CHEMISTRY LETTERS, pp. 979-983, 1973. Published by the Chemical Society of Japan

TIME-RESOLVED PHOSPHORESCENCE SPECTRA OF EDA COMPLEXES OF AROMATIC CARBONYLS WITH ANILINES

Hisaharu HAYASHI
The Institute of Physical and Chemical Research, Wako, Saitama 351

Noboru HIROTA* and Saburo NAGAKURA
The Institute for Solid State Physics, The University of Tokyo, Minato, Tokyo 106

Time-resolved phosphorescence spectra were measured at 77 K for several systems containing benzophenone or p-chlorobenzaldehyde as an electron acceptor and aniline, N-methylaniline, or N,N-dimethylaniline as an electron donor in 2-methyltetrahydrofuran. The phosphorescences of the electron donor-acceptor complexes under consideration showed a strong tendency for bimolecular quenching.

We have hitherto studied the electronic structures of the lowest triplet states of the electron donor-acceptor (EDA) complexes including tetracyanobenzene and acid anhydride as electron acceptors by measuring their phosphorescence, ESR, and triplet-triplet absorption spectra.[1-4] Recently, Arimitsu and Tsubomura[5] studied the emission spectra from the triplet states of the EDA complexes of benzophenone with aromatic amines at 77K in connection with the hydrogen transfer reaction through the excited states. We have undertaken to study the decay process by measuring time-resolved emission spectra and decay curves for several EDA complexes of aromatic carbonyls with anilines at 77 K.

Experimental

Benzophenone (BP) and p-chlorobenzaldehyde (CBA) were purified by repeated recrystallizations from ethanol. Aniline (AN), N-methylaniline (NMA), and N,N-dimethylaniline (DMA) were purified by vacuum distillation. 2-Methyltetrahydrofuran (MTHF) was refluxed with sodium and purified by distillation. A mixture of MTHF and amine (3:1 by volume) was used as a transparent organic matrix at 77 K. The concentrations of carbonyls were about 5×10^{-3} M.

---

* On leave from Department of Chemistry, State University of New York at Stony Brook, New York 11790, USA.

Samples were excited by a pulsed nitrogen gas laser (AVCO EVERETT model 1000) with a duration time of about 10 ns with a peak intensity about 100 kW. Emissions from the samples were detected by an EMI 6256S photomultiplier through a Spex model 1700 monochromator. Time-resolved spectra and decay curves were measured at 77 K by means of a boxcar integrator (PAR model 160) by fixing and changing the delay time after the laser pulse with a constant aperture time (AT), respectively.

Results and Discussion

Emission spectra observed for BP in mixed solvents of MTHF with AN, NMA, and DMA change with time. Immediately after the irradiation of a laser pulse they are composed of the fluorescences of BP⁶⁾ and its ketyl radical⁵⁾ and the phosphorescences of the EDA complexes of BP with the anilines. The emission spectra observed 2.5 μs after the irradiation of a laser pulse, which are shown in Fig. 1, are similar to those obtained by Arimitsu and Tsubomura⁵⁾ and are interpreted to be the phosphorescences of the EDA complexes. Furthermore, 2.5 ms (AT = 1 ms) after the excitation, the phosphorescence of BP itself was observed.

Emission spectra observed with CBA in mixed solvents of MTHF with AN, NMA, and DMA 2.5 μs after the irradiation of a laser pulse are shown in Fig. 2. As is clearly seen in this figure, the phosphorescence of the EDA complexes were observed for these systems, but the fluorescences of CBA and its ketyl radical and the phosphorescence of CBA were not observed.

The phosphorescences of the EDA complexes under consideration showed bimolecular decay at the initial stage. The population of a complex in the lowest triplet state, n, decreases with time according to the following equation:⁷⁾

$$dn/dt = -\alpha n - \beta n^2 \qquad (1)$$

Here α and β are the unimolecular and bimolecular decay constants, respectively, and the former was obtained from the single exponential decay parts of the decay curves observed later than 20 μs after the irradiation of a laser pulse. The integration of equation (1) gives

$$1/n = (\beta/\alpha + 1/n_0)\ \exp(\alpha t) - \beta/\alpha \qquad (2)$$

Here n_0 is the initial value of n.

Plots of 1/I vs exp(αt) are shown in Fig. 3 taking the CBA-NMA system as an example. Here I is the phosphorescence intensity at 480 nm and is reasonably assumed to be proportional to n. In this figure, plots (a) and (b) were obtained with and without a neutral density filter, respectively. As is indicated in Fig. 3, linear lines were obtained and their crossing points with the vertical axis, which represents $-\beta/\alpha$, are common to (a) and (b). The crossing point of the horizontal axis with line (a) or (b) corresponds to $n_0\beta/(n_0\beta + \alpha)$, the ratio of the bimolecular decay to the total decay at the initial time and is equal to 1 for plots (b). This indicates that the phosphorescence decay is almost completely due to the bimolecular quenching at the initial time for the excitation without the neutral density filter. The situation is the same for the other complexes. Table 1 shows the peak frequencies of the phosphorescence spectra observed with the complexes and acceptors and their α values.

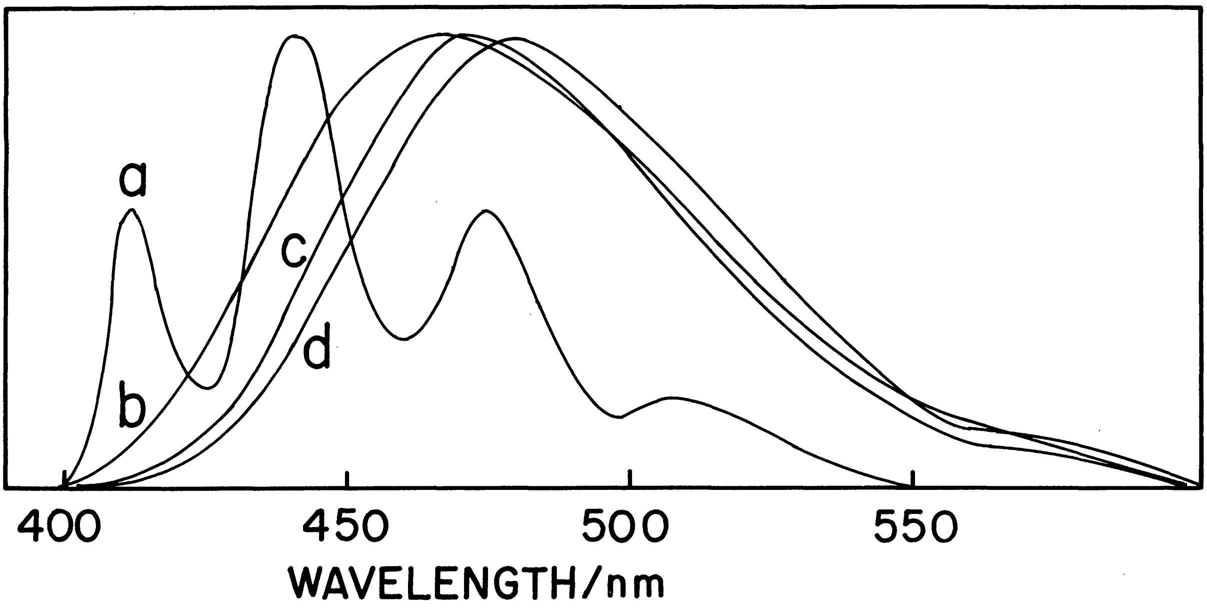

Fig. 1. Time-resolved phosphorescence spectra observed for BP and its complexes with anilines at 77 K 2.5 μs after the excitation.
a: BP in MTHF, b: BP-AN in MTHF, c: BP-NMA in MTHF, d: BP-DMA in MTHF

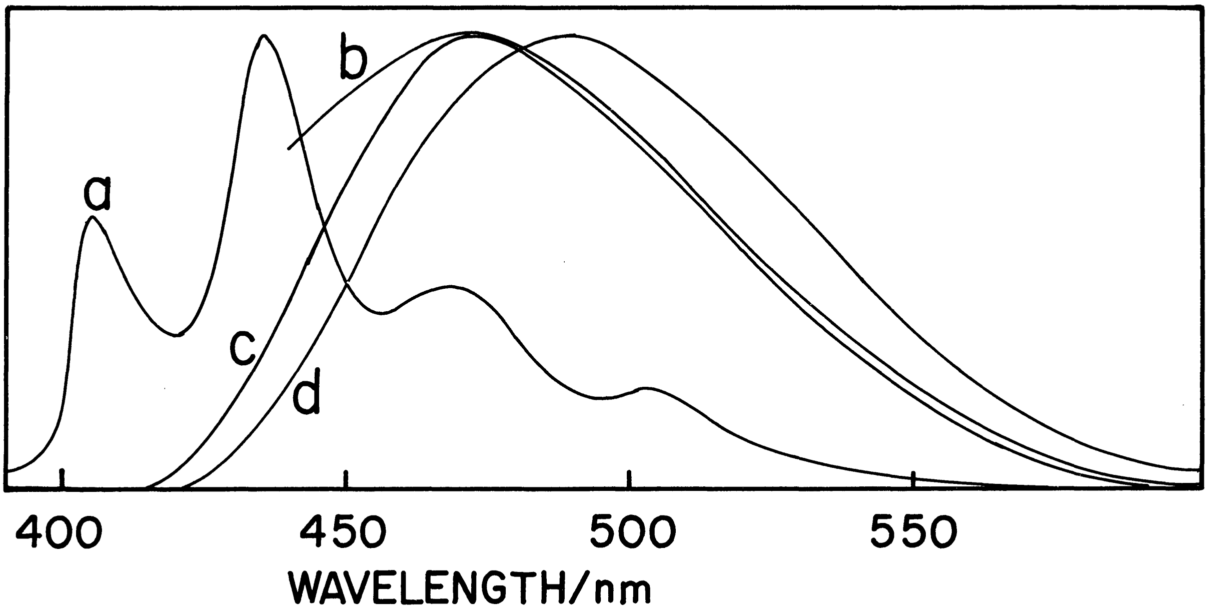

Fig. 2. Time-resolved phosphorescence spectra observed for CBA and its complexes with anilines at 77 K 2.5 μs after the excitation.
a: CBA in MTHF, b: CBA-AN in MTHF, c: CBA-NMA in MTHF, d: CBA-DMA in MTHF

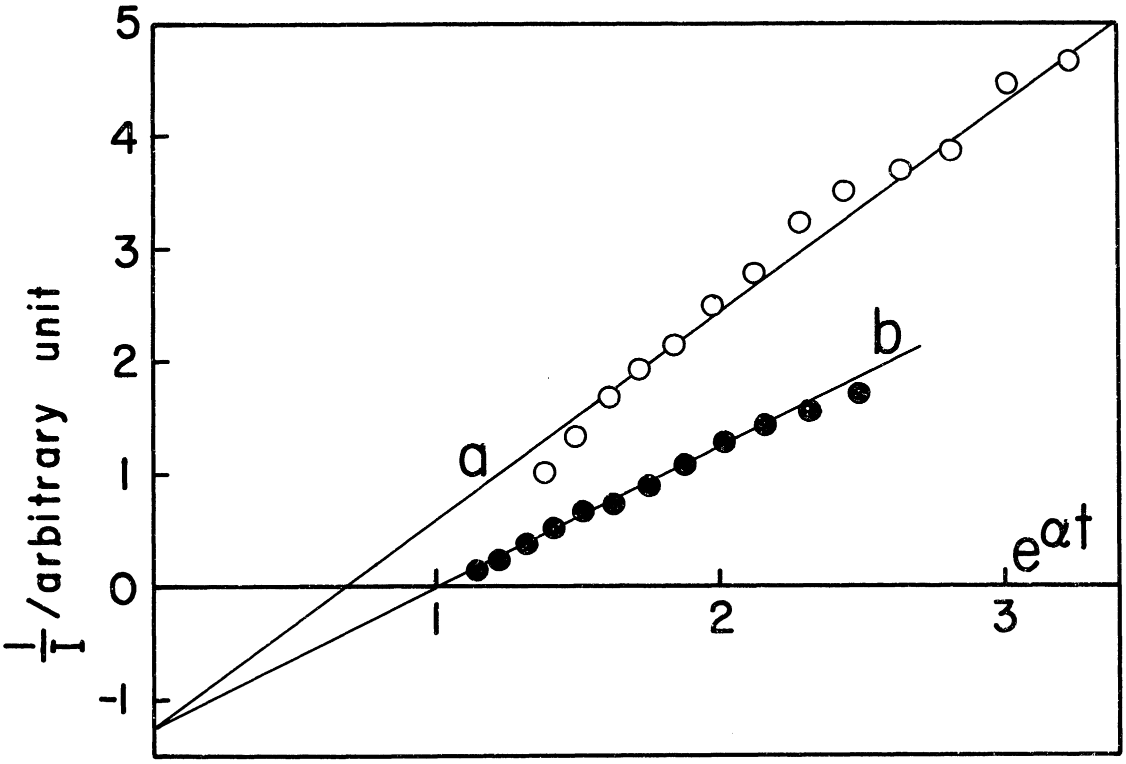

Fig. 3. Plots of 1/I vs exp(αt) for the complex phosphorescence at 480 nm for the CBA-NMA system in MTHF at 77 K : (a) with and (b) without a neutral density filter.

TABLE 1. PHOSPHORESCENCE PEAK FREQUENCIES (P) AND UNIMOLECULAR DECAY CONSTANTS (α_C AND α_A) OBTAINED FOR COMPLEXES AND ACCEPTORS AND IONIZATION POTENTIALS OF DONORS (I_p)

	P 10^3 cm^{-1}	α_C 10^4 s^{-1}	α_A 10^2 s^{-1}	I_p a) eV
BP	24.27 b)	-	2.1	-
BP-AN	21.4	c)	2.5	8.05
BP-NMA	21.2	1.1	2.6	7.73
BP-DMA	20.9	1.1	2.4	7.37
CBA	24.66 b)	-	2.0	-
CBA-AN	21.3	c)	c)	8.05
CBA-NMA	21.2	2.0	c)	7.73
CBA-DMA	20.4	2.5	c)	7.35

a) Ref. (8) b) 0-0 band

c) Phosphorescence was so weak that α was not obtained.

Arimitsu and Tsubomura[5)] showed that the phosphorescence lifetimes of the BP complexes with aromatic amines are about 10 μs. We found that bimolecular quenching is predominant for the BP and CBA complexes with anilines and that their unimolecular decay constants are about 10^4 s^{-1} and 2×10^4 s^{-1} for BP and CBA complexes, respectively. The bimolecular quenching of phosphorescence occurs for the BP[9)] and p-dibromobenzene[10)] crystals. Concerning the complexes under consideration, however, very efficient bimolecular quenching takes place in glassy solution. The reason for this is now under investigation.

The observed phosphorescence peaks and their unimolecular decay constants of the complexes are almost independent of the ionization potentials of donor molecules. Therefore the phosphorescent states of the complexes may be mainly contributed by the zero-order locally excited triplet states of the acceptors, as was pointed out by Arimitsu and Tsubomura[5)] for the BP complexes.

The ketyl radical formation was observed for the BP complexes, but it was not observed for the CBA ones. This difference may be explained by the fact that the lowest triplet states of BP and CBA in MTHF are considered to be of the nπ* and ππ* types,[11-13)] respectively and the former state is efficient for the hydrogen abstracting reaction.[14)]

We have found that a number of aromatic carbonyls including benzaldehyde, biacetyl, and benzil form EDA complexes with anilines.

References

1) S. Iwata, J. Tanaka, and S. Nagakura, J. Chem. Phys., 47, 2203 (1967).
2) H. Hayashi, S. Iwata, and S. Nagakura, J. Chem. Phys., 50, 993 (1969).
3) H. Hayashi and S. Nagakura, Mol. Phys., 19, 45 (1970).
4) S. Matsumoto, S. Nagakura, S. Iwata, J. Nakamura, Chem. Phys. Lett., 13, 463 (1972).
5) S. Arimitsu and H. Tsubomura, Bull. Chem. Soc. Japan, 45, 1357 (1972).
6) R. E. Brown, L. A. Singer, and J. H. Parks, Chem. Phys. Lett., 14, 193 (1972).
7) M. Yagai, S. Nagakura, and H. Hayashi, Chem. Phys. Lett., 18, 272 (1973).
8) D. W. Turner, "Molecular Photoelectron Spectroscopy", John Wiley and Sons, Inc., London (1970) p.300.
9) R. A. Keller, J. Chem. Phys., 42, 4050 (1965); A. N. Faidysh and A. S. Gaevsky, Mol. Cryst. and Liq. Cryst., 19, 13 (1972).
10) One of the authors (N. Hirota) found recently that a bimolecular quenching of phosphorescence occurrs for the p-dibromobenzene single crystal at 77 K.
11) S. Dym and R. M. Hochstrasser, J. Chem. Phys., 51, 2458 (1969).
12) H. Hayashi and S. Nagakura, Mol. Phys., 24, 801 (1972).
13) H. Hayashi and S. Nagakura, Chem. Phys. Lett., 18, 63 (1973).
14) P. J. Wagner and G. S. Hammond, Advan. Photochem., 5, 99 (1968); N. C. Yang and R. L. Dusenberg, J. Amer. Chem. Soc., 90, 5899 (1968).

(Received July 6, 1973)