370. *Charge-transfer Complexes. Part I. Interaction with Solvent*

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Contrary to prediction,[1] it is found that, for a wide range of formally neutral charge-transfer complexes (DA), increase in solvent polarity does not result in a trend of the charge-transfer band to low energies. Small shifts, generally to high energies, are observed, which often echo the effect of solvent on the spectra of the parent molecules. These trends are discussed in terms of current theories for bonding in such complexes, and it is concluded that they are best understood in terms of solvation forces similar to those which operate on the separate, neutral components.

Interaction with polar solvents to give solvated radical-ions is then described as a chemical reaction rather than solvation of ion-pairs, and it is suggested that solid complexes will exist entirely as aggregates of neutral molecules (DA) or entirely as ionic aggregates (D^+A^-), rather than as a mixture of the two.

It is generally accepted that, for a charge-transfer complex DA, whose excited state resembles D^+A^-, the effect of increasing the solvating power of the medium should be to shift the charge-transfer band to low energies.[1-3] This effect would be expected in terms of Mulliken's theory for bonding in such complexes,[4] which requires that there be a slight admixture of the charge-transferred state so that D and A acquire slight positive and negative charges, respectively. The polar solvent molecules will tend to become oriented so as to stabilise these partial charges, and, despite the restriction of the Frank–Condon principle, these polarised molecules will lead to a greater stabilisation of the excited state, and hence to a low-energy shift. Such a shift, however, should be small compared with the shifts to high energies found for the charge-transfer band of complexes having an ionic ground state, such as the alkylpyridium iodides,[5] since, for these complexes, there is a very large interaction with solvent in the ground state.

No systematic study of the effect of solvent on charge-transfer bands seems to have been reported for DA complexes. There is, however, a fairly wide range of scattered results, some typical data being given in Table 1, together with the results of the present study. Foster and Thomson [6] have recently called attention to the " anomalous " high-energy shifts on increasing the solvent polarity for certain complexes, but no explanation was suggested.

It has recently been found that, for complexes between relatively powerful donors (D) and acceptors (A), dissociation into the corresponding radical-ions, D^+ and A^-, occurs in good solvents.[6,7] One aim of the present work is to probe the structure of undissociated neutral complexes, by measuring the effect of changing the environment upon the charge-transfer band, and to study the mechanism of ionisation in mixed solvents, using optical and electron spin resonance spectroscopy. Another aim is to study the structure of crystalline materials obtained from such solutions, using, in the main, the same techniques.

EXPERIMENTAL AND RESULTS

Materials.—Chloranil was recrystallised from benzene, and had m. p. 296—297°. Hexamethylbenzene and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were used without further purification.

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[1] H. McConnell, *J. Chem. Phys.*, 1958, **20**, 700.

[2] J. N. Murrell, *Quart. Rev.*, 1961, **15**, 191.

[3] S. F. Mason, *Quart. Rev.*, 1961, **15**, 287.

[4] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

[5] E. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261.

[6] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, 1962, **58**, 860.

[7] I. Isenberg and S. L. Baird, *J. Amer. Chem. Soc.*, 1962, **84**, 3803.

NN-dimethylaniline was distilled, b. p. 193—195°. *NNN'N'*-tetramethyl-*p*-phenylenediamine was prepared by the action of dilute ammonia on an aqueous solution of the dihydrochloride. The white precipitate was filtered, washed with distilled water, and dried *in vacuo*. The white powder was then distilled under reduced pressure. Solutions of the complexes were prepared by mixing solutions of the components in the appropriate solvent. The solid complex of *NN*-dimethylaniline and chloranil was prepared by dissolving chloranil in the base, and adding one fifth of the volume of alcohol. Excess of solvent was removed from the precipitate by evacuation at room temperature. Complexes of *NNN'N'*-tetramethyl-*p*-phenylenediamine with chloranil or with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were prepared by mixing solutions of the base and the quinone in benzene. The precipitate was freed from excess of solvent in a vacuum desiccator over solid potassium hydroxide.

Diffuse-reflectance Spectra.—The solid complexes were " diluted " with lithium fluoride, and their spectra were measured with a Unicam S.P. 500 spectrophotometer equipped with an S.P. 540 attachment and an RSVSZG.500 photomultiplier. Results for complexes of *NNN'N'*-tetramethyl-*p*-phenylenediamine with chloranil and with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were in good agreement with those of Foster and Thomson,[8] who used Nujol mulls. The *NN*-dimethylaniline–chloranil complex gave bands at 578 and 607 mμ, in marked contrast with solutions of the complex in carbon tetrachloride, which have a single maximum at 650 mμ. As observed by Foster and Thomson, in no instance were peaks due to the charge-transfer complex and the separate ions observed in the same solid complex.

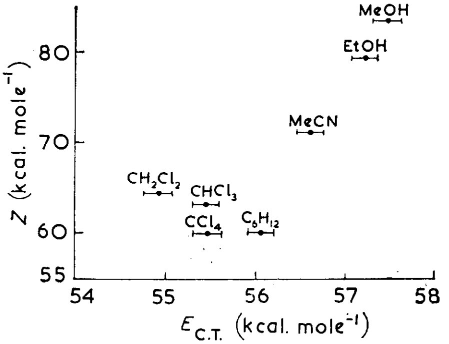

FIGURE 1. Energy of charge-transfer transition of hexamethylbenzene–chloranil complex plotted against the *Z*-value of the solvent

FIGURE 2. Shift of charge-transfer absorption maximum on addition of methanol to carbon tetrachloride

Transmission Spectra.—These were measured with a Unicam S.P. 700 recording spectrophotometer, using cells of 10-mm. path-length. Table 1 shows the effect of varying the solvent on the charge-transfer maximum for several complexes. In Figure 1, the *Z* values [5] of various solvents are compared with the energy of the charge-transfer band for the hexamethylbenzene–chloranil complex in these solvents.

The shift of the band maximum on adding methanol to solutions of the hexamethylbenzene–chloranil complex in carbon tetrachloride is shown in Figure 2. Table 2 shows the effect of varying the solvent on the maxima of individual donors and acceptors. In many cases, the experimental data had to be subjected to band-analysis, as some overlap with the peak of the acceptor occurred. For the hexamethylbenzene–chloranil complex, varying the solvent had no effect on line-width.

In many instances, when a solution of a good donor and a good acceptor were mixed in a polar solvent, a charge-transfer band was not observed, but the spectra of one or both of the ions of the components were observed. These results, which agree with those of Foster and Thomson,[6] were confirmed by means of electron spin resonance measurements, which are not reported in detail here.

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[8] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, 1963, **59**, 296.

TABLE 1

Positions of the charge-transfer absorption maxima (mμ) for a number of complexes in various solvents

	Complex								
Solvent	A	B	C	D	E	F	G	H	I
n-Hexane	465						360		
n-Heptane	466						355		
Cyclohexane	475	387	510	500	558	704			
Carbon tetrachloride	484	395	516				360		
Chloroform	486	390	515				357		
Dichloromethane			521						
1,4-Dioxan	469		504						
Methyl cyanide		374	505	480	544	690		430	395
Ethanol			497					435	408
Methanol			497	454	510				

A, 1,3,5-Trinitrobenzene–*NN*-dimethylaniline (R. Foster and D. L. Hammick, *J.*, 1954, 2685). B, 1,3,5-Trinitrobenzene–hexamethylbenzene (present results; also R. Foster, *J.*, 1960, 1075). C, Chloroanil–hexamethylbenzene (present results). D, *m*-Dinitrobenzene–*NNN'N'*-tetramethyl-*p*-phenylenediamine (ref. 6). E, 2,4,6-Trinitrotoluene–*NNN'N'*-tetramethyl-*p*-phenylenediamine (ref. 6). F, Chlorobenzoquinone–*NNN'N'*-tetramethyl-*p*-phenylenediamine (ref. 6). G, Iodine–naphthalene (G. Briegleb, " Elektronen-Donator-Acceptor-Komplex," Springer-Verlag, Berlin, 1961). H, Chloro-*p*-benzoquinone–hexamethylbenzene (M. E. Peover and J. D. Davies, *Trans. Faraday Soc.*, 1964, **60**, 476). I, *p*-Benzoquinone–hexamethylbenzene (ref. as for H).

TABLE 2

Positions of the maxima (mμ) of a number of donors and acceptors in various solvents

Solvent	Hexamethyl benzene [a]	Chloranil [a]	Chloranil [a]	Aniline [b]	Nitro-benzene [c]	Iodine [d]
n-Hexane						525
n-Heptane				234	252	
Cyclohexane	269	290	364	235	253·5	
Carbon tetrachloride			370			520
Chloroform						514
Dichloromethane		292	374			
1,4-Dioxan				240·5		454
Methyl cyanide	269	286	353	240	262	
Methanol	269	288	364	240		

[a] Present results. [b] W. M. Schubert and J. M. Craven, *J. Amer. Chem. Soc.*, 1960, **82**, 1357. [c] W. M. Schubert, H. E. Steadly, and J. M. Craven, *ibid.* p. 1353. [d] A. L. LeRosen and C. E. Reid, *J. Chem. Phys.*, 1952, **20**, 233.

DISCUSSION

Kosower [5] has observed a well-defined pattern of spectral change with changes in solvent polarity for molecules or ion-pairs which are strongly polar in the ground state, but far less so in the excited state. A comparison of these trends (*Z*-values) with the present results is given in Figure 1. There is no clear correlation of any sort, and the magnitudes of the shifts observed are very small compared with the *Z*-values.

We conclude that the commonly accepted concept for solvent effects on the spectra of charge-transfer complexes has to be abandoned. Furthermore, the results do not accord with the alternative extreme model of an ion-pair ground state, D^+A^-, with the direction of charge transfer reversed.[9]

It is possible, however, that the effect of solvent is to alter the charge-distribution in the ground state, and hence, in effect, alter the electronic structure of the complex. In our view, such modification must either be slight or complete, leading ultimately to solvated ions (see below). Yet another factor to be considered is that the structure of the complex, if depicted as involving a dative bond with, say, a 50% sharing of the outer-electron pair

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[9] J. J. Weiss, *Phil. Mag.*, 1963, **8**, 1169.

of D, would give a complex $D^+–A^-$ with excited states involving the " bonding " electrons having the same charge-distribution (*i.e.*, a $\sigma \longrightarrow \sigma^*$ transition). In such a case, solvent effects would be both small and variable, as is found.

Such a structure would in no sense account for the large trends to low energy found for the charge-transfer bands of complexes having a range of donors with a given acceptor, as the ionisation potential of the donor decreases,[10-12] or having a range of acceptors with a given donor, as the electron affinity of the acceptor increases.[6,13] Furthermore, such a dative bond between π orbitals would surely be weak, and hence one would expect thermal population of triplet states; no evidence for such states has yet been found.

The explanation we favour is that, in all instances, the degree of electron transfer in the ground state is small and that polar solvent molecules are more influenced by local polar centres on D and A molecules than by the small δ^+ and δ^- charges associated with charge transfer. Such solvent interactions should similarly modify the ground states of D and A separately. This will be expected to manifest itself in the effect of solvents upon the spectra of A and of D separately, but solvent shifts will not necessarily parallel those for DA, since excited states will, in general, also be modified.

Solvent effects on spectra are, indeed, frequently found for typical donors and acceptors, and are often comparable in sign and magnitude with those for their complexes. Some examples are given in Table 2.

The trend depicted in Figure 2 is of some relevance, however, since it suggests preferential solvation by carbon tetrachloride. This trend is in accord with the present theory since, for ions or ion-pairs, preferential solvation by methanol is most marked.

Also of significance is the reversal in shift for the hexamethylbenzene complexes of chloranil (C, Table 1) and *p*-benzoquinone (I) on going from methyl cyanide to ethanol. Had the extent of charge transfer in the ground state been an important factor, it would surely have been greater for the former complex, and hence the trend to low energies found for (I) would have been enhanced. In fact, it is reversed. In terms of the present theory, this can possibly be understood on the grounds that hydrogen bonding between ethanol and *p*-benzoquinone is likely to be greater than that between ethanol and chloranil. Thus methyl cyanide, which is a good general solvent for anions, favours the latter, whilst ethanol favours the former.

The shifts recorded are all very small, however, relative to the widths of the bands, and we feel that, since there is a wide variety of factors which could be collectively responsible, detailed discussion is unjustified.

Reaction with Solvent.—If this postulate is accepted, then the formation of radical-ions, D^+ and A^-, when D and A are mixed in polar solvents,[6,8] is best represented as a chemical reaction between the complex, DA, and the solvent:

$$DA + \text{solvent} \rightleftharpoons D^+_{\text{solv.}} + A^-_{\text{solv.}}$$

Reaction will occur when the energy required for electron transfer is less than the net solvation energy of the two ions. If this is the case, then the concept that electron spin resonance signals stem from paramagnetic complexes (D^+A^-) [14,15] is unlikely to be correct, since charge transfer only takes place when the solvent organisation is sufficient to permit dissociation. Indeed, electron spin resonance spectra that have been detected have always been characteristic of the separated ions, and show none of the complications expected for the diradical (D^+A^-).

Structure of Complexes in the Solid State.—Just as it is frequently suggested that 1 : 1

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[10] R. L. Strong, S. J. Rand, and J. A. Britt, *J. Amer. Chem. Soc.*, 1960, **82**, 5053.

[11] G. Briegleb and J. Czekalla, *Z. Elektrochem.*, 1959, **63**, 6.

[12] S. K. Chakrobarti and S. Basu, *Trans. Faraday Soc.*, 1964, **60**, 465.

[13] M. E. Peover, *Trans. Faraday Soc.*, 1964, **60**, 479.

[14] D. Bijl, H. Kainer, and A. C. Rose-Innes, *J. Chem. Phys.*, 1959, **30**, 765.

[15] D. N. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, 1963, **85**, 2557.

complexes in solution can have structures varying from neutral to ionic (D^+A^-), so also it is implied that solid structures can vary progressively from those containing neutral molecules to those containing radical-ions [14] as the donor and acceptor components are varied.

We consider that this viewpoint requires modification. We have frequently observed that, when solutions of donor and acceptor are mixed in a non-polar solvent, the complex DA is immediately formed in high concentration, but some seconds later a solid is precipitated, leaving only very small concentrations of the complex in solution. In such cases, the charge-transfer band characteristic of DA is not detected in the solids, whose electronic spectra consist of a superposition of those of the separate ions. The diffuse-reflectance spectrum is that of the ionic material, while the solution species is still DA. Furthermore, in no instance have we or others [8] detected charge-transfer bands characteristic of DA and of D^+ and A^- in the same solid. That is, one either detects the charge-transfer band of " neutral " DA or the spectra of the individual ions.

These observations are readily understood in terms of our postulate that complexes in the solid state must either be essentially ionic or non-ionic. Consider a situation in which one DA unit in a non-ionic solid becomes D^+A^-. At this stage, the ion-pair gains very little in stabilisation from the " medium," which may be compared with a solvent of low ionising power. Thus, it is an excited state, and will rapidly revert to the neutral condition DA. If, however, we imagine a catastrophic process whereby all DA units simultaneously become D^+A^-, then the ion-pair under consideration is in an ionic medium, and is thereby greatly stabilised. If this stabilisation is sufficient, then an ionic complex will be favoured.

If, in the non-ionic solid, defects can act as electron-sources or -traps, then low concentrations of the separate anions or cations may accumulate, and these are probably responsible for the traces of paramagnetic species often detected in such solids.

This would explain why an ionic solid is obtained from a solution of the neutral complex (DA), and also why there is an induction period prior to precipitation. The neutral complex is likely to be soluble in the non-polar solvent used, whereas the ionic solid is insoluble. A fortuitous agglomeration of many neutral complex molecules is then required before nucleation of the ionic crystals can take place. In general, only those complexes which react with polar solvents to give ions are found to give ionic precipitates from non-polar solvents. This is in accord with the usual observation that stabilisation of ions in ionic crystals is comparable with that in polar solvents.

We have used electronic spectra as our criterion for deciding whether a solid is ionic or neutral. We consider this to be a better criterion than paramagnetism, since the latter is far more sensitive to the perturbing effects of adjacent radicals than is the former. Indeed, little is known about the bulk paramagnetic properties of solids containing radical-ions of the type under consideration. It does seem to be an experimental fact, however, that the overall electronic spectrum does not deviate much from those of the individual ions.

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