$_2$*	Ac·NMe$_2$
$\nu_{max.}$ ArOH	34,800	32,700	32,300	31,800	31,100
$\nu_{max.}$ ArOMe	33,800	33,700	33,400	32,800	31,800
$\Delta\nu_{max.}$ (ArOMe − ArOH) + 1000	0	2000	2100	2000	1700

Solvent	CCl$_4$	MeCN	H$_2$O	Ether	MeOH	EtOH
$\nu_{max.}$ ArOH	33,900	32,500	31,500	33,400	32,100	31,800
$\nu_{max.}$ ArOMe	33,400	32,500	31,600	33,600	32,700	32,800
$\Delta\nu_{max.}$ (ArOMe − ArOH) + 1000	500	1000	1100	1200	1600	2000

Solvent:	MeOH	MeCN	MeCN	MeCN	Ac·NMe$_2$	Ac·NMe$_2$	Ac·NMe$_2$	Ac·NMe$_2$
Anion:	0·1M-Cl$^-$	0·01M-I$^-$	0·1M-I$^-$	0·01M-Cl$^-$	0·01M-I$^-$	0·001M-Cl$^-$	0·01M-Cl$^-$	0·1M-Cl$^-$
$\nu_{max.}$ArOH	32,100	32,500	32,400	31,000	31,100	31,000	30,400	30,000
$\nu_{max.}$ ArOMe	32,700	32,500	32,500	32,500	31,800	31,800	31,800	31,800
$\Delta\nu_{max.}$ (ArOH$_A$ − ArOH$_S$) †	0	0	100	1500	0	100	700	1100

* In cyclohexane. † ArOH$_A$ refers to $\nu_{max.}$ for *p*-nitrophenol in the presence of the anion, ArOH$_S$ to $\nu_{max.}$ in the solvent without the anion.

TABLE 4.

Solvent shifts in $\nu_{max.}$ (cm.$^{-1}$) of ArM$^-$ relative to ArMMe.

(Ar is *p*-nitrophenyl, M is O, S, or Se.)

Solvent:	Ac·NMe$_2$	H·CO·NMe$_2$	H·CO·NH·Me	H·CO·NH$_2$	H$_2$O
$\nu_{max.}$ ArOMe	31,800	31,600	32,100	31,200	31,600
$\nu_{max.}$ ArO$^-$	23,000	23,000	24,300	24,000	24,800
$\Delta\nu_{max.}$ (ArOMe − ArO$^-$)	8800	8600	7800	7200	6800
Blue shift *	0	200	1000	1600	2000
$\nu_{max.}$ ArSMe	28,600	28,700	28,700	28,200	28,600
$\nu_{max.}$ ArS$^-$	19,800	19,800	22,300	22,300	24,100
$\Delta\nu_{max.}$ (ArSMe − ArS$^-$)	8800	8900	6400	5900	4500
Blue shift *	0	−100	2400	2900	4300
$\nu_{max.}$ ArSeMe	27,800	27,800	27,800	—	27,800
$\nu_{max.}$ ArSe$^-$	18,300	18,800	21,900	—	23,800
$\Delta\nu_{max.}$ (ArSeMe − ArSe$^-$)	9500	9000	5900	—	4000
Blue shift *	0	500	3600	—	5500

* Due to hydrogen-bond acceptance by ArM$^-$, relative to ArM$^-$ in Ac·NMe$_2$ and ArMMe in all solvents (see text).

Solvent Effects on the Spectrum of p-*Nitrophenol.*—The electronic transition represented by (a) above can be abbreviated to $\text{Ar–OH} \longrightarrow {}^-\text{Ar=O}^+\text{–H}$. *p*-Nitrophenol in the ground state is a powerful hydrogen-bond donor, but *p*-nitrophenol is an even stronger hydrogen-bond donor in the excited state $^-$Ar=O$^+$–H, because the hydrogen is now bound to positive oxygen and the acceptor molecules are orientated favourably, for hydrogen bonding, before the transition. The result is a red shift in $\nu_{max.}$ (to lower frequencies) in the spectrum of *p*-nitrophenol as the solvent becomes a stronger hydrogen-bond acceptor.

The argument is supported by the results of Table 3, in which are compared the solvent shifts of *p*-nitrophenol relative to the standard, *p*-nitroanisole, in cyclohexane–dimethylacetamide mixtures. Similar effects have been observed with other phenols in non-polar solvents.[15,17] The shift appears to be caused by a specific interaction between *p*-nitrophenol and dimethylacetamide to give a species, which is not *p*-nitrophenoxide ion,[19] in equilibrium with the free phenol.[17,20] Apparently with 0·005M-dimethylacetamide, the equilibrium is already strongly in favour of the *p*-nitrophenol–dimethylacetamide complex, because the absorption band in this solvent does not appear to have a component which could be assigned to absorption by " free " (uncomplexed) *p*-nitrophenol in cyclohexane and the band is not shifted relatively to that for *p*-nitroanisole by more dimethylacetamide. However, the bands in cyclohexane and in cyclohexane–dimethylacetamide are broad and not well separated, so it is difficult to decide if the band in the cyclohexane–dimethylacetamide mixture is due to one or to more species.

The red shifts, produced by basic solvents on the spectrum of *p*-nitrophenol relative to *p*-nitroanisole, decrease in the series EtOH > Ac·NMe$_2$ > MeOH > Ether > H$_2$O > MeCN > CCl$_4$ > Cyclohexane.

Addition of tetraethylammonium chloride to solutions of *p*-nitrophenol in acetonitrile or dimethylacetamide produces a red shift in $\nu_{max.}$ of *p*-nitrophenol. As expected,[9] the shift due to chloride ion, which is a stronger hydrogen-bond acceptor, is much greater than that due to iodide ion. The shift increases progressively with increasing concentration of chloride ion. The band is not broadened, nor does the absorption intensity change significantly, when chloride ion is added. There is no evidence that more than one species of *p*-nitrophenol, corresponding to [ArOH • • • Ac·NMe$_2$], [ArOH • • • Cl]$^-$, and ArOH is present in dimethylacetamide containing *p*-nitrophenol and chloride ion, but the band is broad and in the same region as that for *p*-nitrophenol in dimethylacetamide. Although we cannot with confidence eliminate the possibility of a specific interaction to give [ArOH • • • Cl]$^-$ in equilibrium with [ArOH • • • Ac·NMe$_2$], the effect of chloride ion has more of the features of a general interaction between *p*-nitrophenol and chloride ion.

p-Nitrophenol is approximately 5% ionized in dimethylacetamide at 10^{-4}M-concentration, but the absorption at 23,000 cm.$^{-1}$ due to *p*-nitrophenoxide ion was not changed by 0·5M-chloride ion. Thus, the effect of added phenols on the reactivity of halide ions in dimethylacetamide [5] and acetonitrile [8] is unlikely to be due to proton transfer to form hydrogen halide, but rather to strong general solvation of the halide ion by the phenol.

0·1M-Chloride ion in methanol did not influence the position of $\nu_{max.}$ of *p*-nitrophenol. This is because methanol, at relatively high concentrations, is a more effective hydrogen-bond donor than 10^{-4}M-*p*-nitrophenol.

Solvent Effects on the Spectrum of ArM$^-$.—The electronic transition represented by (b) above can be abbreviated to ArM$^-$ $\longrightarrow$ $^-$Ar=M. The ground state, ArM$^-$, is a much stronger hydrogen-bond acceptor than the excited state, $^-$Ar=M, because the electrostatic interaction between a negatively charged atom, M, and hydrogen is greater than that between an uncharged atom and hydrogen, and the hydrogen-bond donors are orientated in the same way around the M atom in both the ground and the excited state.

The difference in hydrogen-bond solvation of the ground and the excited state produces a large blue shift in $\nu_{max.}$ of ArM$^-$, relative to ArMMe, in the change from aprotic to protic solvent. That some form of hydrogen-bond solvation is responsible for the shift is shown in Table 4, where the blue shift in $\nu_{max.}$ of ArM$^-$ compounds with change of solvent follows the order of strength as hydrogen-bond donors: [5] H$_2$O > H·CO·NH$_2$ > H·CO·NHMe $\gg$ H·CO·NMe$_2$ > Ac·NMe$_2$. The same order has been obtained for the reduction in reactivity of anions in S_N2 reactions by solvents.[5]

The effect of different M atoms must also be considered. In the ground state, *p*-nitrophenoxide ion is a slightly stronger hydrogen-bond acceptor than is *p*-nitrothiophenoxide or *p*-nitroselenophenoxide ion.[1] The differences are not large because hydrogen bonding

[19] Bell and Crooks, *J.*, 1962, 3513.

[20] Joesten and Drago, *J. Amer. Chem. Soc.*, 1962, **84**, 2037.

to anions is electrostatic, and the charge density at the M atom is similar for ArO^-, ArS^-, and $ArSe^-$. In the excited state, $^-Ar{=}O$ is a much better acceptor at oxygen than are $^-Ar{=}S$ and $^-Ar{=}Se$ at sulphur and selenium, respectively. Numerous examples exist of strong hydrogen-bonding to carbonyl compounds and quinones,[17] but similar interactions with C=S or C=Se groups are very weak.[17,18,21] The result is that the blue shift from aprotic to protic solvents is much greater for *p*-nitrothiophenoxide and *p*-nitroselenophenoxide ions than for *p*-nitrophenoxide ion.

The largest blue shift is 5500 cm.$^{-1}$ (*i.e.*, 15·7 kcal./mole) for *p*-nitroselenophenoxide ion relative to *p*-nitrophenylmethylselenide from dimethylacetamide to water.

General Solvation of p-*Nitrothiophenoxide Ion by Water and Methanol.*—The variation of $\nu_{max.}$ for *p*-nitrothiophenoxide ion in mixtures of water and dimethylacetamide is shown in Fig. 1. The effect of methanol on the visible absorption of *p*-nitrothiophenoxide ion in dimethylacetamide is shown in Fig. 2. The $\nu_{max.}$ of the standards, *p*-nitroanisole and methyl *p*-nitrophenyl sulphide in dimethylacetamide, are not appreciably changed by added water or methanol (cf. Table 1).

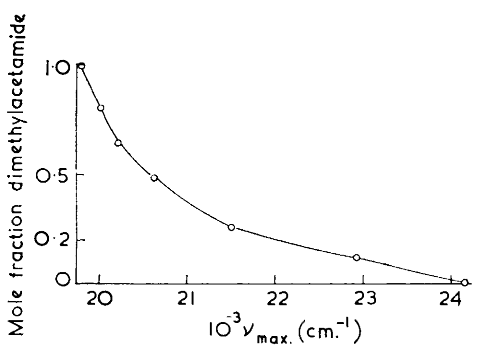


FIG. 1. Effect of added water on $\nu_{max.}$ of *p*-nitrothiophenoxide ion in dimethylacetamide–water mixtures.

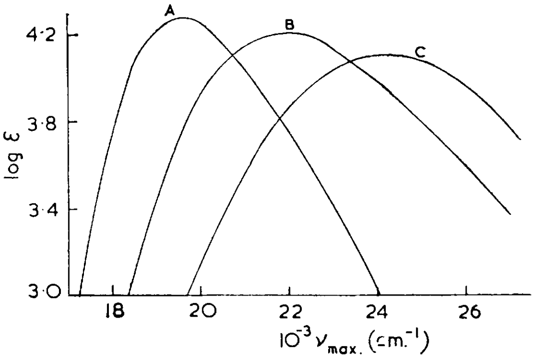


FIG. 2. Absorption spectra of *p*-nitrothiophenoxide ion in (A) dimethylacetamide, (B) methanol–dimethylacetamide (0·6 mole fraction MeOH), and (C) methanol.

In solutions of ArM^- in dimethylacetamide–water mixtures, it seems that water, dimethylacetamide, and ArM^- are competing as acceptors for the protons of the water, so that water in dimethylacetamide is a weak donor towards ArM^-.[5] For this reason, and because the interaction is general rather than specific, comparatively large amounts of water are needed to produce appreciable shifts in $\nu_{max.}$ of *p*-nitrothiophenoxide ions in dimethylacetamide.

The blue shift with increasing mole fraction of water is greater when the mole fraction of water exceeds 0·5 than when dimethylacetamide is in excess over the water (cf. Fig. 1), but in none of the solvent mixtures is there a sharp change in $\nu_{max.}$ of *p*-nitrothiophenoxide ions on the addition of small amounts of water. This is in contrast to the behaviour of *p*-nitrophenol, which in cyclohexane has a specific interaction with dimethylacetamide and has a pronounced red shift on addition of very small quantities of dimethylacetamide (cf. Table 3).

The absorption band of *p*-nitrothiophenoxide ion in dimethylacetamide–methanol mixtures (cf. Fig. 2) is broadened and the intensity decreases slightly as methanol is added. The blue shift of $\nu_{max.}$ as methanol concentration increases cannot be due to formation of two species such as ArS^- and $[ArS^- \cdots HOMe]$ in equilibrium with each other. Despite the band broadening, there is no way that the absorption curves A and C in Fig. 2 can be

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[21] Manojlovich and Edmunds, *Proc. Chem. Soc.*, 1962, 302.

combined to give curve B. Thus the species corresponding to curve B must be different from that of curve A and C. It is thought to be produced by a general electrostatic interaction between *p*-nitrothiophenoxide ions and a large number of methanol molecules, the interaction becoming stronger as the concentration of methanol increases.

It is felt that specific intermolecular hydrogen-bonding interactions may take place between dipolar molecules such as *p*-nitrophenol and dimethylacetamide and that these interactions should be favoured in one particular direction.[22] Anions in protic solvents are solvated, however, by a general anion–dipole interaction, which is undirected, involving a number of protic molecules at various distances from the anion. Since this interaction is so much greater when the positive charge of the dipole is on hydrogen,[9] it is convenient to retain the expression "hydrogen-bonding solvation of anions" to describe the special behaviour of anions in protic solvents,[5] and to refer to anions as hydrogen-bond acceptors. It should be realized, however, that a stoicheiometric hydrogen-bonded anion (*e.g.*, HF_2^-, HCl_2^-)[23] is formed only in exceptional circumstances.

EXPERIMENTAL

Materials.—Solvents were purified by methods already described.[1,9] Cyclohexane was distilled from sodium and absolute ethanol was used without further purification. Dipolar aprotic solvents have been used with advantage in the synthesis of ethers, sulphides, and selenides.[5] Thus *p*-nitroanisole, m. p. 54°, and methyl *p*-nitrophenyl sulphide, m. p. 71—72°, were obtained in $>90\%$ yield from an excess of methyl iodide with sodium *p*-nitrophenoxide and sodium *p*-nitrothiophenoxide, respectively, in dimethylformamide after 5 min. on a steam-bath. The reaction was complete when the deeply coloured solutions became pale yellow. The products were isolated by pouring the solutions into water and were recrystallized twice from methanol.

Methyl *p*-nitrophenyl selenide,[24] m. p. 78°, was prepared by treating di-*p*-nitrophenyl diselenide[12] with 2 mol. of sodium thiophenoxide in dimethylformamide under nitrogen, to give sodium *p*-nitroselenophenoxide and diphenyl disulphide.[12] An excess of methyl iodide was added immediately, the deep red colour disappearing rapidly. The product was isolated by dilution with water and was separated from diphenyl disulphide by recrystallisation from methanol. The yield was 70%. Methyl *p*-nitrophenyl selenide darkened over a period of weeks and was recrystallized shortly before each measurement.

Tetraethylammonium chloride and iodide were used as the source of chloride and iodide ion, respectively. They were recrystallized from dimethylacetamide. *p*-Nitrophenol was recrystallized from water, and its sodium salt, obtained by treatment of *p*-nitrophenol with sodium hydroxide in ethanol, was recrystallized from acetone–ether.

The sodium salts of *p*-nitrothiophenol and *p*-nitroselenophenol are difficult to handle because of oxidation to the disulphide and diselenide, respectively,[12] especially in dipolar aprotic solvents.[25] They were, therefore, prepared in the appropriate solvent just before the spectrophotometric measurements, by treating the stable di-*p*-nitrophenyl disulphide and diselenide,[12] respectively, with a four-fold excess of freshly prepared sodium thiophenoxide[1] in the appropriate solvent, under nitrogen in solutions flushed with nitrogen. The excess of sodium thiophenoxide ensures that any oxidation to disulphide or diselenide does not affect the absorption because reactions such as $ArS{\cdot}SAr + 2PhS^- \longrightarrow 2ArS^- + PhS{\cdot}SPh$ are very fast at room temperature.[12] The presence of an excess of thiophenoxide ion also ensures that the weaker bases, $ArSe^-$ and ArS^-, are not protonated in protic solvents. The visible absorption bands of *p*-nitrothiophenoxide and *p*-nitroselenophenoxide ions were shown not to be influenced by the presence of thiophenoxide ion and diphenyl disulphide, which do not absorb above 360 mμ.[12] Solutions of sodium *p*-nitrophenoxide in protic solvents were made alkaline by the addition (to 0·01M) of sodium hydroxide in the appropriate solvent.

Spectrophotometric Measurements.—These were made on a Beckmann D.U. spectrophotometer at 19—21°. Spectra of oxidizable compounds were measured in freshly prepared

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[22] Allen and Caldin, *Quart. Rev.*, 1953, **7**, 255.

[23] Janz and Danyluck, *Chem. Rev.*, 1960, **60**, 209.

[24] Houben Weyl, "Methoden der Organischen Chemie," Georg Thieme, Stuttgart, Vol. IX, 1955.

[25] Wallace and Schriesheim, *J. Org. Chem.*, 1962, **27**, 1514.

solutions in gas-tight cells flushed with nitrogen. The spectra of ions ArM^- were measured in the regions where ArMH and ArM^- absorb. In no case was the concentration of the conjugate acid $>3\%$, and the absorption of ArMH was sufficiently displaced from that of ArM^- not to interfere with the absorption due to ArM^-. *p*-Nitrophenol was not significantly ionized in cyclohexane or dimethylacetamide.

Other features of the measurements have been discussed in earlier papers.[12,26]

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[26] Parker and Kharasch, *J. Amer. Chem. Soc.*, 1960, **82**, 3071.