

Liquid chromatographic aqueous product characterization of high-energy electron beam irradiated 2-chlorobiphenyl solutions

Nicholas J. Drenzek ^{a,1}, Marianne C. Nyman ^b, Nicholas L. Clesceri ^b, Robert C. Block ^c, Julie A. Stenken ^{a,*}

^a Cogswell Laboratories, Department of Chemistry, Rensselaer Polytechnic Institute, 110 Eighth Street, Troy, NY 12180, USA

^b Department of Civil and Environmental Engineering, Rensselaer Polytechnic Institute, 110 Eighth Street, Troy, NY 12180, USA

^c Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, 110 Eighth Street, Troy, NY 12180, USA

Received 25 July 2002; received in revised form 4 July 2003; accepted 4 July 2003

Abstract

Polychlorinated biphenyls (PCBs) are of environmental concern due to their toxic nature. Ionizing radiation has been suggested as a means to remediate PCB-contaminated samples in complex matrices. A set of experiments was performed to qualitatively and quantitatively determine the aromatic degradation products of 2-monochlorobiphenyl (2-MCB) in an aqueous system exposed to ionizing radiation. The degradation of 2-MCB was observed in aqueous samples that were exposed to radiation from a linear accelerator electron beam source. Analytical measurements performed by liquid chromatography (LC) equipped with an ultraviolet (UV) detector revealed that biphenyl, *o*-hydroxybiphenyl, *p*-hydroxybiphenyl, phenol, chlorobenzene, and other unidentified products were created after 2-MCB irradiation. These results suggest that sensitive and selective analytical methods will be required to account for all degradation products during ionizing radiation of aqueous PCB-contaminated samples.

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Keywords: Ionizing radiation; Liquid chromatography; PCB

1. Introduction

Polychlorinated biphenyls (PCBs) are a class of 209 compounds that were widely used for industrial applications (Durfee et al., 1976; Erickson, 1997). PCBs are

thermodynamically stable compounds causing remediation to be challenging. PCB remediation processes have been heavily researched due to United States regulatory pressures. These remediation technologies include: incineration (Hunt et al., 1984), chemical dechlorination (Yak et al., 1999, 2000), biodegradation (Van Dort et al., 1997; Williams and May, 1997), soil washing, thermal desorption, and ionizing radiation (Curry and Mincher, 1999).

Curry and Mincher (1999) have recently reviewed the applications of ionizing radiation towards PCB remediation in non-polar solvents and soils. Ionizing radiation has been applied to PCB-containing solutions in

* Corresponding author. Tel.: +1-518-276-2045; fax: +1-518-276-4887.

E-mail address: stenkj@rpi.edu (J.A. Stenken).

¹ Present Address: Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, 360 Woods Hole Road, Woods Hole, MA 02543, USA.

aqueous (Schweitzer et al., 1987) and non-polar organic phases (Mincher, 1998; Chaychian et al., 1999). Several groups have designed prototype ionizing radiation facilities for the destruction of PCB-contaminated samples (Singh et al., 1985; Múcka et al., 1997).

For all PCB-related remediation technologies, confirmation and quantitation of PCB destruction and product production is important. For example, ionizing radiation of aqueous samples containing chlorinated organic compounds in complex matrices such as sediments can produce a variety of products (both oxidative and reductive) due to the non-selective nature of irradiation.

During reductive PCB dechlorination, chlorine loss is frequently determined by measuring the solution chloride content using either ion-chromatography (Al-Sheikhly et al., 1997; Mincher et al., 2000) or chloride ion-selective electrodes. Although these methods will give a mass balance on total chloride formed and therefore constrains the amount of chlorinated byproducts formed, they do not allow for measurement or determination of other possible reaction products such as phenols or dioxins. Moreover, chloride monitoring in natural settings, especially estuarine and coastal environments, would be ineffective due to the high background concentrations of natural chloride. Since the United States Toxic Substances and Control Act requires a 99.9999% mass balance on PCB remediation processes, both qualitative and quantitative characterization of all products becomes necessary. For large remediation projects, direct application of ionizing radiation to PCB-contaminated sediments may be an economically viable solution to this persistent environmental problem.

Our focus in this work was to demonstrate a simple and selective analytical method for determining potential aromatic degradation products from aqueous samples spiked with a model PCB, 2-monochlorobiphenyl (2-MCB). By focusing on detection of aromatic degradation products rather than chloride production, a more complete understanding of the chemical nature of these products can be obtained. Liquid chromatography coupled to UV detection was used as a specific analysis system for monitoring aromatic groups derived from 2-MCB destruction.

2. Theory

Organic compound degradation in aqueous solutions using ionizing radiation can occur via two different reaction mechanisms (Spinks and Woods, 1990). The first is by direct incidence of the linear accelerator electron beam upon the target compound. The energy imparted within this beam is substantial as compared to the carbon–chlorine bond dissociation energies associated with

PCBs and their derivatives. The incident electrons can then break the carbon–chlorine bonds causing dechlorination. This mechanism is not favored in these experiments due to the statistical improbability that the electron beam will directly strike a target PCB molecule at such low experimental and environmental concentrations (ppm or μM) as compared to striking a solvent molecule (water $\sim 55 \text{ M}$).

The second degradation method involves an indirect solvent-mediated process. Upon irradiation, water produces a variety of products including hydroxyl radical ($\cdot\text{OH}$), hydrogen radical ($\text{H}\cdot$), hydrated electron (e_{aq}^-), hydrogen gas (H_2), hydrogen peroxide (H_2O_2), and hydronium ion (H_3O^+) as shown in Table 1, Eq. (1). The main species that are generated during water hydrolysis are hydroxyl radical and hydrated electron which both have yields of $0.29 \mu\text{mol J}^{-1}$ (Spinks and Woods, 1990). Aryl halides in aqueous solution will react with hydrated electron as shown in Table 1, Eq. (2) to undergo dehalogenation with rate constants that range between 5×10^6 and $2 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988). Al-Sheikhly et al. (1997) determined the reductive dehalogenation rate for 2,6-dichlorobiphenyl to be $3.8 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ ($3.8 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Aromatic compounds can also react with hydrogen or hydroxyl radicals in solution to form cyclohexadienyl systems that can combine and disproportionate to produce numerous products including phenols (Table 1, Eqs. (3) and (4)). For example, the radiolysis of chlorobenzene has been reported to give *o*-, *m*-, and *p*-chlorophenols which were identified using infrared spectroscopy (Johnson et al., 1951).

Binary solvents containing water and alcohols such as isopropanol or methanol are commonly used to dissolve different hydrophobic analytes including PCBs (Al-Sheikhly et al., 1997). The addition of alcohol to an aqueous solution increases the complexity of the chemical reactions that can occur during solution irradiation. Alcohols can react with hydroxyl radical to give the corresponding alcoxyl ($\text{RO}\cdot$) or hydroxyalcohol ($\cdot\text{ROH}$) radicals shown in Table 1 (Eq. (5)) (Spinks and Woods, 1990). These alcohol-derived radicals can also abstract hydrogen from alcohol or water in solution (Table 1, Eq. (6)) and the resulting alcohol radical can disproportionate or dimerize (Ulanski and von Sonntag, 1999). The hydroxyalcohol radical can reduce aryl halides to give an aryl radical, but has a low rate constant as shown in Table 1, Eq. (7). Finally, when aryl radicals and alcohols are present in solution, the aryl radical can abstract a hydrogen from the alcohol (Table 1, Eq. (8)).

In air saturated matrices, hydrated electron and hydrogen radicals are scavenged by oxygen (Eqs. (9) and (10)) leading to an increased formation of hydrogen peroxide. In many aqueous solutions, trace metals such as Fe^{2+} and Cu^+ exist thus giving rise to a potential for

Table 1
Selected reactions for the irradiation studies and their literature reported kinetic rate constants

$\text{H}_2\text{O} \xrightarrow{\text{Ionizing radiation}} \text{e}_{\text{aq}}^-, \cdot\text{OH}, \text{H}\cdot, \text{H}^+, \text{H}_2\text{O}_2, \text{H}_2$	(1)
$\text{ARX} + \text{e}_{\text{aq}}^- \rightarrow \text{AR}\cdot + \text{X}^-$,	$k = \sim 10^6 \text{ to } 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988)
$\text{AR} + \text{H}\cdot \rightarrow \text{ARH}\cdot$,	$k = 9.1 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Spinks and Woods, 1990, p. 352)
$\text{AR} + \cdot\text{OH} \rightarrow \text{AROH}\cdot$,	$k = 7.8 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Spinks and Woods, 1990, p. 352)
$\text{CH}_3\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}\cdot$ $\text{CH}_3\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_2\text{OH}$,	$k = 9.7 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Spinks and Woods, 1990, p. 323)
$\text{CH}_3\text{O}\cdot \xrightarrow{\text{H}_2\text{O}} \cdot\text{CH}_2\text{OH}$,	Rapid conversion, rate not reported (Ulanski and von Sonntag, 1999)
$\text{ARX} + \cdot\text{CH}_2\text{OH} \rightarrow \text{AR}\cdot + \text{CH}_2\text{O} + \text{H}^+ + \text{X}^-$,	$k = < 10^3 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Al-Sheikhly et al., 1997)
$\text{AR}\cdot + \text{CH}_3\text{OH} \rightarrow \text{AR} + \cdot\text{CH}_2\text{OH}$,	$k = \sim 1 \times 10^3 \text{ to } 10^4 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ * (Fang et al., 1995; *depends on alcohol substitution)
$\text{e}_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^-$,	$k = 1.9 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Spinks and Woods, 1990, p. 323)
$\text{H}\cdot + \text{O}_2 \rightarrow \text{HO}_2\cdot$,	$k = 2.1 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Spinks and Woods, 1990, p. 323)
$\text{AR}\cdot + \text{O}_2 \rightarrow \text{AROO}\cdot$,	$k = 3.3 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Fang et al., 1995)
$\text{AROO}\cdot + \text{HO}_2\cdot \rightarrow \text{RO}_2\text{H} + \text{O}_2$,	Reaction rate not reported (Al-Sheikhly et al., 1997)

hydroxyl radical production or formation of oxidized product via classic Fenton chemistry (Neyens and Baeyens, 2003). Furthermore, addition of molecular oxygen to aryl radicals can occur to create radical organic peroxides as shown in Table 1, Eq. (11). Additionally, organic radical peroxides can react with $\text{HO}_2\cdot$ formed during the irradiation process (Eq. (10)) to form organic peroxides as shown in Eq. (12). In addition to peroxide formation, a variety of other products can be obtained in this complex solvent milieu during exposure to ionizing radiation (Von Sonntag and Schuchmann, 1991). Considering the above arguments and the kinetic rate constants for the reactions outlined in Table 1, the net products in an oxidative solution environment from these various processes might be expected to include

biphenyl as well as phenolic compounds such as *o*-hydroxybiphenyl and *p*-hydroxybiphenyl.

3. Materials and methods

3.1. Chemicals

2-MCB was purchased from Accustandard (New Haven, CT, USA). Biphenyl, phenol, *o*-hydroxybiphenyl, and *p*-hydroxybiphenyl were purchased from Sigma (St. Louis, MO, USA). Chlorobenzene was purchased from Fisher Scientific (Pittsburgh, PA, USA). All the chemicals were used as received. All other chemicals were reagent grade or better.

3.2. LINAC

The irradiation of the samples was carried out at the Rensselaer Polytechnic Institute Gaertner LINAC Laboratory. The LINAC consists of nine RF accelerator sections that accelerate pulses of electrons to a maximum energy in excess of 60 MeV with peak target currents in excess of 3 A. The electron beam can be extracted either after the third or ninth section and can be focused on any target geometry. For the irradiations in this study, the beam extracted from the third section and had an average energy of 15 MeV. This energy was chosen to minimize the amount of radioactive species produced. Use of 15 MeV also ensures that the energy range is greater than the 1.5 cm of water in the test tube.

3.3. Irradiation experiments

A rotating, vertically supported thin aluminum bucket that can travel up and down as it turns in the electron beam has been constructed. This apparatus held 15 borosilicate screw top glass tubes (65 ml capacity) capped with TeflonTM lined silicone septa and sealed with Parafilm, all of which were fitted with inverted U-shaped glass to allow out-gassing. This bucket was suspended in the path of the electron beam, and was rotated about its vertical axis and moved vertically to ensure homogeneous irradiation dosage.

Preliminary tests using radiochromic film placed on the outside of the rotating target assembly were employed to integrate and calculate the dose delivered per pulse (or per time of operation) (Bly, 1988). The radiochromic film was cross calibrated to Harshaw 800 Lithium Borate thermoluminescent dosimeter (TLD) powder by exposing both the radiochromic film and TLD powder to the same radiation field. The TLD powder has been exposed to a radiation field that has been calibrated by the National Institute of Standards and Technology (NIST). Thus the dose rates measured in this experiment were effectively calibrated to the NIST standard. The dose rate in the water decreases by approximately 5% as the electrons pass through it such that the measurement of dose at the outside of the thin glass test tube is within 5% of the dose in the sample (e.g., water).

The 15 MeV beam contains sufficient energy to fully penetrate the ~1.5 cm width of the aqueous sample in the glass test tube with the integrated dose modulated by only 5% over the width of the test tube wall. Increasing dosages were achieved as follows. After the delivery of a pre-determined dose, a set of sample-containing vials were removed from the apparatus and replaced with new tubes that contained water. The remaining sample vials were then subjected to successive irradiation periods, with tubes removed periodically so that a homogenous

set of data points was achieved over the entire 0–8.4 MeV range. After irradiation, the rotational assembly was removed from the system and vials were allowed to return to background radiation as measured by the TLD. Typically the borosilicate glass of the vials returned to the background radiation level within one day.

Two separate irradiations were performed. The first irradiation experiment was performed to test the feasibility of 2-MCB destruction in an aqueous medium and to confirm product elucidation via the analytical method. The second irradiation was used both to refine the techniques discussed above and estimate the reproducibility of the irradiation procedure.

In the first experiment, six test tubes containing 50 ml each of 50 μ M 2-MCB in 95/5 (v/v%) water/isopropanol in glass test tubes were placed into the bucket with the remaining positions filled with placeholder tubes containing only water. The administered dosages to these individual samples were: 1.2, 2.4, 4.8, 6.0, 7.2, and 8.4 Mrad. After irradiation, the samples were stored overnight and analyzed the next day.

For the second experiment, 12 test tubes also containing 50 ml each of the 50 μ M 2-MCB solution in 95/5 (v/v%) water/isopropanol were placed into the bucket apparatus. A control test tube was removed from the rest of the samples prior to irradiation. Duplicate samples were irradiated between 0.5 and 8.4 Mrad. After irradiation, the samples were stored again overnight and analyzed the next day.

3.4. HPLC conditions

Aqueous samples from the electron beam irradiation experiments were analyzed using reverse-phase HPLC with the UV detector operated at $\lambda = 254$ nm. The HPLC equipment consisted of a Thermo Separations Products P1000 pump, UV 1000 variable wavelength detector with PC 1000 data acquisition and control software (Thermo Separations Products, San Jose, CA, USA). Separations were achieved using a Phenomenex Hypersil C18 column (2 mm i.d. \times 15 cm) (Phenomenex, Torrance, CA, USA). The analysis was performed with isocratic flow that consisted of 55/45 (v/v%) water/ acetonitrile with a flow rate of 0.25 ml min⁻¹. The injection volume was 10 μ l. Sample concentrations were determined by comparing peak areas to a standard calibration curve. All calibration standards were prepared in 95/5 (v/v%) water/isopropanol. Calibration standards for biphenyl, *o*-hydroxybiphenyl, *p*-hydroxybiphenyl and 2-MCB ranged between 1 and 100 μ M. All compounds eluted within 20 min as shown for 50 μ M standards in Fig. 1. Although all the standards are the same concentration, the molar absorptivity for each analyte is different resulting in different peak heights for standards with the same concentration.

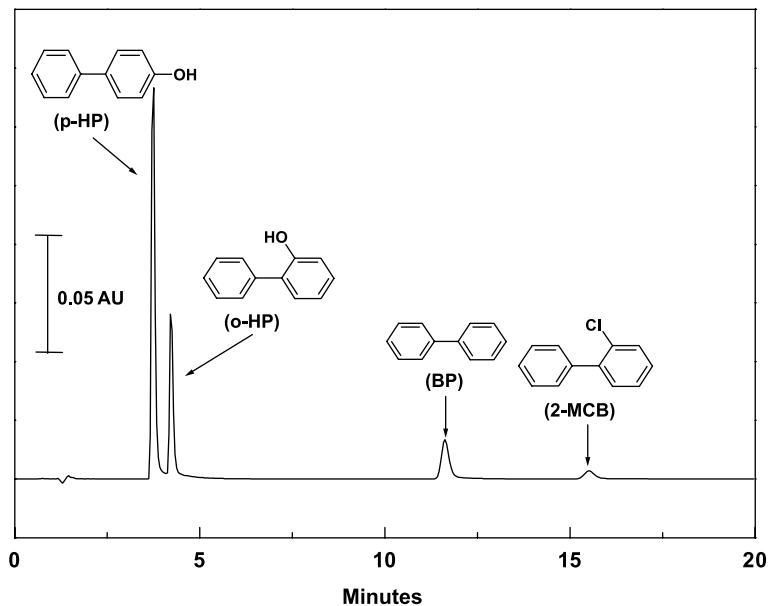


Fig. 1. Chromatogram of 50 μM standards of (1) *o*-hydroxybiphenyl, (2) *p*-hydroxybiphenyl, (3) biphenyl, (4) 2-monochlorobiphenyl.

4. Results and discussion

In previous work, ionizing radiation was applied to solutions containing chlorobenzene in aqueous solvents to ensure that chlorinated products could be eliminated with our experimental design (Porcino, 1998; Porcino et al., 1999). Gas chromatographic flame ionization (GC-FID) analysis of the irradiated samples indicated that many different products were formed upon irradiation. Thus, a quantitative analysis of so many unknown chromatographic peaks was not possible using the GC-FID, which is a non-selective detector. For this study,

we chose to use reversed-phase HPLC coupled with UV detection as a more selective method for detection of the aromatic compounds that were anticipated as potential products of 2-MCB after irradiation.

Fig. 2 shows chromatograms from a control and 0.5 Mrad irradiated 2-MCB solution (50 μM). With this low radiation dose, the 2-MCB concentration was reduced and biphenyl concentration increased in the sample. The formation of additional hydrophilic products including *o*-hydroxybiphenyl and *p*-hydroxybiphenyl was observed in this chromatogram. During reversed-phase HPLC, hydrophilic products will elute earlier in the

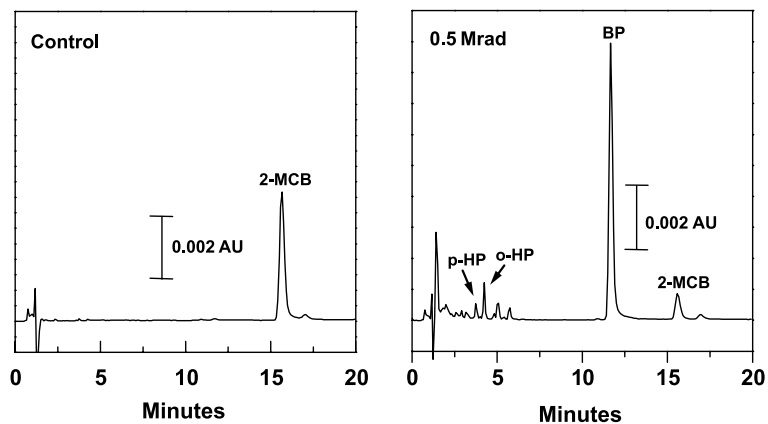


Fig. 2. Chromatograms of control and 0.5 Mrad irradiated 50 μM 2-MCB samples. Abbreviations are as follows: 2-monochlorobiphenyl (2-MCB), biphenyl (BP), *o*-hydroxybiphenyl (*o*-HP), and *p*-hydroxybiphenyl (*p*-HP).

chromatogram (Kaliszan, 1987). As seen in Fig. 2, a variety of different hydrophilic products were produced. These products may include organic peroxides as well as various isomers of chlorophenol.

To determine if phenol or chlorobenzene were produced during irradiation, the retention times for these compounds were measured using the chromatographic conditions for 2-MCB separation. Phenol eluted at 1.9 min, and chlorobenzene eluted at 5.8 min. The short retention time for phenol gives a k' of 0.3, which means that it elutes very close to the non-retained material. Thus, phenol quantitation using these chromatographic conditions is not possible. The chromatograms became more complex as the radiation dose was increased (Fig. 3). As the radiation dose was increased, the size of the peaks that were non-retained (close to the mobile phase retention time, 1.4 min, or void volume) increased. This was an indication that hydrophilic species such as phenols or possibly organic peroxides were being formed during the irradiation process in oxidative conditions. The separation of these non-retained peaks from biphenyl and 2-MCB will require gradient elution HPLC. Determining the identity of these unknown hydrophilic compounds that elute early in the chromatogram will require additional analytical tools such as liquid chromatographic–mass spectrometric (LC–MS) analysis.

As an example of the results from the electron beam irradiation experiments, Fig. 4 illustrates the degradation of 2-MCB in aqueous solution as a function of different irradiation doses for the first experiment. Radiation doses between 0.5 and 2.5 Mrad were effective in dechlorination of 80–90% of 2-MCB. A radiation dose of 5.0 Mrad was effective in eliminating 2-MCB from solution as it was not detected in the chromatogram at this dose. The principal product of this degradation that could be identified by our analytical methods was biphenyl. Additionally low concentrations of *o*-hydroxy-

biphenyl and *p*-hydroxybiphenyl were detected in these samples as shown in Fig. 2. These initial results are in general agreement with the dechlorination studies of 2,6-dichlorobiphenyl (2,6-PCB) in aqueous solution by Al-Sheikhly et al. (1997) and in transformer oil solutions by Chaychian et al. (1999). In their experiments, 2,6-dichlorobiphenyl lost about one half of its total chlorine at a dose of 50 kGy (5 Mrad). In their studies, a plateau of reductive dechlorination (1.5 Cl⁻ out of a total of 2 Cl⁻) was observed between doses of 100 and 200 kGy (10 and 20 Mrad).

Similar results from the second set of 2-MCB irradiation experiments are shown in Fig. 5. In both sets of experiments, biphenyl persisted at higher radiation doses and accounted for approximately 50% of the overall mass balance after irradiation. Low concentrations (<2 μM) of *o*-hydroxybiphenyl and *p*-hydroxybiphenyl were detected in the solutions in this experiment. These results were similar to those of Chaychian et al. (1999) for 2,2',6,6'-tetrachlorobiphenyl in transformer oil, where biphenyl accounted for 70% of the total mass balance at doses of 250 kGy (25 Mrad).

The observed differences between the mass balance between our work and others can be explained by the different sample matrices. Our experiments were performed in an oxygenated water matrix rather than an oil matrix. In an oxygenated water matrix, there is a potential for hydroxyl radical attack in addition to the possibility for organic peroxide formation. Since a variety of different chemical reactions may take place upon irradiation of an organic sample in oxygenated aqueous matrices, it is not unanticipated that that biphenyl only accounted for 50% of the total mass balance in these experiments. However, in contrast to the nearly 100% loss in total measurable products at a 5 Mrad dose in the first experiment, only a 50% loss in total measurable products was observed in the second procedure with

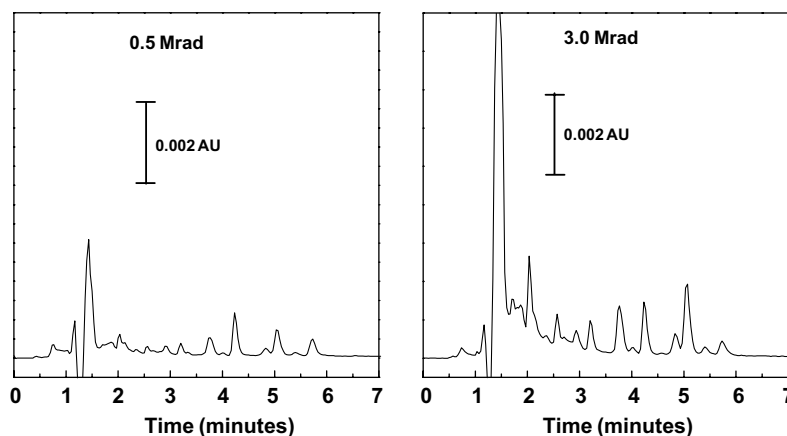


Fig. 3. Chromatograms of 50 μM 2-MCB aqueous solution after receiving radiation doses of 0.5 and 3.0 Mrad.

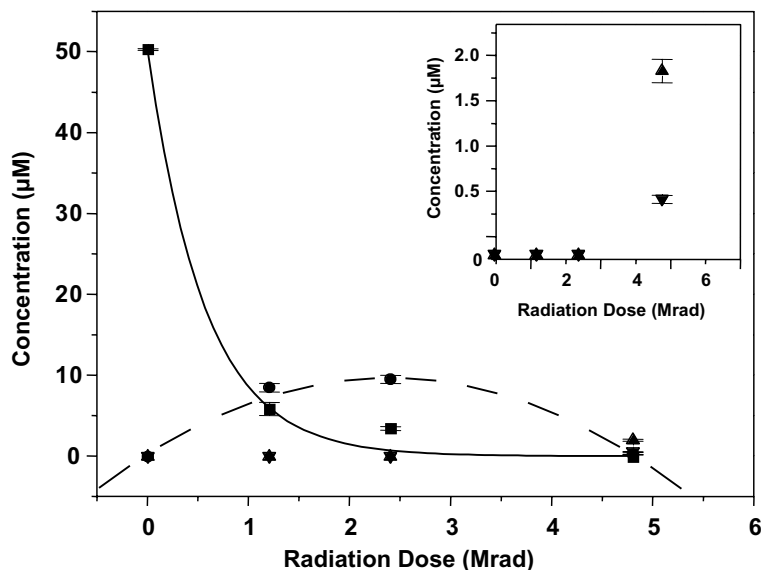


Fig. 4. First degradation experiment of 2-MCB in a solution containing 95/5 v/v% water/2-propanol as a function of radiation dose. Regression lines are meant to aid the eye and do not imply a model for elimination. Symbols are as follows: (■) 2-monochlorobenzene, (●) biphenyl, (▲) *o*-hydroxybiphenyl, and (▼) *p*-hydroxybiphenyl. Error bars represent triplicate analysis of each irradiated sample.

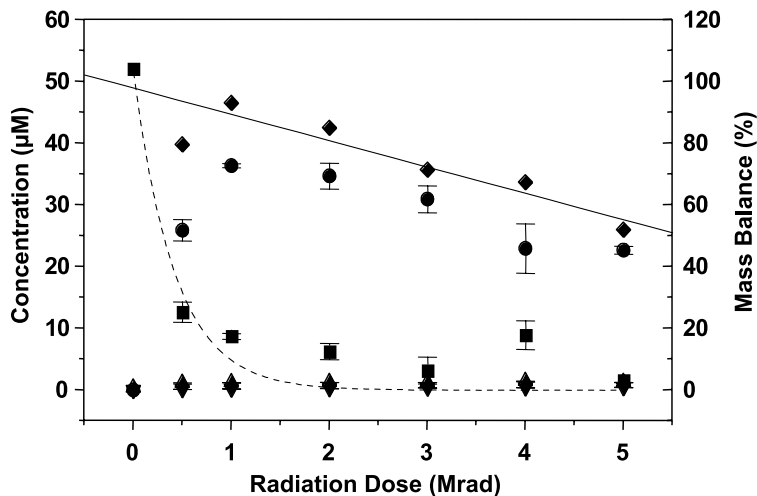


Fig. 5. Second degradation experiment of 2-MCB in a solution containing 95/5 v/v% water/2-propanol as a function of radiation dose. Replicate experiment of 2-MCB irradiation. Regression lines are meant to aid the eye and do not imply a model for elimination. Symbols are as follows: (■) 2-monochlorobenzene, (●) biphenyl, (▲) *o*-hydroxybiphenyl, (▼) *p*-hydroxybiphenyl, and (◆) mass balance. Error bars represent the range of two different samples. Each sample was analyzed once.

minimal sample-to-sample variability. While it is possible that some of the variation may be due to dosimetry differences, radiochromic film calibrations give approximately a 10% variation when compared to Fricke dosimetry (Bibler, 1976). Radiochromic film calibrations are generally used since the experimental procedures to

calibrate are much quicker as compared to Fricke dosimetry. Since radiochromic film can have such a low variability when compared to Fricke dosimetry performed on the aqueous solution, differences in dosimetry estimation from day-to-day does not fully account for the variation observed between the different samples.

5. Conclusions

The predominate product formed from irradiation of a 2-MCB aqueous solution was found to be biphenyl by using liquid chromatography coupled with UV detection. However, biphenyl only accounts for approximately 50% of the overall mass balance after irradiation. In addition to biphenyl, LC clearly demonstrated the production of many other polar components as confirmed by the multiple peaks observed in the chromatograms. Knowledge of the total mass balance is important for remediation studies with PCBs since 99.9999% mass balance is required for compliance with the Toxic Substances Control Act in the United States. In order to meet this strict law, sensitive and selective analytical methods will need to be developed to fully account for the degradation products of remediated samples. For complex remediation problems that include many different Aroclor mixtures, a comprehensive analytical approach to identifying the products formed and the mass balanced will be needed. Such a comprehensive approach may include GC methods including those extensively developed by Frame (1997) or more recent two-dimensional GC methods developed by others (Korytar et al., 2002) for the targeted PCB analytes as well as LC methods for the observed hydroxylated products.

Acknowledgements

A grant from the Aluminum Company of America (NLC and RCB) and Rensselaer Polytechnic Institute start-up funds (JAS and MCN) supported this work. NJD was supported by the Rensselaer Polytechnic Institute Undergraduate Research Program.

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