

$\bar{H}_W'$  = modified partial molar enthalpy of water (Equation 4), J/kmol  
 $N_N^L$  = moles of liquid ammonia, kmol  
 $N_N^V$  = moles of vapor ammonia, kmol  
 $N_W^L$  = moles of liquid water, kmol  
 $P$  = total pressure, N/m<sup>2</sup>  
 $x_N$  = mass fraction of ammonia in ammonia-water aqueous solution

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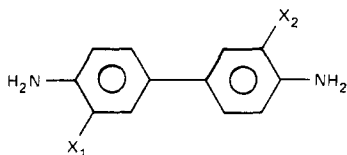
## Photodegradation of 3,3'-Dichlorobenzidine

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■ 3,3'-Dichlorobenzidine (DCB) is very rapidly photodegraded in aqueous solution to give monochlorobenzidine (MCB), benzidine, and a number of brightly colored water-insoluble materials. Disappearance quantum yields for DCB and MCB are high, whereas that for benzidine is much lower. Transients are generated upon photolysis of DCB in acidic solutions or on treatment of DCB with chlorine water. The photolability of DCB is markedly lower in nonaqueous solvents, and the mechanism of dechlorination does not appear to involve simple carbon-chlorine bond homolysis.

DCB (1), a widely used pigment intermediate, is known to induce cancer in animals (1), and is regarded by the Occupational Health and Safety Administration as being hazardous to human health (2). The material may be introduced to the aquatic environment through effluent discharge from manufacturing plants for the chemical and also from DCB pigment wastes containing unreacted DCB. Consequently, adverse health effects might result from the contamination of drinking water supplies or through bioaccumulation in fish which are subsequently used as food. In a preliminary study on several aspects of the environmental degradation of DCB, we found the material to be extremely photolabile (3). We now report more complete data on the photodegradation of DCB and 3-chlorobenzidine (2), and assess the environmental importance of these photoprocesses.



1.  $X_1 = X_2 = \text{Cl}$
2.  $X_1 = \text{Cl}, X_2 = \text{H}$
3.  $X_1 = X_2 = \text{H}$

#### Experimental

DCB, as the dihydrochloride, was kindly provided by the Upjohn Company, and MCB was synthesized according to Branch et al. (4). <sup>14</sup>C-labeled DCB was obtained from the California Bionuclear Corp.

Prior to the initiation of our studies, the maximum water solubility of DCB-2HCl was measured spectrophotometrically in a buffered solution of pH 6.9 and was found to be 3.99 ppm at 22°C. In this medium,  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ) for DCB-2HCl occurs at 282 (28 200) and at 211 nm (57 800).

Quantification of the benzidines was carried out on a Waters M6000A HPLC utilizing a  $\mu\text{C}_{18}$  Bondapack column and a 1:1 mixture of acetonitrile and 5% aqueous acetic acid as the mobile phase. Under these conditions, the retention volumes of DCB, MCB, and benzidine were 11.8, 4.7, and 3.7 mL, respectively. Increase of the acetonitrile content of the mobile phase led to a lower retention volume for DCB and an increase in that for MCB. All samples were diluted with acetonitrile before filtration and introduction to the HPLC, in order to minimize sample adsorption onto the filter.

The identity of the photoproducts was confirmed by GC, using an HP 5730A FID instrument and a 10% UCW 932 on Chromosorb W column maintained at 225 °C, and by mass spectrometry.

Preparative photolyses were conducted in a 1-L immersion well type photoreactor equipped with a 450-W high-pressure Hanovia lamp fitted with a Pyrex filter. Quantum yields were determined in a Rayonet RMR-400 merry-go-round photoreactor at 2537 or 3000 Å.

#### Results and Discussion

**Preparative Photolysis.** Irradiation of aqueous solutions of DCB results in a hypsochromic shift of the UV absorption band of the substrate, and is accompanied by about a 50% decrease in intensity. Extraction of the photolyzed solution by ether after basification, and analysis of the ether concentrate by HPLC, GC, and mass spectrometry revealed the presence of benzidine (3) and MCB. In a separate experiment, aliquots were withdrawn periodically and analyzed for DCB, MCB, and benzidine by HPLC. These results are listed in Table I and suggest that DCB is, in part, degraded sequentially to MCB and benzidine. In addition, DCB is also photodegraded to a number of relatively water-insoluble products which adhere to the walls of the photoreactors. These materials are ether soluble, and TLC (silica gel, ether-hexane, 2:1) of an ethereal concentrate resolved the products into more than five brightly colored components. The extent of conversion to these water-insoluble materials was determined through the photolysis of <sup>14</sup>C-labeled DCB. Aliquots of the aqueous solution were counted periodically, and after 30 min,

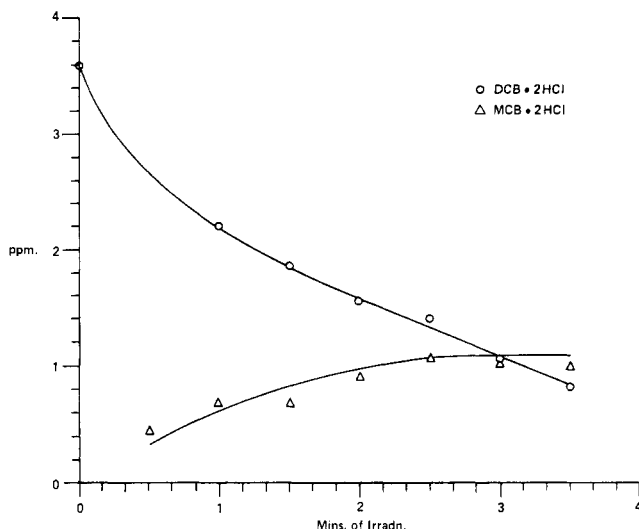


Figure 1. Irradiation of DCB in natural sunlight

Table I. Photolysis of DCB (1)<sup>a</sup>

min of irradi.	DCB·2HCl, <sup>b</sup> ppm	MCB·2HCl, <sup>b</sup> ppm	benzidine·2HCl, <sup>b</sup> ppm
0	0.64	0	
1	0.60	0.034	
2	0.56	0.060	
3	0.42	0.068	
4	0.24	0.114	
5	0.078	0.044	0.044
10		0.044	0.072
15			0.086
45		0.034	0.072

<sup>a</sup> Irradiated with light from a Hanovia 450-W high-pressure lamp filtered through Pyrex. <sup>b</sup> Average of two determinations. The "2HCl" represents the dihydrochloride.

63% of the counts were observed to be adsorbed on the surface of the reactor.

It is evident that very little DCB, MCB, or benzidine remains after 15 min, and the residual spectral absorption probably derives from partial solution of the unidentified products deposited on the reactor walls. Furthermore, less than 40% of the initial substrate gives rise to this absorption, and, consequently, the extinction coefficient is >25 000. Hence, it is probable that these products are dimers or higher analogues of DCB and/or its photoproducts.

**Irradiation in Natural Sunlight.** Five-milliliter aliquots of an aqueous solution of DCB were exposed to noonday sunlight in identical quartz tubes. Tubes were withdrawn every 30 s, covered in foil, and analyzed by HPLC. The results illustrated in Figure 1 confirm the expected photolability of DCB. No benzidine was observed in this experiment, but its presence was detected in prolonged exposures (>20 min) of DCB to sunlight.

**Measurement of Quantum Yields.** The disappearance quantum yields of benzidine and MCB were measured with respect to a ferrioxalate actinometer (5) at 2537 and 3000 Å. The wavelength dependence of the quantum yields was minimal, and the results obtained at 3000 Å are reported in Table II. The limited solubility of DCB in water made direct determination of the quantum yield at 3000 Å difficult, and, consequently, the measurement was made with respect to MCB at 2537 Å. The high quantum yields for DCB and MCB confirm the photolability of these substrates, whereas the relatively low value for benzidine is in keeping with Metcalf's

Table II. Disappearance Quantum Yields for DCB, MCB, and Benzidine

	$\phi$	wavelength, Å	pH
benzidine	0.012	2537, 3000	7.0, 8.2
MCB	0.70	2537, 3000	7.0, 8.2
DCB	0.43	2537	6.7, 8.1

Table III. pH Dependence of the Rate of Disappearance of DCB

pH	$\phi_{rel}(\text{DCB})$	$\phi_{rel}(\text{MCB})^a$
1.96	1.0	1.0
3.96	0.71	0.73
6.01	0.42	0.49
8.28	0.50	0.56

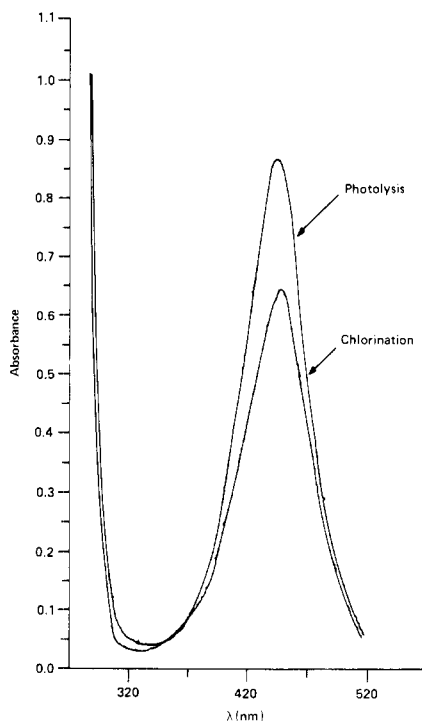
<sup>a</sup> Appearance quantum yield.

finding that the disappearance half-life of benzidine in methanol at 254 nm is about 2 h (6). A number of experiments were also conducted to determine the pH dependence of the quantum yield for DCB. These results, presented in Table III, indicate that the rate of degradation has a slight dependency on pH. The appearance quantum yields for MCB, although less accurate due to the reactivity of this material, also exhibit the same dependency.

Interestingly, in solutions of low pH, brief irradiation of DCB results in a transient green solution whose color decays in the dark. This phenomenon also occurs with MCB, but is absent for benzidine. UV spectra recorded immediately after irradiation show that the absorption maxima for the transients derived from DCB and MCB occur at 425 and 435 nm, respectively. The decay kinetics of the transients are of the first order, are independent of the irradiation time, slightly dependent upon initial substrate concentration, and have a half-life of approximately 7 min in 1 N HCl at 22 °C.

While further work is required to identify the reaction under observation, the position of the absorption maximum of the transient(s) would seem to implicate a diphenoquinone-diimine type of intermediate which could lead to the colored products obtained on prolonged photolysis. These intermediates would arise from oxidation of DCB, and a number of experiments were carried out to identify the oxidant. The involvement of dissolved oxygen was ruled out since the transients could be generated during photolysis under oxygen-free argon. We reasoned that chlorine (atomic or positively charged) produced during the reduction of DCB and MCB could serve as an oxidizing agent and consequently an experiment was carried out to determine whether transients could be formed during the reaction of DCB with chlorine. A solution of DCB in 2 N HCl was divided into parts. One portion was photolyzed for 30 s, and the absorption spectrum of the transient was recorded. A drop of chlorine water was added to the second portion, and the spectrum of the resulting solution was obtained. These spectra, illustrated in Figure 2, clearly indicate that the same (or similar) transient is involved in both processes.

**Photolysis in Organic Solvents.** To determine the photoreactivity of DCB in solvents other than water, a number of preliminary experiments were carried out in hexane, 2-propanol, and methanol. Irradiation of these solutions, under approximately the same conditions under which disappearance of DCB in aqueous solution is complete, showed that virtually no degradation has occurred. For example, irradiation of a 15-ppm solution of DCB·2HCl in 2-propanol at 2537



**Figure 2.** Spectra of transients generated from the photolysis and chlorination of DCB

Å for 1 h led to 28% degradation. Under similar conditions, a 4-ppm aqueous solution of DCB is decomposed to an extent of 42% in 0.3 min. It is, therefore, evident that photodegradation of DCB in water proceeds through a mechanism different from that in organic solvents.

**Mechanistic Considerations.** Recent studies on aromatic dehalogenation in aprotic solvents have shown that the mechanism involves homolysis of the carbon-chlorine bond, followed by hydrogen abstraction from solvent (7-9). In aqueous media, irradiation of chloro aromatics frequently leads to photosubstituted products (10-12), presumably through the nucleophilic photosubstitution mechanism advocated by Havinga and Cornelisse (13). While most of the photochemistry of chloro aromatics may be rationalized in terms of these two mechanisms, examples do exist where other pathways must be considered. Nordblum and Miller (14) observed that irradiation of 4,4'-dichlorobiphenyl in ether containing 2% trifluoroacetic acid gave 4-chlorobiphenyl. In hexane, cyclohexane, acetonitrile, or pure ether, complex product mixtures were obtained. Furthermore, the reduction was accompanied by a kinetic isotope effect, as determined by the use of deuterated trifluoroacetic acid. Simple bond homolysis does not explain the acid catalysis or the large isotope effect.

The photoreduction of DCB would also appear to involve a mechanism different from simple bond homolysis. The relative inertness of the material in 2-propanol or hexane, both of these solvents being appreciably better hydrogen atom donors than water, implies the specific involvement of water in the transition state. While the limited scope of our work does not allow further mechanistic speculation at present, it appears that proton transfer is involved and that the dechlorination process might well proceed through an ionic pathway involving the loss of chloronium ion from the excited DCB molecule. We are presently investigating the mechanism of the reaction in somewhat greater detail.

### Conclusions

DCB is very rapidly photodegraded under environmental conditions through reductive dechlorination and other processes. The reaction is considerably slower in organic solvents and the mechanism of dechlorination does not involve simple carbon-chlorine bond homolysis. From an environmental standpoint, the action of sunlight on DCB will lead to its degradation but not necessarily to its detoxification since benzidine, a relatively photostable carcinogen, is one of the products. Furthermore, the inertness of DCB in hydrocarbon solvents coupled with its high octanol/water partition coefficient (15) might lead to enhanced stability in water contaminated with hydrocarbons.

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