PHOTODECHLORINATION OF 3,3′-DICHLOROBENZIDINE IN WATER

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(Received 11 April 2001; Accepted 14 September 2001)

Abstract—Laboratory experiments have been conducted to elucidate the photochemical behavior of 3,3′-dichlorobenzidine (DCB) and its congeners in aquatic systems. Photodechlorination of DCB was observed in aqueous samples that were irradiated with monochromatic radiation from a variable-wavelength laser at several wavelengths in the range 300 nm ≤ λ ≤ 360 nm. Analytical measurements performed by high-performance liquid chromatography (HPLC) and Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry revealed that 3-chlorobenzidine (MCB) was produced as a transient intermediate in the photodechlorination process, with subsequent photodechlorination to yield benzidine as a stable photoproduct. Data obtained from these measurements also suggest the existence of other (unidentified) reaction pathways and products. The time-course measurements of chlorobenzidine congener concentrations and irradiance history were combined with a simple reaction model to develop estimates of reaction kinetics. Model predictions were consistent with results obtained for all wavelengths investigated.

Keywords—Photodechlorination 3,3′-Dichlorobenzidine Benzidine Laser

INTRODUCTION

A suspected human carcinogen, 3,3′-dichlorobenzidine (DCB), is used as an intermediate in dye manufacturing processes. The carcinogenicity of DCB toward humans is believed to be attributable to dechlorination in the digestive system [1]. This result in the formation of its fully dechlorinated congeners, benzidine, which has been found to be carcinogenic in the human bladder [2].

The fate and transport of hydrophobic organic compounds, such as DCB in the aqueous environment, can be affected by many processes. We have previously reported on the equilibrium partitioning behavior of DCB and benzidine in natural sediments [3,4]. Microbially mediated reductive dechlorination of DCB to benzidine in lake sediments has also been discussed [4]. A transient intermediate, 3-chlorobenzidine (MCB), was found in the microbial degradation process. However, this process was found to be relatively slow (i.e., reaction half-life on the order of months).

The distribution of DCB and its congeners in the environment is also likely to be affected by photochemical reactions. This behavior has been previously studied by Banerjee et al. [5] by irradiating DCB in water using a photoreactor equipped with a 450-W high-pressure Hanovia lamp (a Pyrex filter, [Victoria, BC, Canada] was used to minimize sample exposure to radiation with λ ≤ 300 nm). The photoreactor experiments were reported to result in rapid dechlorination of DCB to MCB, accompanied by the formation of unidentified, brightly colored, low-solubility compounds. Banerjee et al. [5] also conducted experiments involving exposure of DCB to solar radiation. They concluded that no benzidine was formed under conditions of natural solar irradiation. However, their experiments were limited to exposure times of approximately 20 min.

The study by Banerjee et al. [5] implied that (aqueous) DCB would be photostable in most surface waters. However, the results of an extensive field sampling program within a freshwater estuary known to be contaminated with DCB suggested otherwise [6]. As part of this sampling program, water samples were collected from multiple sites within Lake Macatawa (Holland, MI, USA); at each location, samples were taken from near-surface (depth ≤ 0.1 m), middepth, and near the sediment–water interface (depth 3–7 m). A consistent bias toward less chlorinated chlorobenzidine congeners was evident in near-surface samples. In particular, near-surface samples showed benzidine concentrations of as high as 9.4 μg/L; in most of these samples, DCB was present at concentrations below the limit of detection. Samples collected at middepth and near the sediment–water interface were found to contain DCB at concentrations as high as 26.8 μg/L. For perspective, the U.S. Environmental Protection Agency (U.S. EPA) water-quality criteria for benzidine and DCB (based on one in a million increase in cancer risk over the lifetime of an exposed individual) are 0.12 ng/L and 0.010 μg/L, respectively [7]. Since no source of MCB or benzidine is known or suspected to exist in Lake Macatawa, these findings imply that a near-surface process exists that causes relatively rapid dechlorination of DCB. A logical candidate would be direct or indirect photodechlorination [8,9], since the previously described microbially mediated process is likely to be restricted to the anaerobic sediments that characterize the lake bottom [4].

Therefore, a series of experiments was initiated to examine the photochemical behavior of DCB in aqueous solutions. In the work reported herein, well-characterized, monochromatic radiation from a variable-wavelength laser system was imposed on aqueous solutions of DCB, and reaction products were characterized and quantified. All experiments were conducted using radiation intensities and wavelengths comparable to tropospheric solar radiation.
Materials and methods

Solvents and reagents

Acetonitrile, acetic acid, and sodium acetate were HPLC grade and were supplied by Fisher Scientific (Pittsburgh, PA, USA). Anhydrous diethyl ether was obtained from Mallinkrodt Baker (Philipsburg, NJ, USA). Benzidine (Sigma, St. Louis, MO, USA) and DCB (Chem Services, West Chester, PA, USA) were used without further purification. The purities of benzidine (95%) and DCB (99%) were verified using HPLC with ultraviolet-visible detection; confirmatory analyses were conducted with a Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer. Selected properties of DCB and benzidine are given in Table 1. Rhodamine 610, chlorine, DCM, and LDS 698 (Exciton, Dayton, OH, USA) were used as the laser dyes.

Laser experiments

A Nd:Yag-pumped dye laser (Continuum YG61/ND60, Santa Clara, CA, USA), operating at 10 Hz, was used as the source of radiation (Fig. 1). Monochromatic radiation was applied to aqueous DCB solutions (0.57±1.61 mg/L; pH 7.0) without a cosolvent at wavelengths ranging from 300 to 400 nm at 10 nm increments. Table 2 demonstrates the excitation wavelengths in order to minimize intensity variations in the direction of light propagation. The radiation intensity imposed on the samples was measured by placing 5- to 8-mm circular apertures in front of an Ophir Optronics AN-203A-P-CAL power meter (Danvers, MA, USA), and the light intensity was maintained during the experiments between 1.3 and 6.9 mW/cm² (see Table 2). This intensity was chosen to mimic the intensity of solar radiation in the range 300 nm ≤ λ ≤ 400 nm at sea level for a zenith angle of 0° (~4 mW/cm²) [11]. Variation in the intensity of radiation imposed across the face of the sample was measured with this arrangement and was found to be less than 15%.

HPLC analysis

Aqueous samples from the photodegradation measurements were analyzed using reverse-phase HPLC with an ultraviolet-visible detector operated at λ = 285 nm or a photodiode array detector operated at λ = 285 nm and were scanned from 200 to 600 nm at 5.2-nm intervals. The former HPLC system was a Shimadzu Scientific Instruments (Columbia, MD, USA) automated gradient system (LC-10AD pump, FCV-10AL solvent delivery system, SCL-10A system controller, SIL-10A auto injector) equipped with an ultraviolet-visible detector (Shimadzu SPD-10A) and a reverse-phase LC-ABZ+ column (4.6-mm i.d. × 15 cm) obtained from Supelco (Bellefonte, PA, USA). The latter HPLC system contained a Waters (Milford, MA, USA) automated multisolvent delivery system (600E pump, 600E multisolvent delivery system, 600 system controller, 717 plus auto injector) equipped with a photodiode array detector (Waters 991) and the same LC-ABZ+ column. The analysis was performed with isocratic flow that consisted of 40/60, 45/55, or 50/50 volume/volume (v/v) mixtures of acetonitrile and 100 mM acetic buffer (pH 4.7) made of sodium acetate, glacial acetic acid, and 40% water. Solvent was delivered to the system at approximately 1.5 ml/min. The injection volume was 10 μL, and the injection solvent was methanol/water 70/30 v/v solution. The 45/55 v/v solvent ratio gave retention times (tR) of 8.2 and 2.6 min for DCB and benzidine, respectively. The average chromatographic responses resulting from at least two injections of each sample were used to estimate sample concentration by comparison with a calibration curve developed using standards consisting of known amounts of DCB and benzidine dissolved in methanol. The MCB was not commercially available and is difficult to synthesize due to its inherent instability. Therefore, no standard

Table 1. Selected properties of dichlorobenzidine (DCB) and benzidine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Molecular weight (g/mol)</th>
<th>S, b (mg/L)</th>
<th>pK_{a,1}</th>
<th>pK_{a,2}</th>
<th>Log K_{ow}</th>
<th>Molecular ions (mL/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>C12H10Cl2N2</td>
<td>253.13</td>
<td>3.99</td>
<td>1.6c</td>
<td>3.2c</td>
<td>3.5c</td>
<td>252, 254, 256</td>
</tr>
<tr>
<td>Benzidine</td>
<td>C12H12N2</td>
<td>184.23</td>
<td>400</td>
<td>3.3b</td>
<td>4.3b</td>
<td>1.34b</td>
<td>184</td>
</tr>
</tbody>
</table>

a S = water solubility; pK_{a,1} and pK_{a,2} = acid dissociation constants; K_{ow} = octanol–water partition coefficient.

b [15].
c [16].
d [17].
e [18].

Fig. 1. Schematic representation of the irradiation set-up.
was used for MCB. The possible product, MCB, present in the samples was identified based on ultraviolet and photodiode-array chromatograms obtained from the HPLC, with confirmation by FT-ICR mass spectroscopy. The elution time for MCB from the column was estimated from a linear relationship of log \( K_w \) and log \( k_t \) [4,12]. The concentration of MCB was estimated using the arithmetic mean of the DCB and benzidine response factors, approximately \( 1.8 \times 10^{-5} \) and \( 2.6 \times 10^{-5} \), respectively.

### Absorbance measurements

The optical behavior of aqueous solutions of DCB and benzidine was examined using a Perkin-Elmer Lambda 19 ultraviolet (UV)/visible/near infrared (NIR) scanning spectrophotometer (Shelton, CT, USA). Aqueous solutions containing known concentrations of DCB and benzidine were prepared gravimetrically and scanned for absorbance from 190 to 600 nm. Since MCB could not be purchased or synthesized in sufficiently high purity to allow development of a standard, it was not possible to directly measure its absorbance characteristics. For purposes of this investigation, the molar absorptivity coefficient for MCB (\( \varepsilon_{\text{MCB}} \)) was estimated as the arithmetic mean of \( \varepsilon_{\text{DCB}} \) and \( \varepsilon_{\text{benzidine}} \) at each of the wavelengths investigated. The UV response factors for benzidine and DCB (\( 1.6 \times 10^{-5} \) and \( 2.0 \times 10^{-5} \)) were quite close, suggesting that their adsorptive behavior at \( \lambda = 285 \) nm was attributable to a benzidine molecule more so than the substituted chlorine at this wavelength.

### FT-ICR analysis

A FT-ICR mass spectrometer was used for identification and confirmation of reaction products. The FT-ICR consisted of a dual-cell (two identical 2-inch cubic cells) aligned collinearly with the magnetic field produced by a 3 T-superconducting magnet operated at 2.2 T (Extrel) Fourier transform/mass spectrometry (FT/MS) (Finnigan FT/MS, Madison, WI, USA). The dual-cell instrument was differentially pumped to a nominal base pressure of \( \leq 1 \times 10^{-9} \) Torr with two Balzer’s (Hudson, NH, USA) turbomolecular pumps (330 L/s) and backed with Alcatel 2012 mechanical pumps (Hinghim, MA, USA) [13]. The instrument was controlled by an Odyssey data station (Finnigan FT/MS, Madison, WI, USA) based on a Sun computer. The diethyl ether extracts (1:2 diethyl ether:water) obtained from the photodegradation experiments were deposited onto a custom-built disk made from stainless steel. After solvent evaporation, the disk was introduced into the mass spectrometer on a solids probe and heated to approximately 100°C in order to desorb DCB, MCB, benzidine, and other photodegradation products. Molecular ions and ion fragments were generated by electron impact ionization (electron energy = 70 eV, electron current = 8 µA, electron beam time = 1 ms) in one side of the dual cell at a nominal pressure of approximately 0.2 to \( 1 \times 10^{-5} \) Torr. Samples were also analyzed by chemical ionization to generate protonated analyte molecules and avoid fragmentation. Methanol and anhydrous ammonia were used as chemical ionization reagents at nominal pressures ranging between 4 and \( 8 \times 10^{-5} \) Torr; sample pressure in these experiments was maintained at nominal pressures of 0.5 to \( 4 \times 10^{-8} \) Torr. For the chemical ionization measurements, chemical ionization time varied from 1 to 10 s; electron beam time ranged between 70 and 90 ms; electron energy ranged between 13 and 20 eV; and electron current ranged between 6 and 8 µA.

### RESULTS AND DISCUSSION

The parent compound, DCB, demonstrated rapid decay when exposed to laser radiation at wavelengths ranging from 300 to 360 nm. For all wavelengths investigated within this range, MCB was observed as an unstable intermediate, ultimately yielding benzidine as a stable photoproduct. In all cases, only a portion of the DCB initially present in the system was recovered as MCB and benzidine. These results suggest that DCB undergoes sequential photodechlorination when subjected to tropospheric solar radiation. However, DCB and MCB appear to also experience other photochemical reactions under these conditions of irradiation. However, the focus of this investigation was the photodechlorination of DCB and formation of less chlorinated congeners (e.g., MCB and benzidine).

As an example of the results of the photodegradation experiments, Figure 2 illustrates benzidine congener concentration (\( \mu \text{M} \)) as a function of the product of incident radiation intensity and exposure time for an experiment conducted at \( \lambda = 340 \) nm. Photodegradation of DCB in deionized water resulted in a steady decrease of parent compound concentration and the increase of photoproduct concentrations. As can be seen in Figure 2, MCB was created as a transient intermediate in this process. A steady increase in benzidine concentration was observed; benzidine was found to be a stable photoproduct (irradiation up to \( \sim 1 \) h). This finding was qualitatively similar to the previously reported biodegradation results [4], but the time scale for photodechlorination was on the order of minutes, as opposed to a time scale of months for microbially mediated reductive dechlorination.

A reaction scheme that explains the observed experimental results is illustrated in Figure 3. A mathematical model based on this scheme was developed to describe the rate of DCB

<table>
<thead>
<tr>
<th>Experiment ID (nm)</th>
<th>Sampling frequency (s)</th>
<th>Radiation intensity (mW/cm²)</th>
<th>Initial DCB concn. (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.0, 5.3, 10.5, 15.5, 20.6, 30.7, 40.4, 60.3, 142.2, 300.3, 602.7, 1,200.2, 1,664.5</td>
<td>1.3</td>
<td>2.57</td>
</tr>
<tr>
<td>310</td>
<td>0.0, 10.3, 20.0, 30.4, 60.2, 90.1, 120.7, 300.4, 900.3</td>
<td>3.2</td>
<td>6.35</td>
</tr>
<tr>
<td>320</td>
<td>0.0, 5.3, 14.3, 20.5, 40.5, 60.5, 120.8, 300.9, 900.8</td>
<td>3.7</td>
<td>2.63</td>
</tr>
<tr>
<td>330</td>
<td>0.0, 5.4, 10.3, 15.8, 20.4, 40.5, 60.5, 120.5, 344.5, 600.4, 1,200.4</td>
<td>2.1</td>
<td>2.63</td>
</tr>
<tr>
<td>340</td>
<td>0.0, 5.3, 10.1, 40.1, 50.2, 119.9, 179.2, 397.3, 548.1, 600.1, 909.9, 3,590.0</td>
<td>2.9</td>
<td>2.75</td>
</tr>
<tr>
<td>350</td>
<td>0.0, 5.7, 30.3, 45.1, 60.1, 89.9, 150.1, 300.2, 450.1, 650.6, 900.2</td>
<td>4.5</td>
<td>2.75</td>
</tr>
<tr>
<td>360</td>
<td>0.0, 5.7, 15.6, 30.0, 60.2, 120.3, 300.1, 600.2, 1,328.3, 2,602.0</td>
<td>6.9</td>
<td>2.25</td>
</tr>
</tbody>
</table>

\(^{a}\) DCB = 3,3'-dichlorobenzidine.
Photodechlorination of 3,3'-dichlorobenzidine in water

Fig. 3. Hypothesized reaction scheme for photolysis of 3,3'-dichlorobenzidine (DCB) and lower chlorinated congeners. The kinetics of each photochemical reaction are represented by their respective wavelength-specific quantum yields ($\Phi_{i,\lambda}$) and photochemical reaction rate constants ($k_{i,\lambda}$). A, DCB; B, 3-chlorobenzidine (MCB); C, benzidine.

The rate of photon absorbance within an irradiated reaction vessel is a function of the product of incident radiation intensity and exposure time for irradiation at $\lambda = 340$ nm. Lines represent fit of the model to measured chromatographic data for DCB (●), 3-chlorobenzidine (MCB; ■), and benzidine (▲) based on nonlinear regression.

Intensity x Time (mW/cm²)
Based on the schematic presented in Figure 3, the photo-kinetics of the processes observed in this research were represented as:

\[
\frac{d[DCB]}{dt} = -(k_{1a} + k_{2a})_0 [DCB] \\
\frac{d[MCB]}{dt} = k_{1a}I_0[DCB] - (k_{3a} + k_{4a})_0 [MCB] \\
\frac{d[B]}{dt} = k_{3a}I_0[MCB] \\
\frac{d[α]}{dt} = k_{2a}I_0[DCB] \\
\frac{d[β]}{dt} = k_{4a}I_0[MCB] \\
\]  
(12)

where \( [DCB]_0 \) = initial concentration of DCB in reactor (mole/L). This set of equations was solved based on a known value of \( [DCB]_0 \) and under the assumption that all photoproduct concentrations were zero at time \( t = 0 \).

For each wavelength investigated, the model resulting from Equations 7 through 12 was fit to the measured values of the time-dependent concentrations of DCB, MCB, and benzidine using nonlinear regression. From these regressions, estimates of the wavelength-dependent reaction rate constants were developed. The model was judged to provide a reasonable representation of the dynamic behavior of chlorobenzidine congeners at each wavelength (Fig. 2). In particular, the model was able to describe the rapid decrease in DCB concentration, the appearance of MCB as a transient intermediate, and the appearance of benzidine as a stable photoprodut.

Predictions of the photochemical behavior of DCB and MCB in the environment require knowledge of all four rate constants as a function of wavelength. Table 3 provides a detailed summary of these parameters, together with measured and estimated absorbance data for chlorobenzidines; rate constant estimates listed in this table were derived from model fits to the measured time-course chlorobenzidine congener concentrations. It should be noted that the lack of an MCB standard for these experiments represents a potentially important source of error in the estimation of MCB concentration from chromatographic data as well as in the estimation of \( k_3 \) and \( k_4 \). However, available experimental evidence supported the hypothesis that the optical and chromatographic behavior of MCB would be intermediate to those of DCB and benzidine.

A consistent decrease in the values of \( k_1 \) and \( k_4 \) was evident with increasing wavelength. The rate constants for both reactions (e.g., DCB degradation to MCB and MCB degradation to benzidine) were similar at each wavelength and declined to a value \( 2.2 \times 10^{-5} \) and \( 1.0 \times 10^{-5} \) cm²/mole for \( k_1 \) and \( k_4 \), respectively, at 360 nm. As described previously, the homolytic C-Cl bond dissociation energy in DCB is calculated to be 338 kJ/mole, which corresponds to photons of \( \lambda = 352.8 \) nm. The data presented in Table 3 can also be used to estimate disappearance rate constants (\( k_d \)) for DCB and MCB. For DCB, \( k_d \) is defined as the sum of \( k_1 \) and \( k_4 \), whereas for MCB, \( k_d \) is defined as \( k_3 \) + \( k_4 \).

To provide some information regarding the relative photochemical persistence of DCB in the water environment, the half-lives of DCB in water were estimated assuming a pseudo-first-order reaction (ln [DCB] vs time) based on the sampling times for each wavelength (Table 2). The rate constants, regression fits, and half-lives for DCB at each wavelength are summarized in Table 4. The 300- to 320-nm wavelengths had lower photochemical half-lives, ranging from approximately 145 to 279 s for each initial DCB concentration. A steady increase in photochemical half-life was observed with increasing wavelength (e.g., from 145.0 s to 3,013.0 s). The lower half-life for DCB at 310 nm (e.g., 145.0 s) might be explained by the lack of an MCB standard for these experiments.

**Table 3. Measured and estimated molar absorptivities and rate constants for chlorobenzidine congeners**

<table>
<thead>
<tr>
<th>Wave-length (nm)</th>
<th>Molar absorptivity (10⁶ cm²/mole)</th>
<th>Rate constant (cm²/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \varepsilon_{DCB} )</td>
<td>( \varepsilon_{MCB} )</td>
</tr>
<tr>
<td>300</td>
<td>15.30</td>
<td>13.40</td>
</tr>
<tr>
<td>310</td>
<td>10.00</td>
<td>7.90</td>
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<tr>
<td>320</td>
<td>5.00</td>
<td>3.51</td>
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<tr>
<td>330</td>
<td>2.19</td>
<td>1.34</td>
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<tr>
<td>340</td>
<td>1.09</td>
<td>0.59</td>
</tr>
<tr>
<td>350</td>
<td>0.69</td>
<td>0.35</td>
</tr>
<tr>
<td>360</td>
<td>0.61</td>
<td>0.31</td>
</tr>
</tbody>
</table>

\( a \) DCB = 3,3'-dichlorobenzidine; MCB = 3-chlorobenzidine; B = benzidine.

\( b \) The molar absorptivity coefficient for MCB (\( \varepsilon_{MCB} \)) was estimated as the arithmetic mean of \( \varepsilon_{DCB} \) and \( \varepsilon_{ benzidine } \) at each of the wavelengths investigated.

\[ v_{\lambda} = - \frac{d[R]}{dt} = k_{i\lambda}I_0[R] \]  
(6)

where \( k_{i\lambda} \) = reaction rate constant for the \( i \)th reaction (cm²/mJ).
Photodechlorination of 3,3′-dichlorobenzidine in water

The mass/205 peak existed as a photoproduct along with other (smaller) fragments, including carbon dioxide (CO₂).

The mass/205 indicates the presence of a photoproduct of molecular weight 205. The elemental composition of the compound at mass/205 was identified as C₁₃H₁₉NO using accurate mass analysis. The measured mass for this ion was 205.1456, whereas the theoretical mass for C₁₃H₁₉NO is 205.1467; the theoretical masses of 16 other ions with similar molecular weight were also examined and found to deviate more from the measured mass than C₁₃H₁₉NO. The ion of mass/205 was further examined by FT-ICR MS in a chemical ionization mode using CH₃OH as the reagent. Measurements were conducted using reaction times ranging from 200 ms to 2 s. As reaction times increased, the peak in question displayed a shift from mass/205 to mass/206, indicating protonation of the compound responsible for the mass/205. These measurements suggest that the mass/205 was attributable to a parent compound and not a fragment of another compound in the FT-ICR electron ionization analyses.

Acknowledgement—Financial support from Purdue Research Foundation and the Jenny and Antti Wihuri Foundation to M.C. Nyman was greatly appreciated. This work was also supported by grants from the National Science Foundation (CHE-9409644 and CAREER award BES-0093191). Special thanks to Joseph J. Ferra for assistance with laser and FT-ICR studies and Eileen Cruz for the hydrolysis experiments. Thanks are also extended to the reviewers for their helpful comments.

REFERENCES


Fig. 4. Electron impact ionization mass spectrum (70 eV) measured for a composite liquid sample irradiated at 300 nm for 5, 10, and 15 s. Ionized 3,3′-dichlorobenzidine (DCB) (m/z 252), 3-chlorobenzidine (MCB) (m/z 218), benzidine (m/z 184), and other photoproducts, including a compound of m/z 205, were identified in the sample.

with a higher initial DCB concentration at that specific wavelength.

Product confirmation

Confirmation of photodegradation product identities was achieved with the dual-cell FT-ICR mass spectrometer. The benefit of this approach, as compared with other mass spectrometric techniques, include the ability to introduce and analyze the entire sample with minimal sample preparation, thereby minimizing discrimination effects possibly caused by separation of the sample into its components. Furthermore, this instrument allows the accurate determination of the mass of all mixture components and has an extremely high mass resolution. The ability to operate the instrument in electron impact and chemical ionization modes also aids in the identification of reactants and products [14].

Figure 4 demonstrates a mass spectrum collected using 70 eV electron impact ionization of a composite liquid sample irradiated at 300 nm for 5, 10, and 15 s. A composite sample was used to ensure the presence of workable concentrations of all three chlorobenzidine congeners; chromatographic analyses had suggested that none of these irradiation periods would yield sufficient quantities of chlorobenzidine photoproducts independently. The mass spectrum provides evidence for the dechlorination of DCB (m/z 252) to MCB (m/z 218) and benzidine (m/z 184) as well as the formation of other photoprod...


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