Charge-transfer Complexes. Part XII.[1] Viscosity Dependence of the Intensity of Contact Charge-transfer Absorption Bands

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As the viscosity of the solvent is increased by addition of ethylene glycol to ethanol, the intensity of the contact charge-transfer absorption bands of the oxygen complexes of benzene and *NN*-dimethylaniline diminishes, tending towards zero in highly viscous media. This contrasts with the behaviour of the π-molecular complex, chloranil–hexamethylbenzene, which has the intensity of its charge-transfer band essentially independent of viscosity. These results are in accord with the model for contact complexes in which the light absorption to the charge-transfer state occurs during random collisions between the components.

'CONTACT' charge-transfer (C.T.) complexes[2] were originally invoked to explain the anomalous rise in extinction coefficient of the C.T. band as the association constant decreased in series of molecular complexes. Pure contact complexes, *i.e.* those with a zero association constant, have been found for the system iodine–n-heptane[3] and the complexes of molecular oxygen with electron donors.[4] Contact complexes are envisaged as being formed by random collisions of the electron donor and acceptor during which there is sufficient overlap of orbitals to enable a transition to a charge-transfer excited state to take place. The intensity of such transitions may be quite high owing to the 'borrowing' of intensity from an allowed transition of one of the components.[5] Characteristically, no maximum of the band is observed, the transition appearing as an increase in intensity of the long wavelength tail of a component absorption band. Here we present the results of an investigation into the effect of the viscosity of the solvent on the intensity of the contact C.T. bands of the oxygen complexes of benzene and *NN*-dimethylaniline. As a comparison, a similar investigation was carried out on the complex, chloranil–hexamethylbenzene, which has a non-zero association constant.

EXPERIMENTAL

Materials.—Solvents used were of spectroscopic grade and were dried before use. Fluorimetric grade benzene was used. *NN*-Dimethylaniline was distilled under nitrogen and stored under mercury in ampoules until required. Chloranil was recrystallised from benzene, m.p. 297 °C. Oxygen free solutions were prepared in a dry box under nitrogen using dry, nitrogen-purged solvents. Oxygenated solutions were prepared by shaking the nitrogen-purged solutions in an atmosphere of oxygen until constancy of the absorption spectra was obtained.

Spectra.—Absorption spectra were obtained with a Beckman DK2A recording spectrophotometer with a thermostatted cell compartment. The reference cell contained the appropriate oxygenated or nitrogen-purged solvent mixture.

RESULTS AND DISCUSSION

A series of solutions containing a constant concentration of the donor were prepared in mixtures of ethanol and ethylene glycol. For each solution the spectrum was obtained for both the nitrogen-purged and oxygenated solutions. It was found that the nitrogen-purged solutions gave a constant spectrum in all solvent mixtures. Figures 1 and 2 show the effects on the spectra of

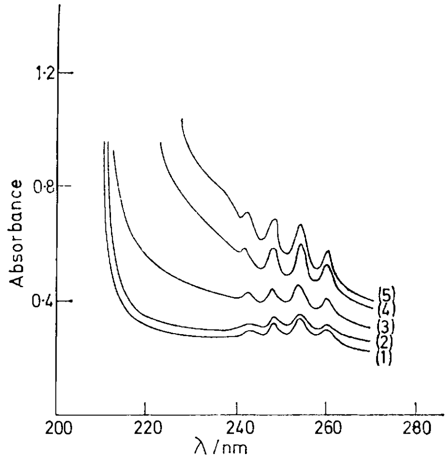

FIGURE 1 Absorption spectra for the system benzene (concentration 5×10^{-5}M)–oxygen in ethanol–ethylene glycol mixtures: (1) nitrogen-purged sample (spectrum invariant with ratio of solvents); oxygenated sample v/v EtOH : $HO(CH_2)_2OH$ (2) 1 : 4; (3) 2 : 3; (4) 3 : 2; (5) 7 : 3.

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the oxygenated solutions of altering the proportion of ethanol to ethylene glycol. The intensity of the contact absorption, observed as an extension to longer wavelengths of the long wavelength tail of the donor absorption, clearly decreases as the proportion of the viscous ethylene glycol increases. No values are available for the absorption coefficient of oxygen in ethylene glycol. Values available for other alcohols show however that there is only *ca.* 20% variation in absorption coefficient over the range of alcohols from methanol to isoamyl alcohol. This compares with a 300% change in intensity of the contact C.T. band in the present work. We feel that this rules out any explanation of the changes on the basis of differential oxygen solubility. The relative viscosity for each solvent mixture was determined using an Ostwald viscometer, the times of flow being used as a measure of viscosity. Figure 3 shows the intensity at a fixed wavelength of the contact absorption, taken as the difference in intensity of the nitrogen-purged and oxygenated solutions, plotted against the fluidity of the solvent mixture taken as the reciprocal of the flow time in the viscometer. A good linear correlation emerges for both complexes. By contrast, the intensity of the C.T. band of the complex, hexamethylbenzene–chloranil, is almost independent of solvent fluidity. This clearly indicates that the formation of the light absorbing species in the two contact complexes is controlled by the bimolecular collision rate in solution between the two components. This is given by the Stokes–Einstein–Smoluchowski relationship $k_2 = 8RT/3000\eta$. This predicts a zero collision rate when the fluidity is zero. The intensity of the contact C.T. band should also be close to zero in rigid media which is in accord with the results in Figure 3 and with the observation of loss of colour on freezing solutions where the contact C.T. band lies in the visible region.[6] Any slight residual absorption is probably caused by ' frozen-in ' contacts. These results are clearly in accord with the model for contact complexes in which the transition to the C.T. state occurs during a collision between the two components.

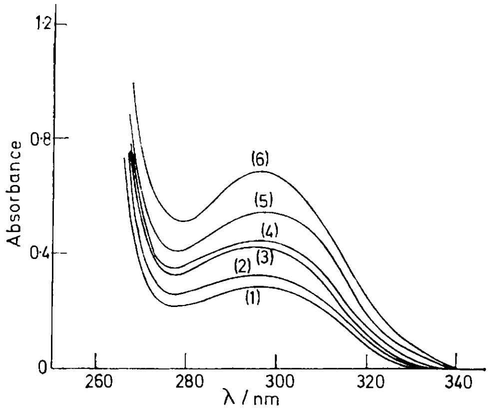

FIGURE 2 Absorption spectrum for the system *NN*-dimethylaniline (concentration 1×10^{-5}M)–oxygen in ethanol–ethylene glycol mixtures: (1) nitrogen-purged sample (spectrum invariant with ratio of solvents); oxygenated sample v/v EtOH : $HO(CH_2)_2OH$ (2) 1 : 9; (3) 3 : 7; (4) 1 : 1; (5) 4 : 1; (6) 9 : 1

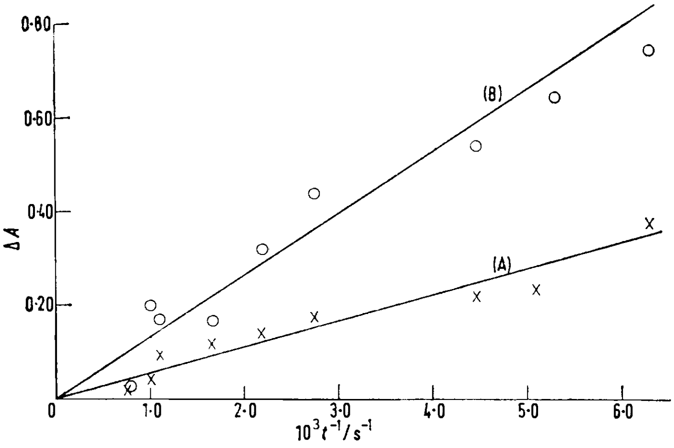

FIGURE 3 The differences in optical density between the nitrogen-purged and oxygenated solutions, ΔA, of benzene (A) at 235 nm (concentration 5×10^{-5}M) and *NN*-dimethylaniline (B) at 268 nm (concentration 1×10^{-5}M), in ethanol–ethylene glycol mixtures plotted against t^{-1}, the reciprocal of the flow time in the Ostwald viscometer

No maximum could be observed for the bands even when the donor concentration was very low, the new absorption appearing to be an extension of the donor high-energy band to longer wavelengths. The general failure to observe maxima for the C.T. bands in these systems may be attributed to the new absorption being caused by a broadening of the donor band due to admixture of the donor excited state with a C.T. state as postulated for the system carbon tetrachloride–tetracene where such broadening with maintenance of integrated intensity has been demonstrated,[7] the intensity of the C.T. transition being ' borrowed ' from the allowed transition of the donor component.

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