

THE PHOTO-INDUCED REDUCTION OF HALOBENZENES WITH DIMETHYLANILINE;  
EVIDENCES FOR INTERMEDIACY OF EXCITED CHARGE-TRANSFER COMPLEX

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In the previous papers,<sup>1)</sup> we reported the photo-induced electron transfer reactions from dimethylaniline (D) to anilinium salts and suggested intermediacy of excited charge-transfer complexes (ex-CTs) between the lowest excited singlet D ( $D^S$ ) and the ground state anilinium salts. On the formation of the ex-CTs, however, definitive evidences could not be obtained on account of insolubility of anilinium salts in non-polar solvents. In an attempt to obtain unambiguous evidences on the formation and intermediacy of ex-CT in photo-induced electron transfer reactions, we chose halobenzenes as electron acceptors instead of anilinium salts. During the course of the investigation, Latowski published the photo-reactions of aromatic amines with aromatic halides and suggested intermediacy of ex-CTs without confirmative evidences.<sup>2)</sup> In the present paper, we wish to report the photochemical reactions of D with halobenzenes (Ph-X:  $I_a$ , X = Cl;  $I_b$ , X = Br;  $I_c$ , X = I) and indicate spectroscopic and kinetic evidences for intermediacy of ex-CTs between  $D^S$  and the ground state halobenzenes ( $I_a$  and  $I_b$ ).

Irradiation of methanolic solutions of D containing  $I_{a-c}$  in the presence of triethylamine\* through a Pyrex filter by a high pressure mercury arc gave triethylamine hydrohalides in quantitative yields along with benzene, diphenyl, N-methylaniline, *o*- and *p*-dimethylaminodiphenyls. It should be noted that

\* In the absence of triethylamine, the photo-reactions were complicated by the formation of D hydrohalides, since D photochemically reacted with D hydrohalides.<sup>1)</sup>

the products other than triethylamine hydrohalides were the same as those obtained from the photo-reactions of D with trimethylphenylammonium halides.<sup>1)</sup>

#### Spectroscopic Evidences

The fluorescence spectrum of D in benzene exhibited an emission maximum at 328 nm. On addition of  $I_a$  ( $I_b$ ) into the benzene solution of D, fluorescence from D was quenched with tailing of the spectrum. When  $I_a$  ( $I_b$ ) was used as solvent, a new weak emission band appeared at 375 nm (412 nm) with total quenching of the fluorescence. On the other hand, methanolic solutions showed only quenching of the fluorescence with  $I_a$  and  $I_b$ , and there were no indications of new emission and of change in the shape of the spectrum. Quenching constants were dependent on dielectric constants of solvents. For example, the fluorescence in methanol was about ten times as quenched as that in benzene with  $I_a$  or  $I_b$ . Dynamic character of the fluorescence-quenching was confirmed by the observation that the uv-absorption spectra of D in  $I_a$  and  $I_b$  did not show any essential difference from those in benzene except for only 2-3 nm bathochromic shift. These observations (appearance of new emission maxima, dynamic property of the fluorescence-quenching and dependency of the fluorescence-quenching on solvent polarity) afford strong evidences for the formation of ex-CTs between  $D^{\ominus}$  and the ground state halobenzenes ( $I_a$  and  $I_b$ ).

With some other aromatic amines such as aniline, N,N-dimethyl-*p*-anisidine, N,N-dimethyl-*m*- and *p*-toluidines, new emissions assigned to ex-CTs could be also observed.

#### Kinetic Evidences

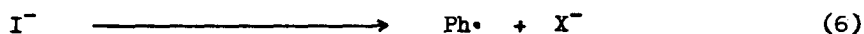
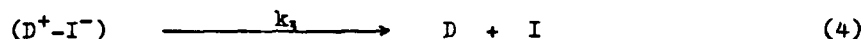
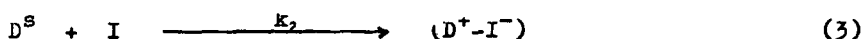
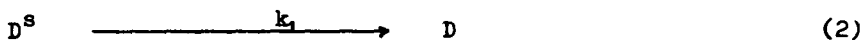
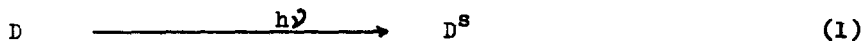
The fluorescence-quenching with  $I_{a-c}$  in methanol strictly obeyed Stern-Volmer relation, from which the quenching constants were determined (Table). Using potassium ferrioxalate actinometer,<sup>3)</sup> the quantum yields for the formation of halide anions from the photo-reactions of D with  $I_{a-c}$  in methanol at 313 nm were determined. Quantitative analyses of chloride and bromide anions were titrimetrically carried out by the method of Volhard,<sup>4)</sup> and that of iodide anion was done by the Jamieson's method.<sup>5)</sup> Reciprocals of the quantum yields were linearly changed against those of concentration of  $I_{a-c}$ . From the slopes and the intercepts of the straight lines, there were obtained the values of

rate-constant ratios (Table).

		Table			Fluorescence-quenching constants		
		Quantum yield measurements					
		$I_a$	$I_b$	$I_c$	$I_a$	$I_b$	$I_c$
$k_2/k_1$	5.7	15.8	62.5	$k_2/k_1$	5.2	13.6	42.0.
$k_3/k_4$	1.0	0.8	0.25				

### Discussion

The results allowed us to propose the following processes 1 - 6, from which the rate equation 7 and Stern-Volmer expression 8 were derived.



$$1/\phi = (1 + \frac{k_1}{k_2(I)})(1 + \frac{k_3}{k_4}) \quad (7)$$

$$F_0/F_q = 1 + (k_2/k_1)(I) \quad (8)$$

The process 2 represents all of the unimolecular decay of  $D^S$  involving unimolecular decomposition, intersystem-crossing, radiative and non-radiative decay.

It is well known that spectroscopic behavior of ex-CTs is dependent on solvents used.<sup>6)</sup> In polar solvents, emission from ex-CTs cannot be observed and fluorescence from fluorescers is only quenched, even though new emission appears in non-polar solvents. Moreover, the quenching constants are highly dependent on dielectric constants of solvents. Therefore, the fluorescence-quenching with  $I_a$  and  $I_b$  can be ascribed to the formation of ex-CTs. For mechanistic elucidation, it is important to note that the values of  $k_2/k_1$  obtained from the quantum yield measurements are in good accordance with the quenching constants which represent  $k_2/k_1$ . This can be easily interpreted by assuming that the same mechanism is operative both in the photo-reactions and in the fluorescence-quenching. On the basis of the results obtained and the above discussion, it is safely concluded that ex-CTs are the intermediates of the photo-induced reduc-

tion of  $I_a$  and  $I_b$  by D. The products also reflect charge-transfer character of the photo-reactions.

Mechanistic details including the photo-reduction of  $I_c$  by D will be discussed in a separate paper.

#### References

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