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Photodissociation of Charge Transfer Complexes based on Aromatic Amines and Bromine-containing Electron Acceptors

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Ionic photodissociation of Am·HBMS donor–acceptor complexes leads to the formation of a primary coloured product that is a diphenylmethane dye and acid $H^+[S(O)_2CBr_3]^-$ if Am is diphenylamine, or *N,N*-diphenylphenylmethyleneiminium bromide and acid $H^+[CBr_2{=}S(O)_2{-}CBr_3]^-$ if Am is diphenylbenzylamine [hexabromodimethylsulfone (HBMS) is the electron acceptor]; the structure of the amine determines the difference in the coloured products.

Polymer layers containing charge transfer complexes based on aromatic amines and electron acceptors are potentially useful in photolithography, new photoregistering systems and other high technology processes.[1,2] As a consequence of the phototransfer of an electron from a donor to an acceptor molecule a coloured product and an acid are formed, the nature of which determine the physico-chemical properties of the illuminated areas. The aim of the present work was to identify the coloured products which are formed on illumination of complexes DPA·A and DPBA·A (DPA = diphenylamine, DPBA = diphenylbenzylamine; A = HBMS or CBr_4). Unlike the DPA·A complexes, DBPA·A complexes form a primary coloured product which is a spectral sensitizer. This allows us to produce highly sensitive photoresists using a process of latent image optical amplification.[1,2]

The complexes were cast on KBr plates from mixtures of Am and HBMS (or CBr_4) in toluene solution. Unlike the individual components, which scatter incident light to a marked degree owing to their crystallization during toluene evaporation, the mixtures formed on the KBr surface are transparent homogeneous films with a wide range of concentrations Am:A. We recorded the IR spectra of the initial unexposed films and also differential IR spectra of the exposed films compared with those of the unexposed films. The films were irradiated using a mercury vapour lamp ($\lambda = 436$ nm) until the absorbance of the coloured product at $\lambda = 665$ nm reached the range $A(665) = 0.15$–0.9. The intensity of the emerging IR bands increases linearly with increasing $A(665)$ and consequently also with the concentration of the coloured product.

The IR spectrum of the coloured product **1** obtained from a DPA·HBMS complex having the composition [DPA]:[HBMS[= 1:2 consists of a quinonoid C═C stretching band[3] (ν_{max}/cm^{-1} 1570 and 1470), a ═CBr— absorption (narrow band at 1650 cm^{-1})[4] and a narrow strong band corresponding to >C═N— group stretching vibrations (1168 cm^{-1}),[5] a C—H out-of-plane deformation band for the *para*-disubstituted benzene ring (830 cm^{-1})[3,6] and also a band at 1140 cm^{-1} which may be attributed to vibration of the dihedral angle[7] in structure **X**. The formation of **1** is accompanied by a decrease in the intensities of the monosubstituted benzene bands: the C═C stretching vibrations (1600–1460 cm^{-1}) and the C—H out-of-plane deformation vibration[3] (ν_{max}/cm^{-1} 750 and 690); and the >N—H bands: the N—H stretching vibrations (ν_{max}/cm^{-1} 3415, 3390 and 1320) and N—H deformation vibrations (ν_{max}/cm^{-1} 1580 and 1520).[3] The IR spectrum of HBMS consists of absorption bands due to symmetric (1155 cm^{-1}) and antisymmetric (1355 cm^{-1}) stretching vibrations of the O═S═O groups and also vibration of the C—Br groups (668 cm^{-1}.[5] Under illumination the intensities of the absorption bands markedly decrease and a new absorption at 1090 cm^{-1} appears. The latter does not appear in the case of the DPA·CBr_4 complex and it may be related to the vibration of the S═O groups in the acid HSO_2CBr_3.[5]

X

The transformation of the primary coloured product **1** into a triphenylmethane dye (with $\lambda_{max} = 605$ nm) on heating proceeds simultaneously with a decrease in the intensity of the ═CBr— absorption, an increase in the intensity of the *para*-disubstituted benzene band and, further, a decrease in the intensity of the benzene ring absorption band. The IR spectra and their transformation with temperature change confirm structure **1** for the primary coloured product with $\lambda_{max} = 665$ nm belonging to the diphenylmethane dye class.[8]

$$Ph{-}\overset{+}{N}H{=}C_6H_4{=}CBr{-}C_6H_4{-}NH{-}PhBr^-$$

1

We have also studied in detail the IR spectra of the DPBA·HBMS and DPBA·CBr_4 complexes. We cast on KBr plates films with the following compositions: [DPBA]:[HBMS] = 1:3 (**I**); 1:1 (**II**); 2:1 (**III**) and also [DPBA]:[CBr_4] = 1:3. As shown in the optical spectra in Fig. 1, illumination of each of these complexes produced a primary coloured product **2** (λ_{max} 665 nm) which converted completely into new compounds when kept at room temperature, for 3, 6 and 24 h (for conversion of complexes **III**, **II** and **I**,

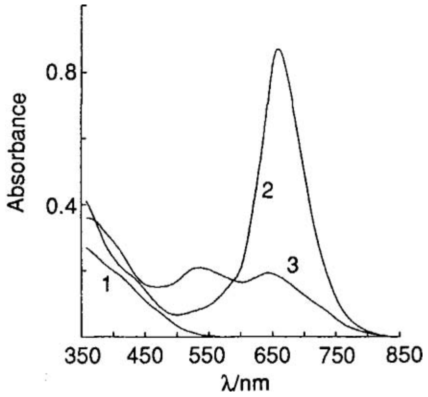

Fig. 1 Electronic adsorption spectra of DPBA · HBMS complexes **I** (1, 2) and **III** (1, 3). Spectra were recorded (1) before and (2, 3) 3 h after illumination.

respectively). In order to determine the structure of **2** and to exclude the contribution of the new compounds to the spectra we recorded the IR spectra of complex **I** immediately after irradiation.

The IR spectra of the DPBA · A complexes show absorptions due to the DPBA benzene rings (ν_{max}/cm^{-1} 3150–3000, 1590, 1496, 1456, 750 and 690), N—CH$_2$ (ν_{max}/cm^{-1} 2920 and 2860) and tertiary amine >N— (ν_{max} 1370 cm^{-1}) groups. The IR spectrum in the region 1700–600 cm^{-1} is shown in Fig. 2(*a*). As mentioned above, if A was HBMS the IR spectrum showed absorption bands at ν_{max}/cm^{-1} 1355, 1155 and 668. When A = CBr$_4$ only the strong 668 cm^{-1} band is present. Scheme 1 has been proposed previously for the phototransformation of DPBA · HBMS into **2** and the acid **I**.[9]

$$\mathrm{Ph_2N{-}CH_2Ph\cdot CBr_3{-}SO_2{-}CBr_3} \xrightarrow{h\nu_{CT}}$$

$$\mathrm{[Ph_2\overset{+}{N}{}^{\bullet}{-}CH_2Ph\cdots Br^-\cdots(CBr_2{=}SO_2^{\bullet}CBr_3)]} \longrightarrow$$

$$\underset{\mathbf{2}}{\mathrm{[Ph_2\overset{+}{N}{=}CHPh]Br^-}} + \underset{\mathbf{I}}{\mathrm{H^+(CBr_2{=}SO_2CBr_3)^-}}$$

Scheme 1

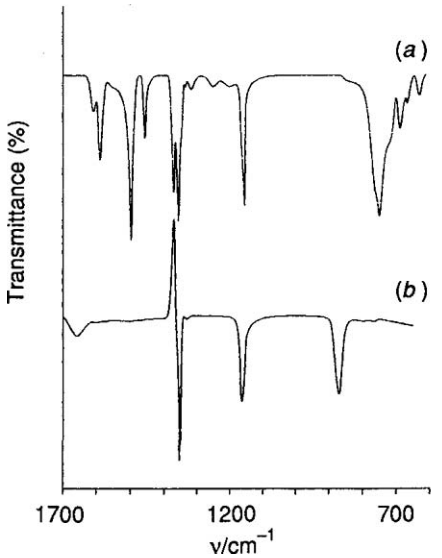

Fig. 2 IR spectra of DPBA · HBMS complex **I** (*a*) before and (*b*) after illumination. Spectrum (*b*) is differential, measured relative to spectrum (*a*).

The electronic spectrum of **2** with λ_{max} = 665 nm (ϵ = 4.5 × 10^4 dm^3 mol^{-1} cm^{-1}),[10] was ascribed to *N,N*-diphenylphenylmethyleneiminium bromide (DPMI$^+$Br$^-$). The formation of DPMI$^+$Br$^-$ is also thought to occur during the phototransformation of the mixture containing the DPBA · CBr$_4$ complex.[10] The IR spectra prove that, unlike DPA, illumination of the DPBA-based compositions does not affect the concentration of the monosubstituted benzene rings. No =CrB— groups or quinonoid structures appeared but the concentrations of the >N— and N—CH$_2$ groups decreased, and an N=C absorption (a broad weak band in the region 1690–1640 cm^{-1}, which is also ascribed to an 'immonium band' $>\overset{+}{\mathrm{N}}{=}\mathrm{C}$,[11] and a narrow strong band at 1168 cm^{-1}) appeared. These changes are entirely consistent with the structure of DPMI$^+$Br$^-$ **2** shown in Scheme 1. At the same time in the CBr$_4$-based complexes the absorption band at 668 cm^{-1} decreases due to the breakup of CBr$_4$ while in the HBMS-based complexes a new band arises at 870 cm^{-1} due to =CBr$_2$ absorption in acid **I**.[4] It should be noted that the transformation of HBMS into acid **I** was accompanied by a small shortwave displacement of the O=S=O antisymmetric vibration band, which is displayed in the increased absorption at 1353 cm^{-1}. This band did not rise when CBr$_4$ was used as an acceptor or if DPA · HBMS was used as a light-sensitive complex.

Illumination of the film with composition **III** results in a rapid transformation of DPMI$^+$Br$^-$ **2** into new compounds having electronic spectrum 3 (Fig. 1). IR absorption bands due to N—H groups (3420–3250 cm^{-1}) and quinonoid structures (ν_{max}/cm^{-1} 1570, 1470 and 1140) appeared. The final product contained neither =CBr— nor disubstituted benzene groups.

The formation of the coloured product DPMI$^+$Br$^-$ **2** from DPBA · A is caused by the reaction of radical species with the chemically reactive α-hydrogen at the N-atom in DPBA$^{+\bullet}$ (see Scheme 1).

The primary coloured products forming optical images in these charge transfer based layers thus have different structures, depending on whether DPA or DPBA is used as the donor component. In the DPA · A complex the coloured product is a diphenylmethane dye and acid H$^+$[S(O)$_2$CBr$_3$]$^-$, while in the DPBA · A complex it is *N,N*-diphenylphenylmethyleneiminium bromide and acid H$^+$[CBr$_2$=S(O$_2$)—CBr$_3$]$^-$.

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