Products of the Triplet Excited State Produced in the Radiolysis of Liquid Benzene

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The radiation chemical yields of the products derived from the triplet excited state produced in the radiolysis of liquid benzene with γ-rays, 10 MeV ^{4}He ions, and 10 MeV ^{12}C ions have been determined. Iodine scavenging techniques have been used to examine the formation and role of radicals, especially the H atom and phenyl radical. For all irradiation types examined here, the increase in hydrogen iodide yields with increasing iodine concentration matches the increase in iodobenzene yields. This agreement suggests that the benzene triplet excited state is the common precursor for the H atom and the phenyl radical. Pulse radiolysis studies in liquid benzene have determined the rate coefficients for the reactions of phenyl radicals with iodine and with the solvent benzene to be 9.3×10^9 M^{-1} s^{-1} and 3.1×10^5 M^{-1} s^{-1}, respectively. Direct measurements of polymer formation, which refers to trimers (C_{18}) and higher order compounds ($>C_{18}$), in liquid benzene radiolysis using γ-rays, ^{4}He ions, and ^{12}C ions at relatively high doses have been performed using gel permeation chromatography. The yields of trimers increase from γ-rays to ^{12}C ions due to the increased importance of intratrack radical−radical reactions that can be scavenged by the radical scavenging reactions of iodine. On the other hand, the $>C_{18}$ product yields decrease from γ-rays to ^{12}C ions. The structure of the polymer consists of a partly saturated ring as determined by infrared and gas chromatography/mass spectrometry studies. A schematic representation for the radiolytic decomposition of the benzene triplet excited state is presented.

Introduction

Many products have been identified in the radiolysis of liquid benzene and other similar aromatic compounds; however, their yields are far less than expected. The discrepancies lead to questions on the pathways for the decomposition of specific transient states.[1] In radiolysis, ionization due to the absorption of energy is quickly followed by neutralization reactions producing the singlet and triplet excited states of benzene.[2−6] For fast electrons, the initial yield of the benzene triplet state due to neutralization reactions is about 4.2 molecules/100 eV.[7,8] The total yield of benzene triplet excited state, including intersystem crossing from singlet excimer to the triplet excimer is about 4.8 molecules/100 eV with γ-rays.[7−9] The triplet forms an excimer by coupling with a ground-state benzene molecule, which decays with a lifetime of about 4.9 ns.[9] The singlet excited state is thought to be the precursor to molecular hydrogen and acetylene, whereas the triplet excited state is believed to decay to a phenyl radical and H atom. These radicals are the precursors to other higher molecular weight hydrocarbon products.[10] Scavenging techniques have identified the total radical yield in benzene to be about 0.7 radicals/100 eV.[11−15] The main hydrocarbon product observed in the radiolysis of neat liquid benzene is biphenyl with a yield of about 0.07 molecules/100 eV.[10,12,16−19] Obviously, there is a large difference between the yield of the triplet excimer and the yields of products thought to be derived from its decomposition.

Most of the phenyl radicals are thought to be consumed in “polymer” formation, which generally refers to the formation of trimers and higher order compounds ($>C_{18}$).[1,12] The yield of polymer in the γ-radiolysis of benzene is estimated to be 0.76 molecule/100 eV, which agrees well with the total radical yield.[20,21] Polymer yields are usually determined by the net loss of benzene using very high doses. This technique for measuring polymer yields is not quantitative and gives limited information on polymer structure or the method of formation. Polymer yields, including the yields of trimers and $>C_{18}$ products, increase with increasing LET (linear energy transfer, $= -dE/dx$) of the incident radiation.[22] This increase is similar to that observed for molecular hydrogen,[10,23] but no direct relationship between the two products has been established. The increased importance of second-order reactions at high LET is an important tool for the elucidation of the pathways to polymer formation.

In this work, the role of the triplet excited state in the radiolysis of liquid benzene is examined. Molecular hydrogen, hydrogen iodide, and polymer production in the radiolysis was determined using γ-rays, 10 MeV ^{4}He ions, and 10 MeV ^{12}C ions. Polymer yields were measured directly using gel permeation chromatography (GPC). The rate coefficients for the reactions of phenyl radicals with iodine and with benzene were determined from transient absorption measurements using pulse radiolysis techniques. A scheme for the decay of the triplet excited state of liquid benzene is proposed.

Experimental Section

Benzene of HPLC grade with purity above 99.9% and iodine (99.999%) from Sigma Aldrich were used without further purification. Radiolysis of all solutions was performed under inert atmospheres.

Heavy Ion Radiolysis. Heavy ion irradiations were performed using ^{4}He, and ^{12}C ions obtained from the 10 MV FN Tandem

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Van de Graaff accelerator of the University of Notre Dame Nuclear Structure Laboratory. The window assembly and irradiation procedure were the same as previously reported.[24,25] Ion energy was determined by magnetic analysis, and energy loss to the windows was calculated using standard stopping power tables.[26] Both ^{4}He and ^{12}C ion energies were 10 MeV incident to the sample. Absolute dosimetry in the scavenging experiments was obtained by collecting and integrating the charge from the sample cell in combination with the ion energy. In experiments on hydrogen iodide production, beam currents were 5.0 nA and total energy deposited was usually 1.6×10^{20} eV in 20 mL of sample to give a total dose of about 1.3 kGy (130 krad). In polymer production, beam currents were 5.0 nA and total energy deposited was usually 6.2×10^{21} eV in 20 mL of sample to give a total dose of about 50 kGy (5 Mrad). The beam diameter was 6.35 mm, and completely stripped ions were used. The sample cell for heavy ion irradiation was made of Pyrex with a mica window of about 5.0 mg/cm^2. The sample was purged with ultra-high-purity helium for 10 min before the irradiation.

γ-Radiolysis. Irradiations of benzene−iodine solutions were carried out using a Shepherd 109−68 ^{60}Co γ-source in the Radiation Laboratory at the University of Notre Dame. The dose rate was 120 Gy/min (12 krad/min) as determined using the Fricke dosimeter.[27] The absorbed dose in the benzene was assumed to be proportional to its electron density relative to that of the Fricke dosimeter.

Pulse Radiolysis. Pulse-radiolysis experiments were performed using 15 ns pulses of 8 MeV electrons from the Notre Dame Radiation Laboratory linear accelerator (TB-8/16-1S linac). Details of the linac, the spectrophotometric detection setup, and the computer-controlled data acquisition and detection systems are described elsewhere.[28] Dosimetry was performed with N_2O-saturated 10 mM SCN^- solutions using the following parameters for the observed $(SCN)_2^-$: $\lambda = 472$ nm, $\epsilon = 7580$ M^{-1} cm^{-1}, $G = 6.14$ molecules/100 eV. KSCN (Aldrich) was of the highest purity commercially available and was used as received. The pulsed electron beam width was 15 ns with a dose of 30 Gy per pulse, as determined by the thiocyanate dosimeter. All measurements were performed at 20 °C in a quartz cell of 1 cm optical path length. The solutions were degassed with ultra-high-purity nitrogen which flowed through the cell continuously throughout the experiment. The concentration of iodine was 0.1−0.4 mM. Transient absoption data and kinetic traces were averaged over six shots. Analysis of the optical absorption time dependence was done using ORIGIN (Microcal) software.

Product Analysis. Molecular hydrogen, H_2, was determined using an inline technique as previously reported.[29] Gas chromatograph (GC) analysis was carried out using an SRI 8610 equipped with a thermal conductivity detector. The column was a 6.4 mm diameter 13× molecular sieve 3 m long, maintained at 40 °C. The sample cell was made from a quartz cuvette and contained 4.0 mL of sample. The sample was purged with ultra-high-purity argon for 10 min at room temperature and the cell was sealed with a four-way valve during the radiolysis. Irradiations of benzene-iodine solutions were performed with initial iodine concentrations of 0.10−3.0 mM. Following irradiation, the sample cell was opened to the column gas stream using the four-way valve. Calibration was performed by injection of pure hydrogen gas.

Hydrogen iodide was determined according to the method reported elsewhere.[15] In γ-radiolysis, the sample cell was made from a glass cuvette and contained 10 mL of sample. The sample was purged with ultra-high-purity nitrogen for 10 min at room temperature and the cell sealed with a rubber septum. Heavy ion irradiations were performed in the same cell used for molecular hydrogen determination. Irradiations of benzene-iodine solutions were performed with initial iodine concentrations of 0.10−3.0 mM. The hydrogen iodide yields reported here were performed at total doses of 1.50 kGy and were determined using UV−visible spectrophotometry and by ion chromatography. The results using both techniques were essentially the same so the data are given as an average of the two. Ion chromatography (IC) was performed with a Dionex DX320 instrument, equipped with a GP50 gradient pump, a GM-3 gradient mixer, a CD25 conductivity detector with ASRS suppression, an EG40 eluent generator, an AS40 automated sampler and thermal compartment containing a Dionex IonPac AS11 (4 mm × 250 mm) analytical column, and an IonPac AG17 (4 mm × 50 mm) guard column. Optimum ion chromatography conditions eluted with 12 mM NaOH for 7 min, pump flow rate = 1.5 mL min^{-1}, suppressor current of 45 mA, and a column temperature of 25 °C. The injection volume was 25 μL. Data acquired during the determination were collected and processed using Dionex CHROMELEON 6.50 software. UV−visible spectra were measured at $\lambda = 226$ nm with a Hewlett-Packard HP8453 spectrophotometer. Potassium iodine aqueous solutions were used for calibration.

Polymer formation consisting of multiples of C_6 units was determined using gel permeation chromatography (GPC). The sample cell was made from a glass cuvette and contained 10 mL of neat benzene or of benzene-iodine solution. The sample was purged with ultra-high-purity nitrogen for 10 min at room temperature and the cell sealed with a rubber septum. Irradiations of benzene−iodine solutions were performed with initial iodine concentrations of 0.1−1.0 mM. Total doses were varied up to 100 kGy (10 Mrad) at room temperature. Following irradiation, the samples were transferred into a volumetric flask and concentrated to exactly one-hundredth of the original volume using a rotary evaporator. Sample concentrations were then diluted to 1 vol %, by adding tetrahydrofuran (THF). The GPC system was composed of a Waters 515 HPLC pump, a 50 μL sample loop injector, an Eppendorf TC-50 temperature controller, an Eppendorf CH-430 column oven, the Phenomenex columns described below, a Shodex SE-61 refractive index detector, an SRI model 203 A/D converter, and a Pentium processor (PeakSimple 329 software). The molecular weights of benzene radiolysis products were measured by GPC at 40 °C with two 300 mm × 7.8 mm Phenomenex Phenogel 5 μm 50 Å columns using THF as an eluent at a flow rate of 0.6 mL min^{-1}, and calculated from a calibration curve ($r^2 = 0.98$) for standardized polystyrene (Sigma-Aldrich, typical M_w 2500 and 800), *p*-terphenyl (Aldrich), biphenyl (Aldrich), 1-benzene-1-cyclohexene (Aldrich), and benzene. The radiation chemical yield of polymers, G(polymer), in the γ-radiolysis of liquid benzene was calculated from the refractive index peak area relative to the biphenyl yield in liquid benzene, 0.075 molecules/100 eV.[10,11] Polymer structures were established using infrared transmittance spectra (FT-IR) and gas chromatograph−mass spectrometry spectra (GC/MS). In the FT-IR measurements, the crude irradiated sample was dropped on a clean KBr film, and benzene solvent was gradually evaporated off. After complete evaporation of the benzene, the prepared film was examined by transmittance FT-IR using a Bruker Vertex 70 FT-IR spectrometer with a resolution 4 cm^{-1} and 256 scans in the range of 400−4000 cm^{-1}. GC/MS spectra were measured by the electron impact method (EIMS) using a Finnigan Trace GC/

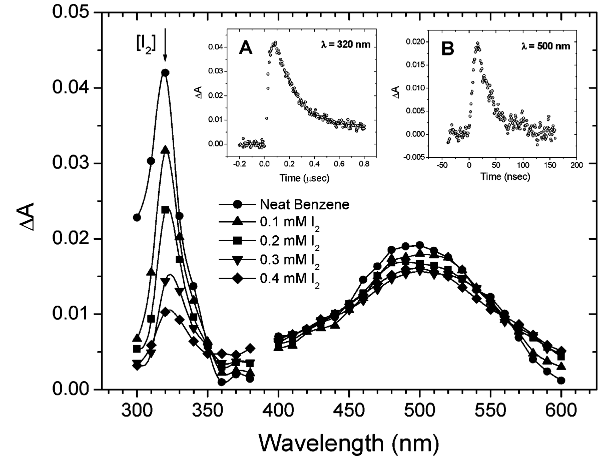


Figure 1. Transient absorption spectra obtained at the absorption maxima (80 ns for the phenyl radical at 320 nm and 15 ns for the singlet excited state at 500 nm) in the pulse radiolysis of a solution of iodine in N$_2$-saturated benzene: (●) neat benzene; (▲) 0.1 mM I$_2$; (■) 0.2 mM I$_2$; (▼) 0.3 mM I$_2$; (◆) 0.4 mM.

MS. Chromatographic separations were made with a 30 m Chrompack CP−Sil-5-CB nonpolar type capillary column. Splitless mode injection of a 1.0 μL solution was used. The initial column temperature was maintained at 120 °C for 10 min during which benzene and iodobenzene were eluted. The temperature was then raised to 200 °C at a rate of 30 °C/min and held for 18 min at this temperature while dimer and trimer eluted.

Radiation chemical yields, *G* values, are given in units of molecules (radicals) formed (or decayed) per 100 eV of total energy absorption.

Results and Discussion

Excimer Formation. The initial products in the pulse radiolysis of liquid benzene are the electron (e$^-$) and the benzene radical cation, which can combine to give benzene singlet and triplet excited states. In the liquid phase, the molecular excited states couple with ground states to give excimers.[32] The benzene singlet excimer is observed in the pulse radiolysis of neat liquid benzene, as shown by the broad absorption band with a maximum at 500 nm (Figure 1). The singlet excimer exhibits a first-order decay with a lifetime of 27 ns (inset B of Figure 1) in good agreement with previous reports.[2,33,34] Little change is observed in the absorption at 500 nm with increasing iodine concentration indicating that iodine quenching of the benzene singlet state is not significant. Consequently, products derived from the benzene singlet excimer are expected to be invariant with respect to the addition of iodine. The benzene triplet excimer is reported to have a lifetime of 4.9 ns,[9] but this species was not observed in the pulse radiolysis experiments. Fast electron pulse radiolysis measurements employing scavengers indicate that the initial yield of the benzene triplet state due to neutralization reactions is about 4.2 molecules/100 eV. [7,8]

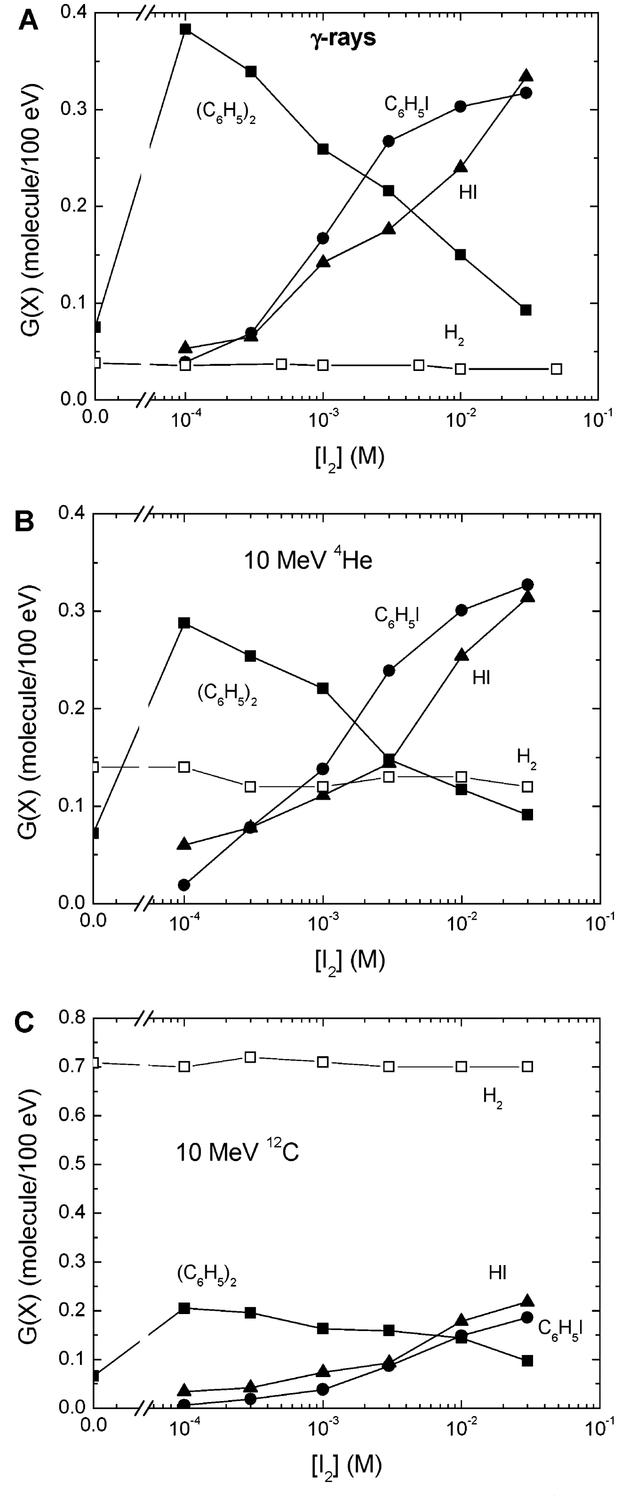


Figure 2. Radiolysis of liquid benzene for (A) γ-rays, (B) ^{4}He ions, and (C) ^{12}C ions as a function of iodine concentration: (■) biphenyl; (●) iodobenzene; (▲) hydrogen iodide; (□) molecular hydrogen.

Molecular Hydrogen Production. The major observed product from benzene radiolysis with high LET radiation is molecular hydrogen, the yield of which increases with LET.[24] One might expect a significant contribution to molecular hydrogen production from H atom abstraction reactions by H atoms produced in the decomposition of the benzene triplet excited state.[35] However, such a reaction is first order and would not show a strong LET dependence. Measurements of the fluorescence in the radiolysis of benzene with a variety of heavy ions show an inverse correlation between fluorescence yields and molecular hydrogen yields as a function of LET, indicating that the singlet excited state of benzene is the precursor of molecular hydrogen.[23] The yields of molecular hydrogen, G(H$_2$), are shown as functions of iodine concentration for γ-rays, ^{4}He ions, and ^{12}C ions in Figure 2. Molecular hydrogen yields in the radiolysis of neat benzene using γ-rays, ^{4}He ions, and ^{12}C ions are 0.038, 0.14, and 0.71 molecues/100 eV, respectively, and are in good agreement with previously reported values.[10] The molecular hydrogen yields in the radiolysis of benzene with added iodine are independence of iodine concentration. This result is consistent with the invariance of the singlet excimer with added iodine, giving further indication that the singlet excimer is the precursor of molecular hydrogen even at high LET.

Hydrogen Iodide Production. The initial radical species produced by the decay of the benzene triplet excimer are a phenyl radical and a hydrogen atom.[1] In iodine solutions, these radicals react to give iodobenzene and hydrogen iodide, as shown in reactions 1−3, respectively.

$$C_6H_6{}^*(T) \rightarrow C_6H_5{}^\bullet + H^\bullet \tag{1}$$

$$C_6H_5{}^\bullet + I_2 \rightarrow C_6H_5I + I^\bullet \tag{2}$$

$$H^\bullet + I_2 \rightarrow HI + I^\bullet \tag{3}$$

Excited states are written here as monomers for simplicity even though the excimer is implied. Previous iodine scavenging studies in the γ and heavy ion radiolysis of benzene identified phenyl radicals through the yield of iodobenzene,[10,11] but quantification of the hydrogen iodide has not been performed at high LET. Figure 2 shows the yields of hydrogen iodide as a function of iodine concentration for γ-rays, ^{4}He ions, and ^{12}C ions. It can be seen that hydrogen iodide yields increase with increasing iodine concentration for all the radiation types examined here and that the yield of hydrogen iodide closely follows that of the iodobenzene. The results at different LET strongly suggest that there is a common precursor for H atoms and phenyl radicals. The most likely source of these radicals is the benzene triplet excited state.

The increase in hydrogen iodide yields with increasing iodine concentration is similar for both γ-rays and ^{4}He ions. An increase in hydrogen iodide yield is also observed with ^{12}C ions, but the highest yield at 30 mM iodine is only 65% of that observed with γ-rays. The lower yields for hydrogen iodide with ^{12}C ions can be attributed to combination reactions of the H atom and phenyl radical or a decrease in the benzene triplet excited state, possibly by triplet−triplet annihilation. The ^{12}C ions of 10 MeV energy have a track average LET of 686 eV/nm compared to the 0.2 eV/nm for γ-rays.[26] Radical−radical reactions are enhanced in LET ion tracks with no effect due to LET expected on the first-order radical-iodine scavenging reaction.[10,35] No independent evidence exists for a decrease in benzene triplet excimer yields at high LET so the reason for the decrease in H atom yields with increasing LET is uncertain.

In neat benzene, H atoms will react with a solvent molecule to give the cyclohexadienyl radical, reaction 4.

$$H^\bullet + C_6H_6 \rightarrow C_6H_7{}^\bullet \tag{4}$$

On the addition of iodine, the formation of the cyclohexadienyl radical occurs in competition with the production of hydrogen iodide. Reaction 4 occurs with a rate constant of about 1.1 × 10^9 M^{-1} s^{-1} in aqueous solutions, so that the lifetime of the H atom is about 80 ps in neat benzene.[36,37] The rate of iodine reaction with phenyl radicals, reaction 2, is 9.3 × 10^9 M^{-1} s^{-1} as given below, and a similar rate is normally expected for the iodine reaction with H atoms, reaction 3. However, using the value of 9.3 × 10^9 M^{-1} s^{-1} for the rate coefficient of reaction 2 at an iodine concentration of 30 mM gives 3.6 ns as the lifetime of H atoms resulting in the iodine scavenging of only 2% of the H atoms. Since the assumed iodine scavenging rate coefficient is nearly diffusion-controlled, the results suggest that H atom scavenging by benzene is not nearly as efficient as previously thought, i.e., use of the measured rate coefficient in aqueous solution greatly overestimates the value in neat benzene.

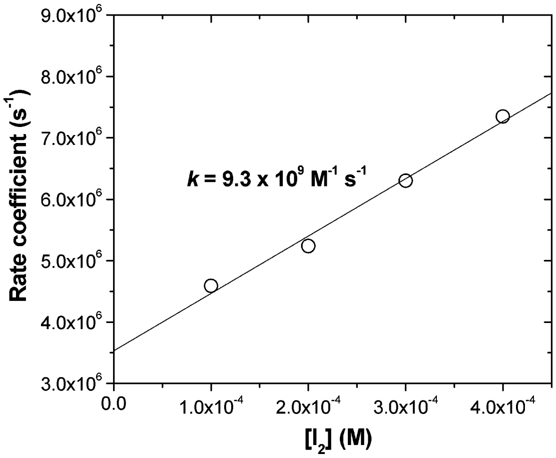


Figure 3. Rate coefficients for iodine reaction with phenyl radical as a function of iodine concentration.

Phenyl Radical Reactions. In the radiolysis of liquid benzene, the benzene molecule is decomposed to give a phenyl radical and an H atom by the decomposition of the triplet excited state, reaction 1. The phenyl radicals will react with benzene to give the phenylcyclohexadienyl radical ($C_6H_5{-}C_6H_6{}^\bullet$), reaction 5.[12,19,35,38]

$$C_6H_5{}^\bullet + C_6H_6 \rightarrow C_6H_5{-}C_6H_6{}^\bullet \tag{5}$$

In the presence of iodine, the formation of the phenylcyclohexadienyl radical is in competition with the production of iodobenzene, reaction 2. The observed rate coefficients for the alkyl radical−iodine reaction in neat liquid cycloalkanes of C_5 to C_{10} are proportional to a combination of a diffusion-controlled rate coefficient, which scales inversely with viscosity of the media, and an activation-controlled rate coefficient, which is the same for all media.[39] The rate of iodine reaction with cyclohexyl radical in cyclohexane is 1.2 × 10^{10} M^{-1} s^{-1}, and the rate for the phenyl radical in reaction 2 is expected to be similar.[39]

The rate of iodine reaction with phenyl radical in liquid benzene radiolysis was determined from transient absorption measurements using pulse radiolysis techniques. Phenyl radical formation by the decay of the benzene triplet excited state could not be observed on the time scales used in these experiments. Figure 1 shows the transient absorption spectra obtained in the pulse radiolysis of benzene with various amounts of added iodine. A sharp absorption band at 320 nm is detected in neat benzene. This transient is assigned to the phenyl radical and it has a first-order decay with a lifetime of 165 ns (inset A of Figure 1) in agreement with previous reports.[9,33,40] The corresponding rate coefficient for the phenyl radical addition to benzene is 5.4 × 10^5 M^{-1} s^{-1}.

In the presence of iodine, the band at 320 nm decreases markedly with increasing iodine concentration due to the reaction of iodine with phenyl radical. The rate coefficients for the reaction of phenyl radicals with iodine were determined by the optimized fits to the decay of the absorbance of the phenyl radical at 320 nm with each iodine concentration. A plot of the rate coefficients as a function of iodine concentration is shown in Figure 3. The results show a linear correlation with a slope of 9.3 × 10^9 (r^2 = 0.99) and an intercept of 3.5 × 10^6. The rate coefficient of reaction 2 is estimated to be 9.3 × 10^9 M^{-1} s^{-1}, which is similar to the diffusion-controlled rate coefficient

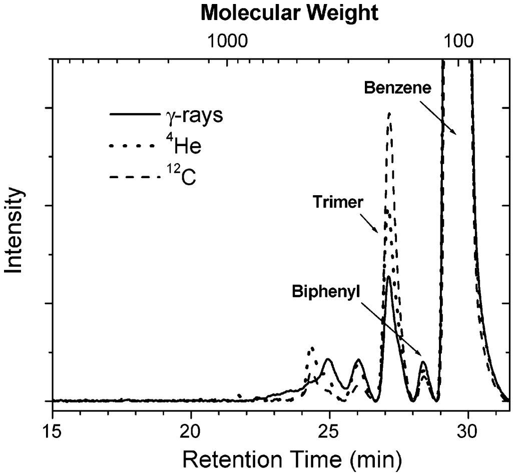


Figure 4. GPC profiles of polymer production obtained by the radiolysis of neat benzene for γ-rays, ^{4}He ions, and ^{12}C ions with a dose of 50 kGy (5.0 Mrad).

of 1.2×10^{10} M^{-1} s^{-1} for the reaction of iodine with cyclohexyl radicals in cyclohexane.[39] The intercept of the fitted line in Figure 3 is due to the phenyl reaction with benzene, reaction 5. The value of the intercept is 3.5×10^6 s^{-1} and thereby the rate coefficient of reaction 5 is estimated to be 3.1×10^5 M^{-1} s^{-1} (3.5×10^6 s^{-1}/11.2 M) in reasonable agreement with the directly determined value of 5.4×10^5 M^{-1} s^{-1} given above.

Biphenyl Production. Biphenyl can be formed by the combination of phenyl radicals, reaction 6.[7,8]

$$C_6H_5^{\bullet} + C_6H_5^{\bullet} \rightarrow (C_6H_5)_2 \qquad (6)$$

Alternatively, biphenyl production is possible through the disproportionation reactions of the phenylcyclohexadienyl. Biphenyl yields as a function of iodine concentration and LET have been discussed at length elsewhere.[10] The most likely source of biphenyl is not reaction 6, but instead it is due to a first-order process since its yield is independent of LET.

Polymer Production. Polymer yields in liquid benzene radiolysis were determined by direct measurements using GPC techniques. This direct approach to measure polymer helps clarify the role of the benzene triplet excimer at high LET. Figure 4 shows the GPC time profiles of polymer production obtained by the radiolysis of neat benzene for γ-rays, ^{4}He ions, and ^{12}C ions with a dose of 50 kGy (5 Mrad). GPC gives a very good estimate of mass for a given class of compounds. The molecular weights of benzene radiolysis products are shown on the upper axis of Figure 4. A major peak in the chromatograph is observed at an elution time of 27.1 min and is assigned to trimers by comparing the elution time with that of a standard. The peaks in the molecular weight region higher than that of trimers are attributable to tetramers and higher molecular weight compounds. The elution times are 26.1 min and lower than 25.5 min, respectively. The average molecular weight of the broad band observed below 25.5 min is about 500 Da. The peaks of biphenyl and benzene are observed at elution times of 28.5 and 29.4 min, respectively.

Polymer yields were determined by scaling the relative GPC responses to that for the biphenyl found in γ-radiolysis, for which the absolute yield is known from previous studies.[10] The resultant yields of biphenyl are given in Table 1 as 0.075, 0.057, and 0.045 molecules/100 eV for γ-rays, ^{4}He ions, and ^{12}C ions, respectively, and are in good agreement with previous estimates.[10] The yields of trimers in the radiolysis of neat benzene are 0.39, 0.58, and 0.83 molecules/100 eV, respectively, for γ-rays, ^{4}He ions, and ^{12}C ions as shown in Table 1. Specific trimer isotopes could not be identified by GPC. Trimer yield increases with increasing LET and the yield of trimers for ^{12}C ion radiolysis is 2.1 times higher than that for γ-radiolysis. A possible source of trimers is the combination of the phenylcyclohexadienyl radical with the cyclohexadienyl radical, which are produced in reactions 5 and 6, respectively.

TABLE 1: Polymer Yields in the Radiolysis of Liquid Benzene[a]

	neat solutions			γ-rays	
product	γ-rays[b]	^{4}He[b]	^{12}C[b]	0.1 mM I$_2$	1 mM I$_2$
biphenyl	0.075[c]	0.057	0.045	0.38[c]	0.26[c]
trimer	0.39	0.58	0.83	0.29	0.10
>C$_{18}$	0.18	0.14	0.10	0.12	0.010
polymer[d]	0.57	0.72	0.93	0.41	0.11

[a] Dose of 50 kGy (5Mrad). [b] Track average LET: γ-rays, 0.2 eV/nm; ^{4}He, 99 eV/nm; ^{12}C, 686 eV/nm. [c] Reference 10. [d] Sum of trimer and >C$_{18}$.

$$C_6H_5{-}C_6H_6^{\bullet} + C_6H_7^{\bullet} \rightarrow C_{18}H_{18} \qquad (7)$$

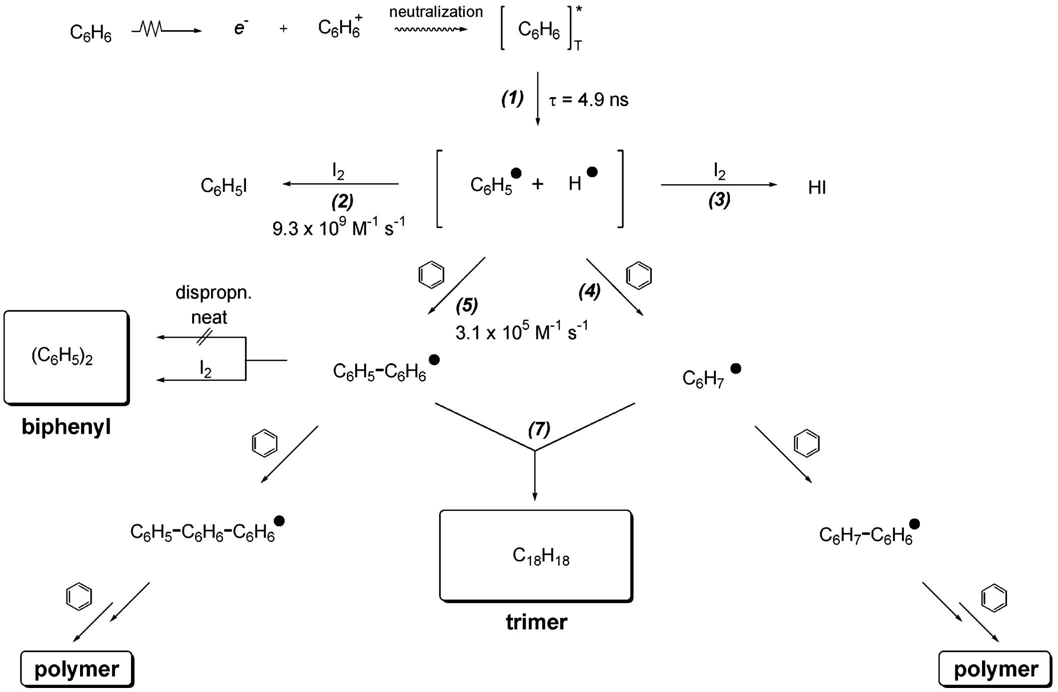
Carbon ions of 10 MeV energy have a track average LET of 686 eV nm^{-1} compared to the 0.2 eV nm^{-1} for γ-rays.[26] Reaction 7 as a source of trimers is consistent with an increase in the number of radical−radical reactions with increasing LET due to the increase in local radical concentrations.[31] On the other hand, products with mass greater than that of trimers (>C$_{18}$) show a decrease in yields with increasing LET; see Table 1. The lower yields for >C$_{18}$ products with increasing LET can be explained by the increased importance of radical−radical reactions and subsequent reduction in the number of radical−solvent reactions. [31,41−43] The >C$_{18}$ products in benzene probably depend on reactions of the benzene with $C_6H_7^{\bullet}$ or with $C_6H_5{-}C_6H_6^{\bullet}$ produced in reactions 4 and 5, respectively. These reactions are first order and not dependent on LET. However, since reaction 7 is enhanced at higher LET the yield of higher polymers (>C$_{18}$) actually decreases.

Iodine scavenging has been used to probe the pathways to polymer formation in benzene irradiated with γ-rays. Phenyl radicals can be scavenged by iodine,[10,11] and their role or that of other radical precursors to polymer formation can be affected by the addition of iodine. As shown in Table 1, trimer yields are 0.29 and 0.10 molecules/100 eV at iodine concentrations of 0.1 and 1 mM, respectively. The yields of >C$_{18}$ products also decrease with increasing iodine concentration. Polymer yields, which include the yields of trimers and products >C$_{18}$, are found to decrease markedly with increasing iodine concentration indicating the predominance of radical precursors. Phenyl radicals and H atoms produced by the decomposition of the benzene triplet excimer are the likely precursor radicals leading to polymer formation.

Spectroscopic examination of the polymer was performed to obtain structural information. The crude solutions obtained by the radiolysis of neat benzene with γ-rays, 10 MeV ^{4}He ions, and 10 MeV ^{12}C ions to a dose of 50 kGy (5 Mrad) are yellow in color with the depth of color increasing with the LET of the radiation. The UV−visible spectrum of neat benzene has an absorption edge at $\lambda = 280$ nm with complete absorption at shorter wavelengths. All of the irradiated solutions exhibited a broad absorption band with a shoulder at $\lambda = 320$ nm and with an absorption edge at about $\lambda = 480$ nm that appears to be mainly due to scattered light.

The FT-IR spectra of the polymers obtained by the radiolysis of neat benzene for γ-rays, ^{4}He ions, and ^{12}C ions to a dose of

SCHEME 1: Decomposition of the Triplet Excited State in Liquid Benzene Radiolysis



50 kGy (5 Mrad) are shown in Figure 5. The peak at 3021 cm^{-1} is assigned to an aromatic C−H (ν_{as}(CH)) stretching vibration. Irradiation led to new peaks at 2915 and 2848 cm^{-1}, which are assigned to asymmetric (ν_{as}(CH$_2$)) and symmetric (ν_s(CH$_2$)) methylene stretching vibrations, respectively. The frequency of aromatic ν_{as}(CH) vibrations decreases with increasing LET, whereas the frequency of both ν_{as}(CH$_2$) and ν_s(CH$_2$) increases significantly especially with ^{12}C ion radiolysis. The frequency of methylene stretching is well-known to increase when the methylene group is part of a strained ring.[44] An increase in the frequency of methylene stretching strongly suggests that the polymer possesses a partly saturated ring. Furthermore, the spectra of two trimers isolated using GC/MS show fragment signals at $m/z = 232$, 155, 77 and at $m/z = 234$, 155, 79 which can be assigned to the partly saturated trimers of $C_{18}H_{16}$ and $C_{18}H_{18}$, respectively. The FT-IR and GC/MS results both suggest that the structure of trimer possesses a partly saturated ring.

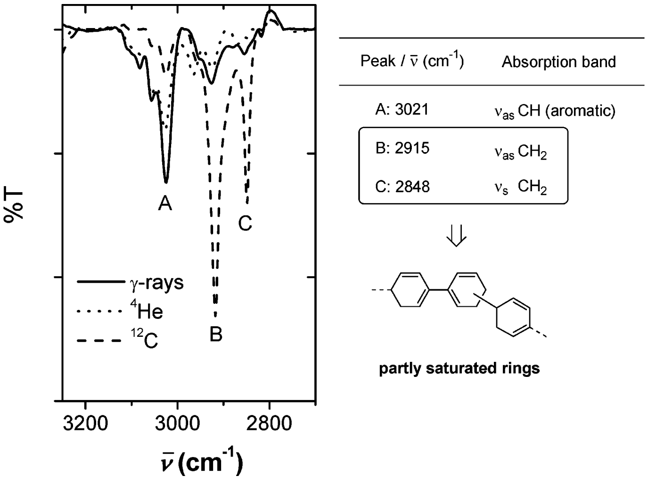


Figure 5. FT-IR spectra of polymer production obtained by the radiolysis of neat benzene for γ-rays, ^{4}He ions, and ^{12}C ions with a dose of 50 kGy (5.0 Mrad).

Decay Pathway of the Triplet Excited State. The preceding discussion on formation of specific products is summarized in Scheme 1, which shows the proposed pathways for the decay of the benzene triplet excited state produced in liquid benzene radiolysis. The total yield of benzene triplet excited state, including intersystem crossing from singlet excimer to the triplet excimer is about 4.8 molecules/100 eV with γ-rays.[7−9] Triplet excited-state yields in benzene are enhanced in the tracks of high LET ions because of the near homogeneous distribution of electrons (e$^-$) and radical cations ($C_6H_5^{\bullet+}$) within the axial direction of the track leading to the statistical maximum of 75% of combination reactions.[23] The triplet excited state then forms an excimer in the liquid by coupling with a ground-state benzene molecule, with a first-order decay lifetime of 4.9 ns.[8] The benzene triplet excimer decays to phenyl radicals and H atoms, reaction 1. The addition of phenyl radical to benzene occurs with a rate constant of 3.1×10^5 M^{-1} s^{-1} to give the phenylcyclohexadienyl radical, reaction 5. The H atoms react with benzene solvent to give cyclohexadienyl radicals, reaction 4. The phenylcyclohexadienyl radical then reacts with cyclohexadienyl radical to give trimers, reaction 7. An increase in the yield of timers with increasing LET is observed suggesting that reaction 7 is the predominant mechanism for trimer formation. The phenylcyclohexadienyl radical undergoes negligible disproportionation to give biphenyl, but the addition of a small amount of iodine efficiently converts phenylcyclohexadienyl radicals to biphenyl.[10,11]

An alternate decay pathway for the phenylcyclohexadienyl radical is to react with benzene to give trimer radicals. The addition of benzene to radicals will continue to make higher molecular weight polymers until radical termination occurs. Such a step−growth radical addition reaction with benzene will also occur with the cyclohexadienyl radical. Decreasing polymer ($>C_{18}$) yields are observed with increasing LET because of the increased importance of radical−radical reactions like reaction 7 over first-order radical addition to benzene reactions. This result shows that intratrack radical−radical reactions have a great influence on the yield of polymers in liquid benzene radiolysis at high LET, but high molecular weight polymers ($>C_{18}$) are not the predominant product. The sum of all the hydrocarbon products with γ-rays is 0.65 molecule/100 eV, which is only

14% of the estimated initial yield of 4.8 molecules/100 eV for the benzene triplet excited state. The lack of radiolytic products suggests that there is an efficient pathway for relaxation of the benzene triplet excited state to the ground state.

Conclusions

The radiation chemical yields of the products formed from the benzene triplet excited state in the γ-ray, 10 MeV ^{4}He ion, and 10 MeV ^{12}C ion radiolysis of liquid benzene have been determined. Iodine scavenging techniques have been used to examine the formation and role of the phenyl radical and of the H atom in liquid benzene radiolysis. Hydrogen iodide yields increase with increasing iodine concentration, matching the iodobenzene yields even at high LET and suggesting that the H atom and phenyl radical have the benzene triplet excimer as a common precursor. Decreasing hydrogen iodide yields are observed with increasing LET due to intratrack radical–radical combination reactions, triplet–triplet annihilation, or due to quenching of the benzene triplet excimer. Pulse radiolysis studies determined the rate coefficients for the reactions of phenyl radicals with iodine and with benzene to be 9.3×10^9 M^{-1} s^{-1} and 3.1×10^5 M^{-1} s^{-1}, respectively. Direct measurements of polymer formation, which refers to trimers and higher order compounds ($>C_{18}$), in liquid benzene radiolysis using γ-rays, ^{4}He ions, and ^{12}C ions at relatively high doses have been examined by using gel permeation chromatography. The yields of trimers increase due to the enhancement of intratrack radical–radical reactions with increasing LET. However, the increased importance of radical–radical reactions leading to trimer formation results in a decrease in the yields of $>C_{18}$ products with increasing LET. Infrared and gas chromatography/mass spectrometry studies found that the trimer possesses a partly saturated ring. A schematic representation for the radiolytic decomposition of the benzene triplet excited state has been proposed.

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