Radiolysis of Aqueous Solutions of Benzoate Ion: A Radiation Chemistry Experiment for Undergraduates

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Abstract: This investigation describes the chemical effects of ionizing radiation on dilute aqueous solutions of benzoate ion. We have composed an experimental procedure that allows undergraduate chemistry students to identify and to quantitatively determine the amount of the products that are produced. The student investigators determine the absorbed dose that a sample receives when exposed to a ^{60}Co source, irradiate dilute aqueous solutions of benzoate ion, and analyze the resulting mixture of hydroxybenzoate ions using high-performance liquid chromatography. The radiolysis of dilute solutions of benzoate ion results in the formation of a mixture of *ortho-*, *meta-*, and *para-*hydroxybenzoate ions that are readily separated on a C_{18} μ-Bondapak column. By the use of appropriate calibration curves, the yield (*G* values) of each of the isomers may be determined and compared.

[‡]Introduction

This article describes an experiment that has been employed in a nuclear chemistry course to illustrate the chemical effects that result from the interaction of ionizing radiation with matter. The experiment demonstrates the ability of ionizing radiation to generate free radicals that can react with dissolved solutes in aqueous solution.

At our institution the experiment has been employed as part of a course on nuclear chemistry and radioactivity. This is a nonmajors chemistry course that has evolved into a course [1] on the chemistry of nuclear waste. This one semester course consists of three sections: an introduction to nuclear chemistry, radiation chemistry, and applications of nuclear and radiation chemistry. The course has been popular with biology, chemistry, geology, and physics majors and an occasional nonscience major. Students are primarily in the upper division of their undergraduate education.

The Journal of Chemical Education has published an excellent group of articles on various aspects of radiation chemistry. The State of the Art Symposium on Radiation Chemistry [2] provides an excellent collection of articles that consists of introductory papers, applications of radiation chemistry techniques to fundamental research in chemistry, and industrial applications of radiation processing. There is one comprehensive radiation chemistry textbook that can readily provide the necessary background for an undergraduate course [3].

Fundamental research in radiation chemistry has been and continues to be a very active area [4] of investigation. This includes employing new instrumentation (femtosecond lasers) and techniques (picosecond radiolysis) to study fast reactions that occur in radiation chemistry. These techniques have been employed to study electron-transfer reactions and surface and interface processes. Considerable efforts have also been made in the use of radiation in industrial and environmental problems. In our course on nuclear and radiation chemistry where we employ the experiment described in this article, the final section of that course is devoted to nuclear and radiation chemical applications. Most popular with the students are applications that relate to techniques that are useful in solving environmental problems. A recent review article [5] on the radiolysis of soil and sediments is extremely useful. It discusses the radiation chemistry, radiation sources, and economics that are involved in using radiation to clean up contaminated sites. The use of radiation to preserve various foods [6a, 6b] and to generate unusual valence states [7] and metal ion clusters [8] are also of great interest.

Purpose of the Experiment

The experiment is an excellent way to introduce the chemical effects of ionizing radiation. It serves as a starting point for the discussion of the chemistry related to radiation damage that results when primary radicals generated by the ionizing radiation react with biological compounds. We have used the experiment in a special topics course [1] on the chemistry of nuclear waste. It may also be used to introduce students to high-performance liquid chromatography.

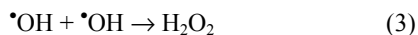### Radiation Chemistry and the Generation of Radicals

A variety of sources have been used in radiation chemical studies, but the most convenient are commercial ^{60}Co irradiators that have been developed to carry out experiments in radiation chemistry and biology. ^{60}Co emits γ-rays that have energies of 1.17 MeV and 1.33 MeV. The chief mode of energy loss by the high-energy γ photons is the Compton and photoelectric effects; both result in the formation of high-energy electrons. These physical processes are adequately described in nuclear chemistry textbooks [9].

[‡]This paper was presented at the 15th Biennial Conference on Chemical Education, Waterloo, Ontario, Canada, August 1998 by N. Zevos and at the 26th Northeast Regional Meeting of the American Chemical Society by Evon Powell.

The electrons that result from the ionization process lose energy through a series of coulombic interactions with the electrons of the atoms in the absorber. With an absorber that is a dilute aqueous solution, the energy deposition is almost exclusively in the solvent molecules. The end result is ionization of the solvent, in this case water, with the production of free radicals. This primary interaction results in the formation of solvent cations (i.e., H_2O^+), which then rapidly react with another solvent molecule. In a picosecond process, the original ion pair results in the formation of a reducing species [hydrated electron, $e^-(aq)$] and an oxidizing species (hydroxyl radical, $^\bullet OH$).

$$H_2O \rightarrow H_2O^+ + e^- \xrightarrow{H_2O} {}^\bullet OH, e^-(aq), {}^\bullet H \qquad (1)$$
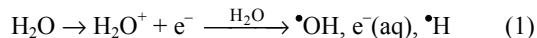
The pH of the solution plays an important role in determining the final state of these two primary species [10]. For example, the hydrated electron will react very readily ($k = 2.4 \times 10^{10}$ M^{-1} S^{-1}) with hydronium ions that are present in an acidic solution; therefore, the final state of the reducing species in highly acidic solutions will be a hydrogen atom: $e^-(aq) + H_3O^+ \rightarrow H^\bullet + H_2O$. Once produced, these primary radicals may react with each other to produce molecular products (reactions 2–4).

$$H^\bullet + H^\bullet \rightarrow H_2 \qquad (2)$$

$$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \qquad (3)$$

$$H^\bullet + {}^\bullet OH \rightarrow H_2O \qquad (4)$$

or diffuse through the solution and react with any dissolved solute that may be present.

The reactions of the hydroxyl radical with a large number of compounds is by electron transfer and addition. For example, hydrated metal ions readily react with the hydroxyl radical.

$$Fe^{+2} + {}^\bullet OH \rightarrow Fe(OH)^{2+} + OH^- \qquad (5)$$
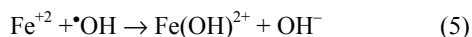
With saturated organic compounds, the usual reaction is abstraction of a hydrogen atom to form water and another free radical. With aromatic organic compounds

$$CH_3OH + {}^\bullet OH \rightarrow CH_2\overset{\bullet}{O}H + H_2O \qquad (6)$$
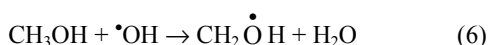
hydroxyl radicals rapidly react by addition to the ring to form hydroxylcyclohexadienyl radicals, **I**. For example, with benzene dissolved in water:

$$C_6H_6 + {}^\bullet OH \rightarrow C_6H_6\overset{\bullet}{O}H \qquad (7)$$
$$\mathbf{I}$$
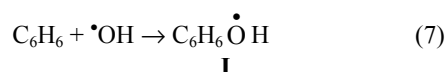
The rate constants for the formation of **I** are usually diffusion controlled. The subsequent fate of **I** depends on the composition of the solution (i.e., pH, presence of oxidants such as metal ions, and organic oxidants).

Overview

The laboratory exercise consists of two parts. Initially, the students calibrate a ^{60}Co radiation source using the Fricke dosimeter. This establishes a relationship between the amount of energy absorbed by the sample and the time that the sample is exposed to the radiation.

In the second part of the study, the students expose a dilute aqueous solution of benzoate ion and $Fe(CN)_6^{-3}$ to the radiation. Analysis of the sample is carried out by high-performance liquid chromatography. By determining the exposure time of the irradiated sample, the amount of energy absorbed by the sample may be calculated. From the HPLC analysis, the concentration of the products may be determined, and then, the radiation chemical yield (i.e., the number of molecules of product formed per 100 eV of energy absorbed) may be determined.

## Calibration of Radiation Source

The amount of energy absorbed by the sample must be determined in any radiation chemical study. The most convenient dosimeter in a study of this type is the Fricke or ferrous sulphate dosimeter. This dosimeter essentially consists of a millimolar solution of $FeSO_4$ in 0.4 M sulfuric acid. When this solution is exposed to ionizing radiation the radicals produced by the radiation, oxidize ferrous ions to ferric ions. The extent of reaction is determined by measuring the increase in absorbance at 304 nm. The increase in absorbance at this wavelength is due to the production of ferric ion by the ionizing radiation. The absorbed dose, or the energy absorbed by the solution for the period of time that it is exposed to the radiation, may be calculated from the following equation if cells with a 1-cm path length are used to determine the absorbance.

$$D = 2.77 \times \Delta A \text{ Gy} \qquad (8)$$

where D is the absorbed dose and ΔA is the change in the absorbance at 304 nm for the irradiated and unirradiated solution. The derivation of this equation and the chemistry involved in the dosimeter is discussed by Spinks and Woods [11]. This particular equation may be used for ^{60}Co sources. The value for the yield of Fe^{+3} will differ with the type of radiation employed. A large number of chemical yields for various types of radiation sources have been determined and are reported in the literature [12].

Radiolysis of Dosimeter Solution

The spectral changes that occur during the radiolysis of a dilute solution of ferrous sulfate are shown in Figure 1. The arrow in the diagram points out the growth that occurs at 304 nm due to the formation of ferric ion from the reaction of ferrous ion with the radicals produced by the ionizing radiation. The inset shows the curve that results when the change in absorbance is employed to calculate the absorbed dose from eq 8. Using the equation that results from the linear regression would allow calculation of the time required to deliver a specific dose to a sample using that particular radiation source.
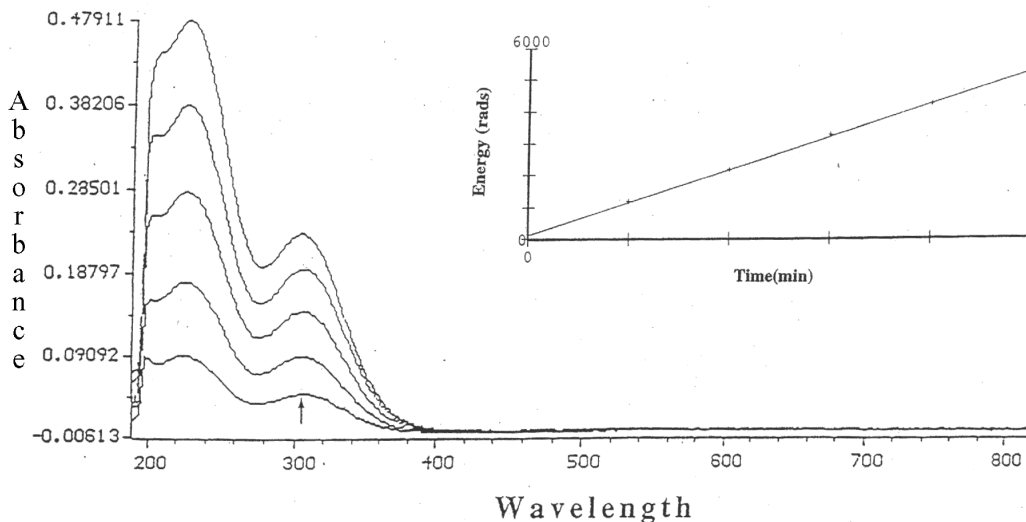
Figure 1. Radiolysis of Fricke dosiometer solution. Consecutive spectra show the growth of ferric ion at 304 nm (arrow) at various exposure times. The insert shows the data fitted to eq 8.

## Radiolysis of Aqueous Solutions of Benzoate Ion

The radiation chemistry of aqueous solutions of benzoate ion has been studied extensively. Armstrong et al. [13–15] developed a sensitive chemical dosimeter based on fluorometric analysis of irradiated aqueous solutions of calcium benzoate. These studies indicated that the main organic products of the radiolysis are *ortho-*, *meta-*, and *para*-hydroxybenzoate ions. Mathews and Sangster [16] have reported on radiolysis of aqueous solutions of ^{14}C labeled benzoate ion. This study indicated that a small quantity of phenol is formed from decarboxylation of the benzoate, but the bulk of the products, greater than 90%, are the ortho, meta, and para isomers.

The radiolysis of benzoate with ionizing radiation has also been investigated by pulse radiolysis methods. These investigations have shown that both of the primary radicals produced by ionizing radiation undergo reactions with benzoate. The initial reaction that occurs between the hydrated electron and benzoate results in the formation of an anion radical [17]. The rate constant for the formation of the anion radical is readily determined by monitoring the decrease in absorbance of the hydrated electron.

The hydroxyl radical also reacts very rapidly with benzoate ($k = 4.3 \times 10^9$ M^{-1}S^{-1}) to produce a hydroxycarboxycyclo-hexadienyl (HCHD) radical [18].


II   (9)
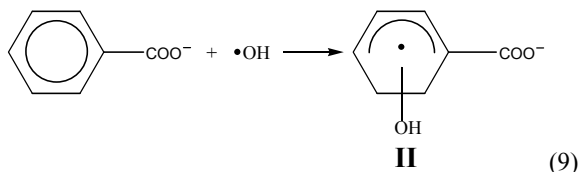
The UV/Vis spectrum and extinction coefficient for **II** have also been reported. Once formed, the HCHD radicals in the absence of oxidants disproportionate [18] to form products.

$$2(HO)\overset{\bullet}{C}6H5COO^- \xrightarrow{2k} \text{products} \qquad (10)$$
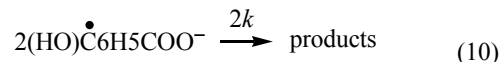
For benzoate ion $2k = 0.5 \pm 0.2 \times 10^9$ M^{-1}S^{-1} for reaction 10. The chemistry of many of the HCHD radicals has been investigated and the reactions that occur after the rapid formation depend on reaction conditions. Product formation may proceed spontaneously or by a catalyzed path. Radicals of this type may be oxidized to produce the final product and a variety of oxidants have been employed to carry this out. The rate of disappearance of the radicals is relatively slow in the absence of suitable electron-transfer agents such as metal ions, metal complexes, and quinones. Volkert and Schulte-Frohlinde [19] found that carrying out the radiolysis in the presence of ferricyanide produced all three isomers.

Schuler [20] and co-workers have carried out the radiolysis reaction in N$_2$O-saturated 1 mM benzoate ion solutions containing 0.5 mM ferricyanide and found that reactions at the ortho, meta, and para positions are very nearly statistical. They also report that the phenolic products formed react very rapidly with OH radical. A 5% reduction in yield occurs at a 10% conversion of benzoate ion. The procedure employed in our experiment is similar to that used in this report.

The separation of the reactants and the products is shown in Figure 2b. Quantitative separation using this column and solvent mixture is excellent. Students readily determine the concentration of the isomers by reference to solutions of known concentration. Typical student chromatograms are shown in Figure 2d and c. A chromatogram of the nonirradiated solution is shown in Figure 2a. The ferricyanide/ferrocyanide peaks elute immediately after sample injection and the benzoate ion elutes with a retention time of 13.9 min. The chromatogram of a benzoate solution irradiated with an absorbed dose of 2.2 Krads is shown in 2c. This dose produces quantities of each isomer that may be readily integrated. The order of elution is *p*-hydroxybenzoate ion (3.7
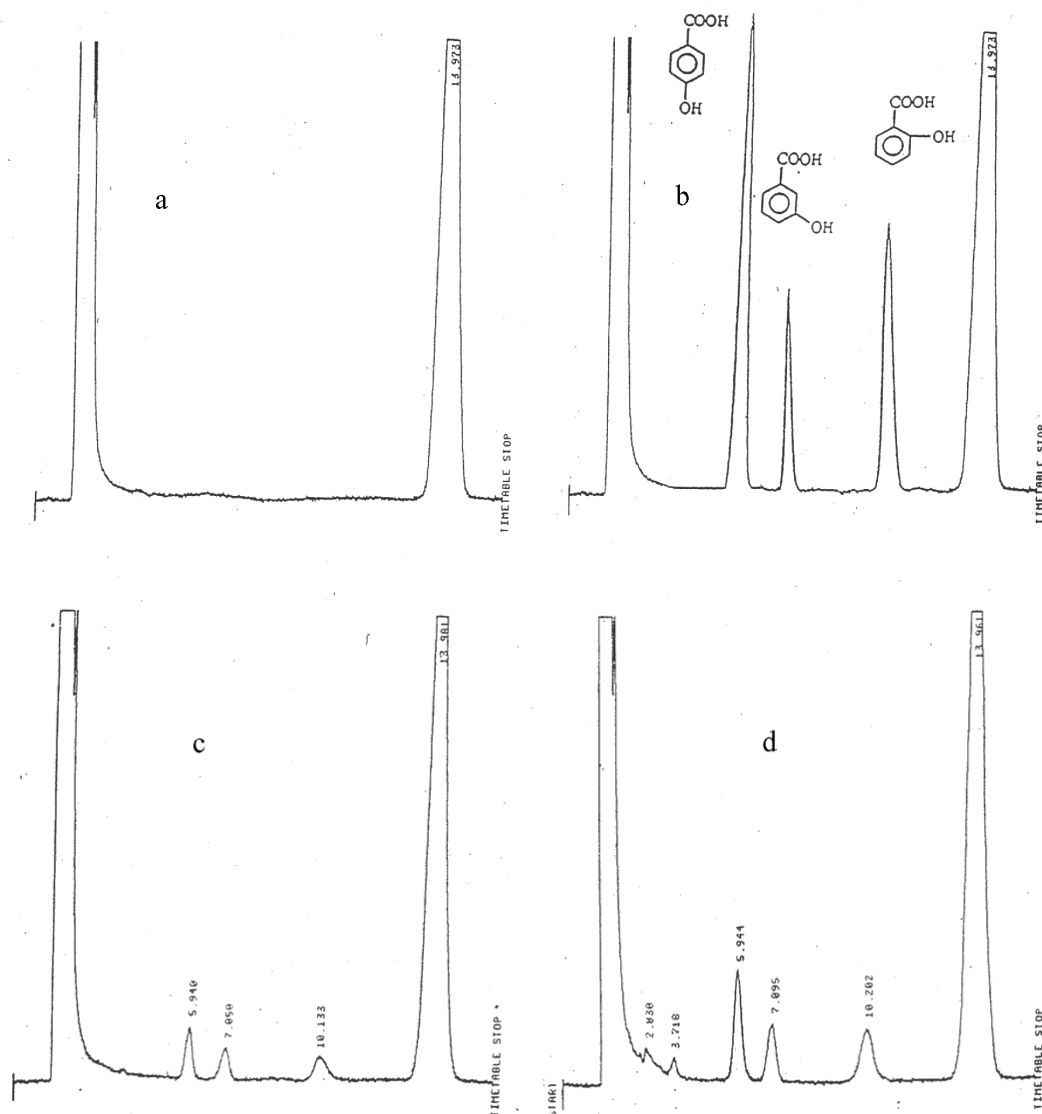
Figure 2. Chromatograms (a) unirradiated solution; (b) solution of reactants and products; (c) absorbed dose = 2.2 Krad: *p*-HBA (5.9 min), *m*-HBA (7.0 min), *o*-HBA (10.1 m); (d) absorbed dose = 4.4 krad: secondary dihydroxy products at 2.8 min and 3.7 min.

min) *m*-HBA (5.9 min) and *o*-HBA (10.2 min.). A trace quantity of secondary products is formed at this absorbed dose. The result of increasing the absorbed dose to 4.4 Krads is shown in Figure 2d. The peaks of the monohydroxy products increase in concentration and the peaks due to secondary (dihydroxy) benzoate ions are readily observed. These secondary products elute at shorter retention times (2.8 and 3.7 min).

Hazards

Radiation sources should be operated only after their proper use has been thoroughly explained by the instructor. Procedures established by a radiation safety committee should be closely followed.

1. Benzoate ion (CAS 65-85-0): irritant, causes eye irritation.

2. Potassium Ferricyanide (CAS 13-146-66-2): light sensitive, may be harmful if swallowed or inhaled.
3. Ferrous Sulfate (CAS 7782-63-0): irritant.
4. Sulfuric Acid (CAS 7664-93-9): oxidizer, corrosive

Students should be very careful in handling the Fricke dosimeter solutions because of the high concentrations of sulfuric acid present.

Conclusions

Depending on the amount of chemistry background that students have, other topics may be discussed. From the amount of isomer that has been produced and the amount of energy that has been absorbed by the analyzed samples, the radiation chemical yield or "*G*" value may be readily calculated [16]. The amount of each isomer is an indicator of the degree of hydroxylation at each position of the benzoate ion molecule. The relative amounts of each isomer produced should be

determined and compared. For students that have a physical chemistry background, a more rigorous kinetic/mechanistic approach involving the free radical and electron transfer reactions that are involved in the hydroxylation reaction may be discussed.

Supporting Material. A description of the ^{60}Co Source, compositions of the dosimeter and the benzoate ion solution, analytical instrumentation and conditions, and the benzoate ion dissociation are included in a Zip file (http://dx.doi.org/10.1007/s00897020614b).

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21. Radiation Units:

Energy: 1 electron volt (eV) per particle, 1.60×10^{-19} J per particle

Absorbed dose: 1 rad (rd), 0.01 J per kg of water, 1 Gray (Gy) = 100 rads

22. Values for the rate constants for the species produced by ionizing radiation may be accessible through the Notre Dame Radiation Laboratory (NDRL), Radiation Chemistry Data Center Web site. http://www.rcdc.nd.edu/ (accessed Sept 2002). This provides a link to bibliographic or kinetics information.

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