

Although the plots superficially suggest that two such functions might suffice, detailed analysis shows that at least three in a narrow range are needed, but we have not found convincing arguments to distinguish among different possibilities. The shape of the complex curves changes slightly with temperature, and activation energies of 8.0 and 6.2 kcal/mole are required to describe the temperature dependence of the low- and high-frequency parts of the dispersion.

These features of the dispersion differ considerably from typical behavior in high-temperature solid rotator and liquid phases, where single, mostly simple exponential, decays with much shorter relaxation times and activation energies of order 1–2 kcal/mole have been found.^{2,4}

Unfortunately, the crystal structures of the solid phases of $CBrCl_3$ are unknown and we are unable to rule out several possible explanations of the dispersions, of which the most likely would be nonequivalent molecular-orientation sites. Similar effects observed in solid solutions of CH_2Cl_2 in CCl_4 will be described later. We note finally that the temperature dependence of $\epsilon_0 - \epsilon_\infty$ must change at lower temperatures to give a temperature-independent state consistent with third-law requirements.

* Supported by the Advanced Research Projects Agency.

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Influence of Charge-Transfer Complexing on the Donor's Phosphorescence

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(Received 4 February 1966)

CHARGE-transfer complexes of acceptors containing heavy atoms, e.g., tetrachloro- or tetrabromophthalic anhydride, with donor aromatic hydrocarbons show a large increase in the $T \rightarrow S$ transition probability of the donor.^{1–3} Although there is a significant change in the triplet lifetime it is found that the donor phosphorescence spectra of all aromatics complexed with TCPA or TBPA heretofore studied are essentially the same as the phosphorescence of the free molecules.⁴ Unlike these earlier results, experiments in this laboratory on chloronaphthalenes with TBPA or in a propyl iodide solvent show gross changes in the donor phosphorescence. A possible role in the charge-transfer state in enhancing the $T \rightarrow S$ transition and altering the vibrational character of the donor phosphorescence is discussed.

The phosphorescence spectra of naphthalene and the chloronaphthalenes for the uncomplexed and TBPA complexes were determined in an EPA glass at 77°K. The heavy-atom experiments were conducted at 77°K in a 16 parts ethanol, four parts methanol, and one part propyl iodide solvent. The TBPA complexes and the propyl iodide complexes were excited at 3660 and 3130 Å, respectively, using a 500-W Hg lamp. The emission was recorded using a $\frac{3}{4}$ -m Czerny–Turner spectrometer.

If the complexing of the donor increases the singlet-triplet mixing already present in the uncomplexed molecule without introducing new coupling schemes, then the vibrational features of the donor phosphorescence should be the same whether complexed or free. For the cases of $C_{10}H_8 + PI$ and $C_{10}H_8 + TBPA$, Fig. 1, the phosphorescence, apart from some broadening, appears the same as the free $C_{10}H_8$ emission. For β - $C_{10}H_7Cl$, significant changes have occurred on complexing, Fig. 1. The out-of-plane bands, i.e., the 0–0 band and all successive totally symmetric modes have been enhanced relative to the in-plane bands.⁵ Clearly, the effect of complexing does not simply increase the coupling already present in the donor molecule.

The different results for naphthalene versus the chloronaphthalenes can be reconciled if the charge-

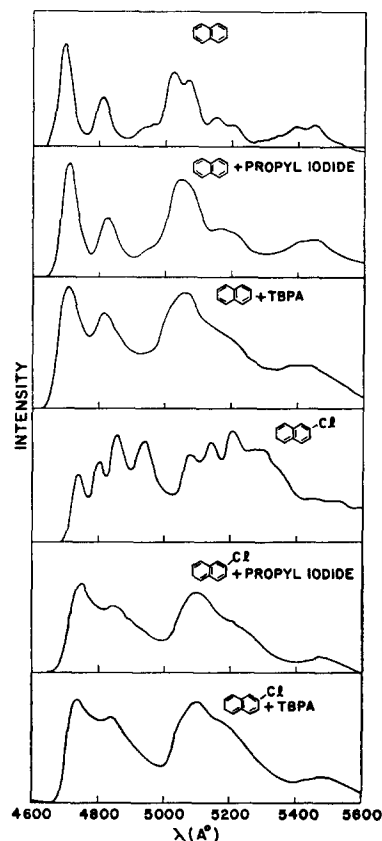


Fig. 1. The effects of complexing on the naphthalene and β -chloronaphthalene phosphorescence spectra.

transfer state is assumed to play an important role in the donor phosphorescence. The electronic mixing of the donor triplet with the charge-transfer singlet or possibly with some final perturbing singlet via the charge-transfer singlet would lead to an enhancement of the 0-0 band as well as all successive totally symmetric vibrational bands of the donor.⁶ Thus, for the naphthalene phosphorescence spectrum one would expect no change in the triplet emission as is shown in Fig. 1. The free chloronaphthalene emission consists of two subpectra⁷; (a) the naphthalene type and (b) a new coupling arising from vibrational and spin-orbit interaction appearing to the red of the 0-0 band.⁷ On the basis of the aforementioned role for the CT state, one would expect the naphthalene-type emission, i.e., the 0-0 band and the successive totally symmetric bands, to be enhanced relative to the (b)-type emission. This would explain the donor emission in the complexed form as shown in Fig. 1.⁸

The increase in the intensity of the 0-0 band can only be effected by states which have the same polarizations as the 0-0 band. For the sandwich complexes involving TBPA the CT band is in the same direction as the 0-0 band and therefore the subsequent totally symmetric bands (naphthalene type). However the CT band is perpendicular to the in-plane bands in the chloronaphthalenes and therefore it cannot contribute directly to their intensities. For the complexes with propyl iodide the most likely geometry is one for which the propyl iodide lies above the plane of the donor molecule. One would therefore expect the CT band to have its primary moment perpendicular to the plane of the donor and consequently in the same direction as the triplet 0-0 band. The major contribution that the CT band can make would therefore be to the out-of-plane 0-0 and totally symmetric bands rather than to the in-plane bands. These arguments provide an explanation for the similar effects of TBPA and propyl iodide on the naphthalene and chloronaphthalene spectra.

For those complexes of TBPA with naphthalene and the chloronaphthalenes, the polarization of the phosphorescence is found to be consistent with a perturbing CT state. The polarized emission of the complexed chloronaphthalenes is significantly more positive for the out-of-plane (naphthalene-type bands), than for the in-plane bands relative to absorption into the CT state.

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On the Charge Recombination in Gamma-Irradiated Alkane Glasses

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(Received 19 April 1966)

IT is known that electrons produced in the gamma radiolysis of certain alkane glasses at 77°K can be trapped even at a state of relatively high purity and that charge recombination is a slow process.¹⁻³ The latter process can be accelerated by heat or infrared light. A common interpretation for the mechanism of acceleration is that electrons are released from their traps and then diffuse to positive ions for completion of the charge neutralization.

The purpose of this note is to point out that the nature of the charge carrier in the recombination process depends both upon the purity (or chemical composition) of the sample and the method of bleaching. In the case of pure alkanes and thermal bleaching, the positive charge is the principal moving entity, whereas in the case of doped alkanes (such as 3-methylpentane with small added component 2-methyl-1-pentene) and thermal bleaching the electron becomes the moving entity. In the case of optical bleaching the electron is essentially the only charge carrier.

The relevant feature of the pure alkane glasses, in contrast to other types of molecular solids, is the fact that the positive charge can be trapped at every molecular site while the electron can be trapped only at certain intermolecular sites which are separated from each other by 10 Å or more.⁴

The above remarks on the nature of the charge carrier are based upon the two premises: (1) the parent alkane ion can exist as a stable entity at 77°K, in agreement with the suggestion of Shida and Hamill,³ (2) the charge transport of electrons or positive charges in alkane glasses is described properly by the narrow-band approximation (hopping mechanism) of Holstein.⁵ According to the latter, the diffusivity D of the charge in the simplest case is given by

$$D = \omega_0 a^2 \frac{J^2}{\hbar^2 \omega_0^2} \left[\frac{2\pi}{2\gamma \operatorname{csch} \frac{1}{2} \beta \hbar \omega_0} \right]^{\frac{1}{2}} \exp\left(-2\gamma \tanh \frac{\beta \hbar \omega_0}{4}\right),$$

where ω_0 is the angular frequency of molecular vibration which is coupled with the motion of the charge, a is the "lattice spacing," distance between the adjacent trap