Heavy Ion Radiolysis of Liquid Benzene

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The mechanisms responsible for the main products in liquid benzene radiolysis (biphenyl, molecular hydrogen, and phenyl radical) are probed with protons, helium ions, and carbon ions of a few to 30 MeV energy. Phenyl radical yields have been examined using iodine scavenging techniques. The results are combined with similar data for γ-rays and suggest that phenyl radicals mainly react with benzene to give a long-lived adduct, which leads to polymer formation. Iodine can react with this adduct to give enhanced yields of biphenyl. Biphenyl is the predominant single hydrocarbon product in the radiolysis of neat benzene with a yield of 0.075 molecule/100 eV. Its yield is nearly independent of radiation type and energy suggesting that its formation in neat benzene is due to a fast ion−molecule process and not due to phenyl radicals. The total yield of 0.7 radicals/100 eV is almost entirely due to phenyl radicals and H atoms. A reexamination of the fluorescence from the singlet excited state of benzene suggests that this state is the precursor for molecular hydrogen and acetylene, whereas the triplet excited state decays to phenyl radicals and H atoms. Most of the excited states formed in the γ-radiolysis of benzene seem to decay to ground without formation of any product.

Introduction

Liquid benzene is generally considered to be radiation inert because the observed product yields are much lower than corresponding aliphatic compounds; however, the reason for this stability is not fully understood.[1] Benzene, and by analogy other aromatic compounds, were postulated to offer protection from radiolytic decay when mixed with aliphatic hydrocarbons because of this presumed stability.[2] For such a common molecule, there is still considerable uncertainty in the mechanism of benzene decomposition. The phenyl radical is thought to be the main precursor of the hydrocarbon products, but until recently, the evidence has been circumstantial.[1] A recent study using selective scavenging techniques has directly identified the phenyl radical formation in liquid benzene and determined that its yield can make up a substantial fraction of the total radical yield.[3] The work presented here extends that study to include an examination of the production of phenyl radicals in the radiolysis of benzene with different types of radiation. This fundamental knowledge of the radiolysis of benzene is extremely important because it can be used as a basis of models for other aromatic systems.

The main hydrocarbon product observed in the radiolysis of neat liquid benzene is biphenyl with a yield of about 0.07 molecules/100 eV.[4−8] It is believed that excited benzene formed by the radiation initially decomposes to a phenyl radical and a hydrogen atom.[1] Spin trapping of the radicals in the radiolysis of solid benzene gives evidence for the phenyl radical.[9] Early scavenging studies in the liquid could not identify the phenyl radical, and it was proposed that its addition to benzene was too fast for it to be observed.[4] Labeling studies suggest that the phenyl radical adds to benzene to give the phenylcyclohexadienyl radical, which leads to biphenyl and lesser amounts of other dimers.[4,10] However, experiments with scavengers have show that the total radical production in benzene is about 0.7 molecules/100 eV.[4,11,12] This value is almost an order of magnitude greater than the yield of biphenyl. Most of the benzene decomposition is thought to lead to “polymer” formation consisting of multiples of C_6 units.[1,4] The phenyl radical is believed to have a major role in the formation of almost all of the major hydrocarbon products from the radiolysis of benzene. Therefore, a thorough examination of its chemistry would give a significant amount of information on the radiolysis of liquid benzene. Iodine scavenging techniques have successfully examined primary radical formation in cyclic alkanes[13−15] and more recently in the γ-radiolysis of benzene.[3] These techniques are expanded in this work to include different types of radiation in order to provide fundamental information on the fate of the phenyl radical in the radiolysis of liquid benzene. Variation in particle LET (linear energy transfer, $= -dE/dx$) influences radical decay kinetics, which can be useful to distinguish between different mechanisms.

The major observed product from benzene radiolysis at high LET is molecular hydrogen, see ref 16 and references therein. Burns and co-workers have long proposed that second-order reactions of the singlet excited state of benzene lead to the formation of molecular hydrogen.[8,17,18] Recent studies attempted to examine the fluorescence induced by the radiolysis of benzene with different types of radiation in order to directly compare excite state yields with those of molecular hydrogen.[19] Unfortunately, it was later discovered that an artifact of the experimental setup was contributing to the observed fluorescence at high LET. These experiments have been repeated using a slightly different experimental radiolysis cell, and the results are reported here. Correlation of a given product with its precursor state allows one to predict radiation chemical yields with various types of radiation and for compounds difficult to examine directly.

In this work, the radiolysis of benzene and its solutions with iodine were examined with protons, helium ions, and carbon ions and are compared to that found in γ-radiolysis. Very low doses have been used in the scavenging studies to avoid secondary reactions and to enable the use of low iodine

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concentrations. Iodine concentrations were varied from 0.1 to 30 mM. The dependences of biphenyl and iodobenzene yields on iodine concentration are used to examine the temporal variation of the phenyl radical. Fluorescence yields were measured and compared to previous results on the yield of molecular hydrogen formation. A general scheme for the overall radiolysis of benzene is presented.

Experimental Section

Particle irradiations were performed using ^{1}H, ^{4}He, and ^{12}C ions obtained from the 10 MV FN Tandem Van de Graaff of the University of Notre Dame Nuclear Structure Laboratory. The window assembly and irradiation procedure were essentially the same as previously reported.[16,20] Particle energy was determined by magnetic analysis, and energy loss to the windows was calculated using standard stopping power tables.[21] Absolute dosimetry in the scavenging experiments was obtained by collecting and integrating the charge from the sample cell in combination with the particle energy. Beam currents were 5 nA, and total energy deposited was usually $(1-5) \times 10^{20}$ eV in 20 mL of sample to give a total dose of about 100−500 Gy. The beam diameter was 6.35 mm, and completely stripped ions were used. The sample cell for particle irradiation was made of Pyrex with a mica window of about 5 mg/cm^{2}. The sample was purged with ultrahigh purity helium before and during the irradiation.

Irradiations with γ-rays were made using a Gammacell 220 ^{60}Co-γ source having a dose rate of 16 Gy/min. The sample cell was made from a quartz cuvette and contained about 4 mL of sample. The sample was purged with ultrahigh purity helium and the sample cell sealed with a rubber septum before the radiolysis. Dosimetry was made in the same sample cell with the Fricke dosimeter.[22] A correction due to the relative electron densities of the two media was applied. The yields reported here were performed at total doses of 2500 Gy. Product yields were found to be independent of total dose from 1 to 10 kGy.

Fluorescence experiments were performed in exactly the same manner as previously reported using single photon counting techniques.[19] The present experiments utilized a titanium cell window instead of the mica used in the previous studies. Mica appears to scintillate strongly in the region of interest when irradiated with very high LET particles. The sample cell, optics, and photomultipliers were located in a light-tight box capable of accepting the accelerator beam exit window or a small ^{90}Sr−^{90}Y beta source. Therefore, a direct comparison of the fluorescence efficiency with fast electrons and with heavy ions could be made.

Measurements of hydrocarbon product yields were performed with an EXTREL model ELQ-400-1 gas chromatograph-mass spectrometer operating in the selective ion monitoring mode. Iodobenzene was detected at masses 51 and 77, whereas biphenyl was detected at masses 51 and 154. Chromatographic separations were made with a 30 m Chrompack CP-Sil-5-CB apolar type capillary column. Splitless mode injection of a 0.5−1.0 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 11 min at this temperature while biphenyl eluted. A typical chromatogram took about 25 min.

Benzene from Aldrich with a purity of about 99.9% was percolated over activated silica. No detectable quantities of the products formed during the radiolysis, or any unsaturated species, were detected with the mass spectrometer.

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

Selective ion monitoring techniques using a gas chromatograph/mass spectrometer have allowed the usage of doses down to 1 kGy for accurate determination of the biphenyl yield in liquid benzene. The radiation chemical yield of biphenyl in neat liquid benzene has been found to be linear with dose in the range of 1−10 kGy in γ-radiolysis.[3] Linearity was also observed for the heavy ions used in these studies, suggesting that dose effects on secondary reactions are insignificant at the doses used in this work.

Radical Production. The employment of a number of different radical scavengers has shown that the total radiation chemical yield, G value, of radicals in the γ-radiolysis of liquid benzene is 0.72 radicals/100 eV of energy absorbed. [4] Radical identification and their specific yields have proven to be more problematic. The radiolysis of liquid benzene is thought to lead to an excited state that decomposes to a phenyl radical and a hydrogen atom:[1]

$$C_6H_6 \rightsquigarrow C_6H_5^{\bullet} + H^{\bullet} \tag{1}$$

$$H^{\bullet} + C_6H_6 \rightarrow C_6H_7^{\bullet} \tag{2}$$

$$C_6H_5^{\bullet} + C_6H_6 \rightarrow C_6H_5^{\bullet}{-}C_6H_6 \tag{3}$$

Hydrogen iodide formation from iodine solutions demonstrates the production of the H atom, and quantitative analysis gives the HI yield in liquid benzene as 0.7 molecule/100 eV.[23] This value corresponds well with the total iodine, $G(-I_2)$, loss of 0.33.[11] Apparently, the radicals produced in reactions 2 and 3 react with iodine to give HI as previously suggested.[7] Reaction 2 occurs with a rate constant of about 1.1×10^{9} M^{-1} s^{-1}, so in liquid benzene, the lifetime of the H atom is about 80 ps.[24,25] The cyclohexadienyl radical produced in reaction 2 has been identified by ESR studies,[26] but very little is known about its chemistry.

Phenyl radical formation in the radiolysis of liquid benzene has been proposed because of studies based on spin trapping in the radiolysis of solid benzene.[9] Labeling experiments suggest that the phenyl radical reacts with benzene to give a phenylcyclohexadienyl radical, a phenyl radical−benzene adduct.[4,8,10] Evidence for such a radical has been observed in the solid phase.[27] Pulsed ESR experiments have determined that the addition of the carboxyphenyl radical to benzene occurs with a rate constant of about 5×10^{6} M^{-1} s^{-1}, and the rate for the phenyl radical should be similar in magnitude.[28] Therefore, the lifetime of the phenyl radical is only about 18 ns but sufficiently long to be detected with selected scavenging experiments. In the radiolysis of benzene with added iodine, the phenyl radicals will compete in their reactions with iodine to give iodobenzene, reaction 4, and with benzene to give the phenylcyclohexadienyl radical, reaction 3:

$$C_6H_5^{\bullet} + I_2 \rightarrow C_6H_5I + I^{\bullet} \tag{4}$$

Measurement of the iodide yield as a function of iodine concentration gives a good estimation of the temporal dependence of the phenyl radicals. Recent experiments with iodine scavenging in the γ-radiolysis of benzene positively identified phenyl radicals using this technique.[3] The results of these experiments and additional data using ^1H (LET$_o$ = 12 eV/nm),[29] ^4He (LET$_o$ = 99 eV/nm), and ^{12}C (LET$_o$ = 686 eV/nm) ions all at 10 MeV incident energy are shown in Figure 1. It can be seen that iodobenzene yields increase with increasing iodine concentration with similar results for γ-rays, protons, and helium ions. An increase is also observed with carbon ions, but the highest yield at 30 mM iodine is only 60% of that observed with γ-rays.

At the maximum iodine concentration of 30 mM, the iodobenzene yield is 0.32 molecule/100 eV with γ-rays. The limiting phenyl radical yield at infinite iodine concentration is expected to be about 0.37 radical/100 eV, which agrees very well with the total radical yield of 0.72 radical/100 eV.[4] Total radical yields include both the parent radical and the H atom or its adduct. The results suggest that decomposition of the benzene excited state gives only phenyl radicals and H atoms, reaction 1. Formation of other radicals can be considered to be negligible.

The lower yields for iodobenzene with carbon ions can be attributed to faster radical chemistry or lower initial radical yields. Decreasing radical yields with increasing LET were observed with cyclic alkanes.[13−15] Carbon ions of 10 MeV energy have a track average LET$_o$ of 686 eV/nm compared to the 0.2 eV/nm for γ-rays. Radical−radical reactions are enhanced in carbon ion tracks because of the increase in local radical concentrations.[30] The rate of iodine reaction with phenyl radicals is not known, but it can be assumed to be similar to cyclohexyl radicals in cyclohexane, 1.2×10^{10} M^{-1} s^{-1}.[31] The scavenging capacity is defined as the product of the rate coefficient for the scavenging reaction and the scavenger concentration. Scavenging capacities for the phenyl radical by iodine are shown on the upper axis of Figure 1. The inverse of the scavenging capacity is equal to the lifetime of the reactive species. At an iodine concentration of 30 mM, the lifetime of phenyl radicals is about 3 ns. About 40% of the total phenyl radicals produced in 10 MeV carbon ion tracks have reacted in this very short time, probably in combination reactions with H atoms. It is not possible from the iodine scavenging experiments alone to determine if the initial phenyl radical yield is dependent on LET.

Biphenyl Formation. Biphenyl can be formed by the recombination of phenyl radicals, reaction 5, in a manner analogous to the dimer formation in the radiolysis of cyclic alkanes:[13−15]

$$C_6H_5^{\bullet} + C_6H_5^{\bullet} \rightarrow (C_6H_5)_2 \tag{5}$$

$$C_6H_5^{\bullet}{-}C_6H_6 + R\,(R^{\bullet}) \rightarrow (C_6H_5)_2 + RH^{\bullet}\,(RH) \tag{6}$$

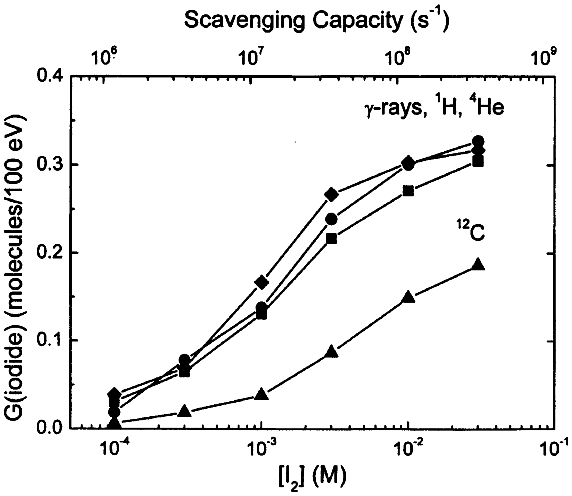

Figure 1. Iodobenzene yields as a function of iodine concentration for 10 MeV ions: (■) ^1H, (●) ^4He, and (▲) ^{12}C ions, this work, and (◆) γ-rays, ref 3.

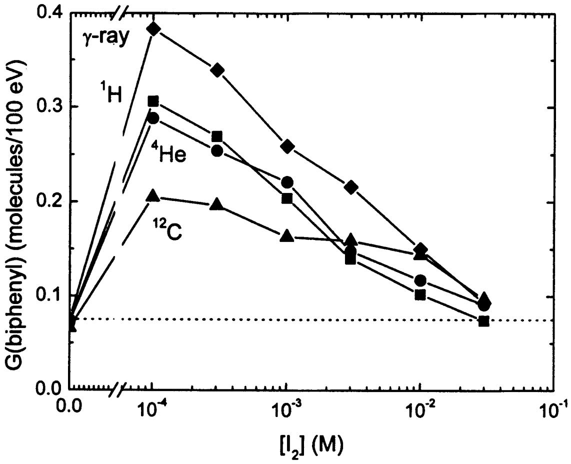

Figure 2. Biphenyl yields as a function of iodine concentration for 10 MeV ions: (■) ^1H, (●) ^4He, and (▲) ^{12}C ions, this work, and (◆) γ-rays, ref 3.

It can also be formed by a hydrogen atom transfer reaction from the phenylcyclohexadienyl radical, reaction 6. Figure 2 shows the radiation chemical yields of biphenyl as a function of iodine concentration for γ-rays and 10 MeV protons, helium ions, and carbon ions. It can be seen that on the addition of 0.1 mM iodine the yield of biphenyl increases substantially. This increase is from 0.073 to 0.31 for protons, 0.073 to 0.31 for helium ions, and 0.066 to 0.21 molecules/100 eV for carbon ions. Iodine may interfere with the neutralization of the benzene cation or it may quench the excited benzene molecule, but both processes are likely to lead to a decrease in product formation.[32−34] An increase in biphenyl must indicate that iodine is causing the phenyl radical−benzene adduct to produce more biphenyl than would normally occur. This result may be due to a simple hydrogen abstraction reaction leading to biphenyl and HI.[7] The reaction by such a small amount of iodine would indicate that the phenyl radical−benzene adduct is relatively long-lived. Several studies have observed anomalous effects when iodine is added post irradiation to benzene, which may be due to reactions of this or other long-lived species.[33−35]

An increase in the iodine concentration leads to a decrease in the biphenyl with a concurrent increase in iodobenzene. Iodine appears to compete effectively with benzene for the scavenging of phenyl radicals. It can be seen from the data of Figure 2 that the yields of biphenyl and iodobenzene are equal at an iodine concentration of about 2 mM for γ-rays, protons and helium ions. This value suggests that the ratio of the rate coefficients k_4 to k_3 is about 5.6×10^3. Assuming the rate coefficient of iodine reaction with phenyl radicals is similar to that for cyclohexyl radicals in cyclohexane, 1.2×10^{10} M^{-1} s^{-1}, gives a value of k_4/k_3 of about 2400 when using the estimated rate coefficient of 5×10^6 M^{-1} s^{-1} for reaction 3.[28] Because the rate coefficient for iodine addition is virtually diffusion controlled, the measured value for the rate coefficient for reaction 2 must be too large by about a factor of 2. The rate coefficient for the addition of phenyl radicals to benzene is probably about 2×10^6 M^{-1} s^{-1}.

The complementary dependence of biphenyl and iodobenzene yields on iodine concentration strongly suggests that the main reaction of the phenyl radical is its addition to benzene. However, the formation of biphenyl in neat benzene is probably

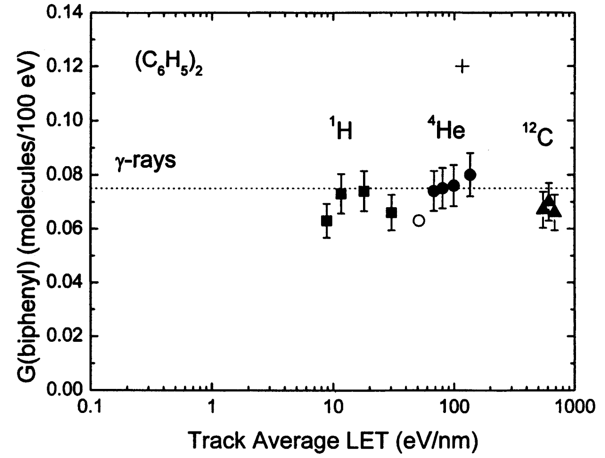

Figure 3. Production of biphenyl as a function of track average LET: (■) ^{1}H, (●) ^{4}He, and (▲) ^{12}C ions, this work; (○) ^{4}He, ref 36; and (+)^{4}He, ref 17. The dotted line is the γ-ray yield.

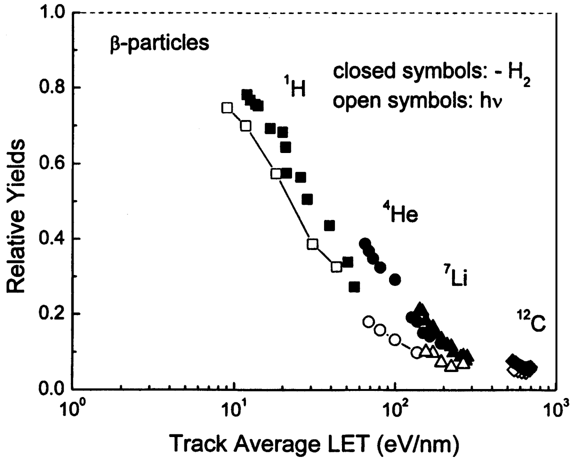

Figure 4. Relative fluorescence yields and inverse relative H_2 yields as a function of track average LET: (□) ^{1}H, (○) ^{4}He, (△) ^{7}Li, and (◇) ^{12}C ions, fluorescence yields, this work; solid symbols are H_2 yields, ref 16.

due to a different mechanism than the subsequent reaction of the phenyl radical−benzene adduct. The yields of biphenyl as a function of track average LET are shown in Figure 3. There are small variations for a given type of ion, but the biphenyl yield in benzene is nearly independent of LET. The LET affects the local concentrations of reactive species and thereby the kinetics. The results for biphenyl suggest that it is produced by a first-order process.

The addition of phenyl radical to benzene is a first-order process, but this reaction is not overall independent of LET. Phenyl radicals are expected to undergo second-order reactions with H atoms leading to a decrease in their yields with increasing LET. This trend can be observed for the iodobenzene formation for carbon ions at high iodine concentrations, see Figure 2. Similar results are observed for parent radical formation in cyclic alkanes.[13−15] It can also be observed for γ-rays, protons, and helium ions that at the highest iodine concentrations essentially all phenyl radicals have been scavenged, but the biphenyl yield is not zero. For all of the radiations used here, the biphenyl radical yield never decreases below a value of about 0.075 molecule/100 eV, as shown by the dotted line in Figure 3. This limiting yield must be due to some other process dominated by a unimolecular reaction. As discussed below, the singlet excited state of benzene is very dependent on LET so it is probably not the source of biphenyl. Biphenyl may be formed in the decay of a triplet excited state, because it is not known if this state is dependent on LET. Previous studies on alkanes show that there is an overall singlet to triplet transition due to random recombination of spin states in high LET tracks.[36] It is not known if this phenomenon is significant in benzene. Another alternative for the production of biphenyl is an ion−molecule reaction of the parent cation with benzene. This reaction is expected to be slow, but the yield of biphenyl is small and probably due to a minor process like this.[37]

Molecular Hydrogen Production. Molecular hydrogen is one of the most examined products in the radiolysis of benzene, especially at high LET.[16] The production of molecular hydrogen in hydrocarbons is usually due to H atom−H atom combination or H atom abstraction reactions. The latter are not expected to be significant in benzene.[38] Scavenger studies with *m*-terphenyl and iodine show that very high solute concentrations are required to lower molecular hydrogen yields in the radiolysis with low LET radiation.[37,39] At 0.2 M iodine, the molecular hydrogen yield is decreased 23% with γ-rays.[39] If a rate constant of 1.2×10^{10} M^{-1} s^{-1} is assumed for H atom reaction with iodine, the scavenging capacity for this reaction at 0.2 M iodine, 2.4×10^9 s^{-1}, is not fast enough to compete significantly with H atom addition to benzene 1.2×10^{10} s^{-1} (11.2 M × 1.1×10^9 M^{-1} s^{-1}). The decrease in molecular hydrogen yields with the addition of *m*-terphenyl or iodine is probably due to a decrease in the yield of the precursor to the H atom.

The most striking feature about benzene radiolysis is that the molecular hydrogen yields increase by over an order of magnitude with increasing LET from γ-rays to 10 MeV carbon ions.[16] The ratio of the molecular hydrogen to acetylene yields is observed to be about 2 and independent of LET, suggesting that these two species are due the same precursor.[8,17,18,35,39,40] Burns and co-workers have long proposed that second-order reactions of excited states of benzene are responsible for both molecular hydrogen and acetylene.[17,18]

The fluorescent yields in the radiolysis of benzene were recently measured with a variety of heavy ions.[19] These measurements showed a dramatic decrease in fluorescence yields with increasing LET suggesting a decrease in the singlet excited state yield. The original published results found a decrease in fluorescence followed by an increase at very high LET. Subsequent experiments found that this increase is due to scintillation of the mica window induced by passage of the high LET ions. This extra emission is at relatively long wavelengths and is not observed with a 300−400 nm band-pass filter, which corresponds to the region of emission by the singlet excimer of benzene. The fluorescence yields observed using the same identical techniques as ref 19 using a band-pass filter or a titanium window give the scintillation yields observed in Figure 4. Here, the fluorescence yields are given relative to that found with fast electrons. It can be seen that the fluorescence yields decrease by an order of magnitude with increasing LET from γ-rays to 10 MeV carbon ions.

The excited singlet state of liquid benzene couples with the ground state to give an excimer.[41] The pseudo-first-order rate for the singlet excimer formation is about 1.2×10^{11} s^{-1},[42] whereas its lifetime is about 27 ns.[43−45] Within a few hundred picoseconds following the absorption of energy, the singlet excimer−monomer excited states of benzene are in equilibrium.[43] Benzene strongly self-absorbs light at wavelengths below about 280, so it is actually the excimer decay that is monitored in these experiments. Because the excimer and monomer states are in equilibrium, it is not important which state is being observed and they will be treated as one unit. Cutoff filters also eliminate any emission from higher lying excited states.

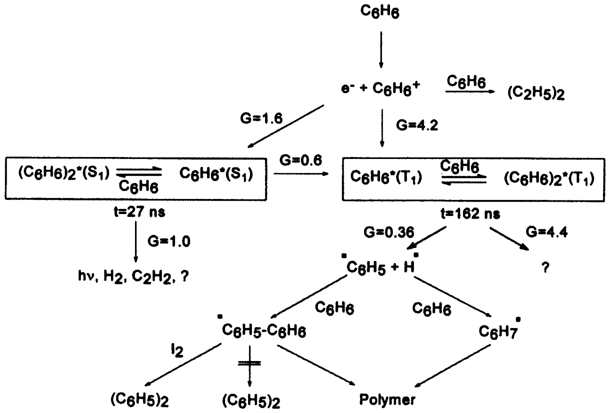

Figure 5. Schematic representation for the radiolytic decomposition of benzene.

The inverse of the molecular hydrogen yields relative to that found with γ-rays, i.e., $G(H_2)_{\gamma-\mathrm{ray}}/G(H_2)_{\mathrm{heavy\ ion}}$, is shown in Figure 4 with the observed decrease in relative fluorescence yields. The agreement between the relative increase in molecular hydrogen yields and the decrease in fluorescence yields is excellent. These results strongly suggest that molecular hydrogen production is due to the decay of a single singlet excited state of benzene. It is not possible in these experiments to determine if it is the singlet state or its precursor that decreases with increasing LET. Because the acetylene yields track those of hydrogen as a function of LET, it must also come from the same singlet excited benzene. Isotopic studies suggest that molecular hydrogen production involves significant scrambling, whereas acetylene essentially has a single benzene molecule as a precursor.[32] Migration of H atoms can be expected from the excimer−monomer excited-state equilibrium. There is an inverse correlation between fluorescence yields and molecular hydrogen yields as a function of LET. Because the molecular hydrogen yield with γ-rays is very small, the normal mode of singlet decay is by fluorescence or intersystem crossing to the triplet state. A second order process must be involved in order to exhibit an LET dependence, so two excited singlet states must be reacting together or the singlet state is reacting with a radical. Fluorescence is thereby decreased and molecular hydrogen yield increased. Only one singlet state decomposes to molecular hydrogen. The benzene singlet excite state has a lifetime of about 27 ns.[44,45] In order for significant reaction between excited states to occur, they must diffuse together within this time period.

Benzene Decomposition Scheme. The absorption of energy by benzene leads to ionization giving an electron and the parent cation with a lifetime of 10−20 ps.[46] Neutralization reactions then produce the singlet excimer−monomer equilibrium state discussed above and the triplet excited state. The yield of the singlet state with γ-rays is about 1.6 molecules/100 eV.[44,47] Measurements of molecular hydrogen yields with a variety of heavy ions extrapolate to a high LET limit of about 0.85 molecules/100 eV.[16] Burns et al.[18] report a molecular hydrogen yield of 1.12 for 21 MeV neon ions, and Boyd and Connor[48] report a yield of 2.14 with fission fragments, which is probably an overestimate. Clearly, most of the singlet excited states can lead to molecular hydrogen production at high LET. There are also obviously other products formed in conjunction with the molecular hydrogen and acetylene. These products have not been identified, and future studies should focus in this area. A simple overview of the formation of the excited states and the products from them are shown in Figure 5.

Neutralization reactions can also lead to the triplet because of the relaxation of spin or cross combination from the multiple ionic pairs formed from the single initial energy loss event. The tracks of higher LET particles lead to an enhancement of triplet formation because of the near homogeneous distribution of electrons and cations within them. At an LET above 100 eV/nm, cross combination reactions dominate the neutralization reactions in alkanes.[36] Specific experiments have not been performed in benzene, but similar results are expected. For fast electrons, the initial yield of benzene triplet state due to neutralization reactions is about 4.2 molecules/100 eV.[49,50] Like the singlet excited state, the triplet also forms an excimer by coupling with a ground-state benzene molecule.[50,51] Both the triplet and singlet excimers are probably in equilibrium with their respective monomers, and both equilibriums are expected to be predominantly in the excimer state.[43] The triplet excimer state decays with a lifetime of about 162 ns.[51] Because radical yields decrease only slightly or remain constant with increasing LET, they are probably due to the decomposition of the triplet excimer. The quantum yield for intersystem crossing from the singlet excimer to the triplet state is 39%,[51] so the total triplet excited-state yield with γ-rays is expected to be about 4.8. It is interesting that the measured total radical yield is about 0.36 radical pairs, so most of the triplet states are decaying to ground without product formation or there are substantial yields of products not yet determined.

Polymer formation in benzene generally refers to the formation of trimers and higher order compounds.[4] The yield of polymer in the γ-radiolysis of benzene is 0.76 molecule/100 eV,[52] which agrees well with the total radical yield and the scheme in Figure 5. Polymer yields increase with increasing LET.[53] This increase is similar to that observed for molecular hydrogen, but polymer formation has not been extensively studied at high LET. However, it is possible that the triplet excited state makes a significant contribution to product formation in the radiolysis of benzene at high LET. Polymer formation is usually determined by the loss of benzene at relatively high doses. Direct measurements of specific products, such as trimers or tetramers, would help clarify the role of the triplet excited state of benzene at high LET.

Conclusions

Phenyl radicals and H atoms make up almost all of the radicals produced in the radiolysis of benzene with a total yield of 0.7 radical/100 eV. These radicals add to benzene and ultimately lead to polymer formation. The phenyl radical−benzene adduct is relatively long-lived and can react with scavengers such as iodine to give enhanced yields of biphenyl. Biphenyl is the predominant single hydrocarbon product in the radiolysis of neat benzene with a yield of 0.075 molecule/100 eV. Its yield is nearly independent of radiation type and energy suggesting that its formation in neat benzene is due to a fast ion−molecule process and not due to phenyl radicals. The similarity of the LET dependence of the fluorescence yields with that of the molecular hydrogen yields suggests that the excited singlet state of benzene is the precursor of molecular hydrogen. The triplet excited state decays to phenyl radicals and H atoms. Most of the excited states formed in the γ-radiolysis of benzene seem to decay to ground without formation of any product. However, extensive product formation may occur through triplet and singlet excited states of benzene at high LET.

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