ARTICLES

Heavy Ion Radiolysis of Liquid Pyridine

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The radiation chemical yields of the main products produced in liquid pyridine radiolysis (molecular hydrogen and dipyridyl) have been examined as a function of particle linear energy transfer (LET) with protons, helium ions, and carbon ions of a few to 30 MeV and compared to γ-radiolysis published in a previous work (*J. Phys. Chem. A* **2005**, *109*, 461). Anthracene and biphenyl scavenging techniques have been used to clarify the role of the triplet excited state. An increase in triplet scavenger concentration leads to a decrease in pyridine triplet excited state with a concurrent decrease in dipyridyl, but formation of the latter does not primarily involve pyridyl radicals expected to be produced in the decomposition of the triplet excited state. A decrease in the yield of dipyridyl and an increase in molecular hydrogen are observed with increasing track average LET. The dipyridyl yield with 10 MeV carbon ions is 0.20 molecules/100 eV, which is only 16% of that of observed with γ-rays. The low yield of dipyridyl with carbon ions is attributed to intratrack triplet−triplet (T−T) annihilation processes due to the increase in local triplet excited-state concentrations with increasing LET. An increasing yield of molecular hydrogen with increasing LET is probably due to an increase in the formation and subsequent decay of singlet excited states produced by the T−T annihilation. A complete mechanism for the radiolysis of liquid pyridine is presented.

Introduction

The formation and decay of excited states play important roles in the radiation chemistry of hydrocarbon liquids. Energy deposited by the passage of ionizing radiation in hydrocarbon liquids is quickly followed by combination reactions of ion pairs, electron-cation, to produce the singlet and triplet excited states.[1] Singlet and triplet excited states yields in the tracks of a heavy ion are different than those of a fast electron because the much higher rate of linear energy transfer (LET) ($= -dE/dx$, the stopping power) increases the concentration of ion pairs in the ion tracks. A fast electron generates a few ion pairs in close proximity, and geminate recombination dominates the decay of the charge species to give singlet excited states. At sufficiently high LET, the combination reactions of ion pairs are completely random because of the near homogeneous distribution of ion pairs along the particle path. Probabilistic arguments then give the relative production of singlet to triplet excited-state formation at 1:3.[2,3] The increase in local concentrations of triplet excited states may lead to different decomposition pathways and thereby affect final product yields.

The effect of LET and ion track structure in radiation chemistry has been examined in the heavy ion radiolysis of various saturated hydrocarbons.[1,4−14] Few products are formed in liquid cycloalkanes and analysis of their yields can lead to estimates of the relative ratio of triplet to singlet excited-state formation. For instance, the observed ratio of the triplet to singlet excited-state formation in liquid cyclooctane radiolysis is 1.3 for fast electrons and increases to about 3.0 with increasing LET. This trend agrees well with the theoretical ratio of the triplet to singlet excited state formed on ion recombination in spurs; the value of triplet/singlet $= 3(n - 1)/(n + 1)$, where n is the number of ion pairs in the spur.[3] Furthermore, the ratio of singlet to triplet excited states observed in the magnetic field dependence of the luminescence from alkane solutes in cyclohexane is 1:3 at LET above 200 eV/nm, which again suggests that most of the chemistry in the high LET track involves a near homogeneous distribution of ion pairs. Fluorescence studies for heavy ion radiolysis of liquid benzene show that the yield of benzene singlet excited state or its precursor decreases with increasing LET, whereas molecular hydrogen yields increase.[15,16] Iodine scavenging studies find that the yields of phenyl radical and H atom formed through the benzene triplet excited state decrease with increasing LET.[17] The exact mechanisms for the decay of pyridine, benzene, and other aromatic hydrocarbon excited states are not known.

Pyridine is the simplest of all nitrogen hetrocycles[18] and relatively few products are formed (molecular hydrogen and dipyridyl isomers) in fast electron or γ-radiolysis.[19,20] The total yield of pyridine triplet excited state is estimated to be 1.30 molecules/100 eV.[21] Dipyridyl is the predominant condensed phase product in the γ-radiolysis of liquid pyridine with a yield of 1.25 molecules/100 eV. Iodine scavenging studies suggest that most dipyridyl has a radical precursor, but only about 10% of that is due to the pyridyl radical, which is the product expected from triplet excited-state decomposition.[19] The pyridine singlet excited state is thought to be the precursor of molecular hydrogen with a yield of 0.027 molecules/100 eV.[19] The yields

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of molecular hydrogen and dipyridyl as a function of particle LET in liquid pyridine will be used as a probe to elucidate the relative roles of singlet and triplet excited states in the radiolysis of pyridine.

In this work, the contributions of the singlet and triplet excited states in the heavy ion radiolysis of liquid pyridine have been examined. The radiation chemical yields of molecular hydrogen and dipyridyl produced in liquid pyridine radiolysis have been determined as a function of particle LET with protons, helium ions, and carbon ions of a few to 30 MeV and compared to γ-radiolysis. Selected scavengers of the pyridine triplet excited state are employed to ascertain its role in final product formation. Polymer yields for γ-rays were measured directly using gel permeation chromatography (GPC) to determine the total radiolytic decomposition of pyridine. A complete scheme for the radiolysis of liquid pyridine is proposed, especially the singlet and triplet excited-state interactions at high LET.

Experimental Section

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

Heavy Ion Radiolysis. Heavy ion 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 the same as previously reported.[22,23] Ion energy was determined by magnetic analysis, and energy loss to the windows was calculated using standard stopping power tables.[24] Absolute dosimetry was obtained by collecting and integrating the charge from the sample cell in combination with the ion energy. Beam currents were 1.0 nA. 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 samples were purged with ultrahigh-purity argon for 10 min before the irradiation.

γ-Radiolysis. Irradiations were carried out using a Shepherd 109−68 ^{60}Co γ-source in the Radiation Laboratory at the University of Notre Dame. The sample cell for γ-irradiation was made from a quartz cuvette and contained 4.0 mL of sample. The dose rate was 100 Gy/min (10 krad/min) as determined using the Fricke dosimeter.[25] The absorbed dose in the pyridine was assumed to be proportional to its electron density relative to that of the Fricke dosimeter.

Product Analysis. Molecular hydrogen was determined using an inline technique as previously reported.[26] Gas chromatographic (GC) analysis was carried out using an SRI 8610 equipped with a thermal conductivity detector. The column was a 6.4 mm diameter 13X molecular sieve 3 m long, maintained at 40 °C. The sample was purged with ultrahigh-purity argon for 10 min at room temperature and the cell was sealed with a four-way valve during the radiolysis. In the triplet excited-state scavenging experiments, the concentration of anthracene was 0.1−100 mM and biphenyl was 0.01 to 3 M. Dose dependent studies were performed with 5.0−20 kGy (500−2000 krad). Following the irradiation, the sample cell was opened to the column using the four-way valve. Calibration was performed by injection of pure hydrogen gas.

Dipyridyl isomers formed in liquid pyridine radiolysis were measured as a function of LET using heavy ion irradiation and as a function of anthracene concentration using γ-irradiation. The dipyridyl isomers were analyzed with a Thermo−Finnigan Trace gas chromatograph−mass spectrometer operating in the selective ion ($m/z = 156$) monitoring mode and under the conditions as previously reported.[19] The sample was purged with ultrahigh-purity helium for 10 min at room temperature, and the cell was sealed with a rubber septum during the radiolysis. The concentration of anthracene was 0.1−100 mM. The dipyridyl yields reported here were performed at total doses of 500 Gy (50 krad).

Polymer formation in the γ-radiolysis of liquid pyridine was determined using GPC as described previously.[17] The sample cell was made from a Pyrex cuvette and contained 10 mL of neat pyridine or of pyridine−iodine solution. The sample was deaerated with ultrahigh-purity helium for 10 min at room temperature, and the cell was sealed with a rubber septum. The concentration of iodine was 0.1−1.0 mM. Total doses were varied up to 50 kGy (5 Mrad) at room temperature. Calibration curves ($r^2 = 0.98$) were determined using standardized polystyrene (Sigma-Aldrich, Typical Mw 2500 and 800), *p*-terphenyl (Aldrich), biphenyl (Aldrich), 2,2′-bipyridyl (Aldrich), 4,4′-bipyridyl (Aldrich), and pyridine. The radiation chemical yield of polymers, G(polymer), in the γ-radiolysis of liquid pyridine was calculated from the refractive index peak area relative to the dipyridyl yield in liquid pyridine, 1.25 molecules/100 eV.[19] Studies to establish the polymer structures were performed using infrared transmittance spectra (FTIR). The crude irradiated sample was dropped onto a clean KBr film and parent pyridine was gradually evaporated. After complete evaporation of the pyridine, the prepared film was examined by transmittance FTIR using a Bruker Vertex 70 FTIR spectrometer with a resolution 4 cm^{-1} and 256 scans in the range of 400−4000 cm^{-1}.

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

The radiolysis of liquid pyridine leads to pyridine singlet and triplet excited states following the neutralization reactions of the electrons with molecular radical cations. The triplet excited state can decompose to a pyridyl radical and an H atom, reaction 1.[19,20] The total radical yield is about 2.8 radicals/100 eV.[27] Combination reactions of pyridyl radicals or their addition to pyridine followed by H atom elimination lead to dipyridyl (dimer) production, which is the predominant condensed phase product observed in the γ-radiolysis of liquid pyridine with a yield of 1.25 molecules/100 eV.[19,20] The corresponding dimer product in liquid benzene is biphenyl with a yield of 0.075 molecules/100 eV.[16] In the presence of iodine, the formation of the dimer is in competition with the production of iodopyridine, reaction 2.

$$C_5H_5N^*(T) \rightarrow C_5H_4N^\bullet + H^\bullet \qquad (1)$$

$$C_5H_4N^\bullet + I_2 \rightarrow C_5H_4IN + I^\bullet \qquad (2)$$

Analogous reactions occur in the radiolysis of liquid benzene with added iodine. Figure 1 shows the yields of dimers and molecular iodides as a function of iodine concentration for the γ-radiolysis of liquid pyridine and of liquid benzene. The benzene results are taken from previous studies.[16] Both systems show an increase in dimer yield on the addition of a small amount of iodine due to the dehydrogenation of the molecular radical−parent molecule complex. This complex would normally lead to polymer formation as discussed below. In benzene, an increase in the iodine concentration leads to a decrease in the biphenyl yield with a concurrent increase in iodobenzene

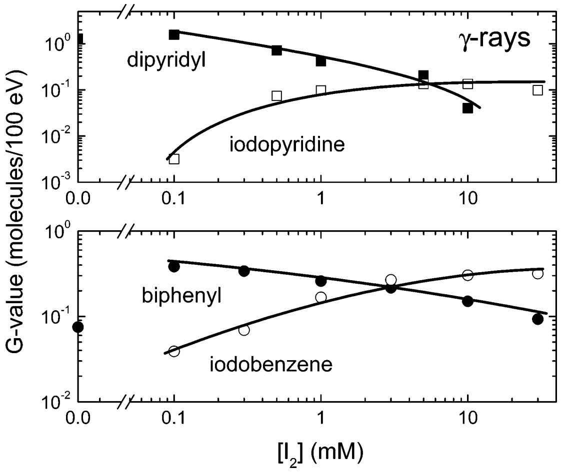


Figure 1. The yields of dimer and iodoaromatics as a function of iodine concentration for the γ-radiolysis of liquid pyridine and of liquid benzene (ref 16): (■) dipyridyl, (□) iodopyridine, (●) biphenyl, and (○) iodobenzene.

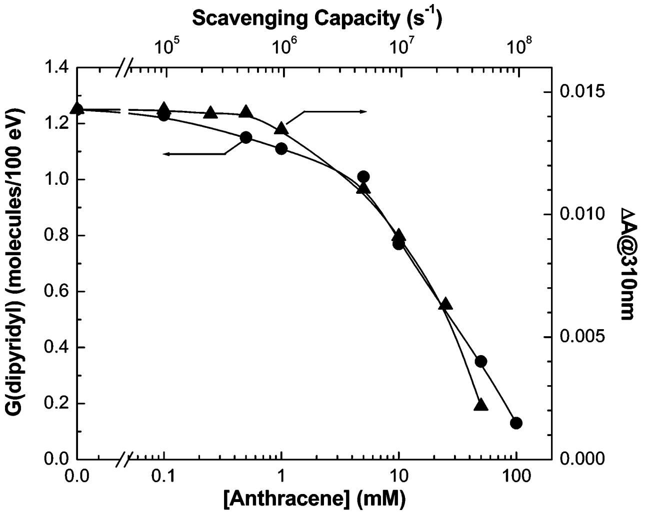


Figure 2. The yields of dipyridyl with γ-rays and the absorption of the pyridine triplet excited state, monitored by pulse radiolysis at 310 nm (ref 21), as a function of anthracene concentration, [Q].

yield. At 30 mM iodine, the yield of iodobenzene rises to 0.32 molecules/100 eV, which agrees well with the yield of biphenyl at 0.1 mM iodine. The symmetrical dependence of the yields of biphenyl and iodobenzene on iodine concentration suggests that the formation of biphenyl in the presence of iodine is due in part to the radical mechanism involving phenyl radical addition to benzene. At the very highest iodine concentration, the biphenyl yield is essentially the same as the value in neat benzene. This limiting biphenyl yield is invariant with LET, as discussed below, and probably is due to a nonradical mechanism. In pyridine, the yield of iodopyridine also increases with increasing iodine concentration. At 30 mM iodine, most of the dipyridyl is scavenged, but the yield of iodopyridine is only about 10% of the yield of dipyridyl at 0.1 mM iodine or in the neat liquid. The results suggest that 90% of the formation of dipyridyl occurs by a mechanism that does not include a pyridyl radical precursor. A few percent of the original dipyridyl yield remains at the highest iodine concentration possible suggesting that most of the dimer has a radical precursor. At most, only a few percent of dimer formation is due to a nonscavengable process.

Pyridine Triplet Excited-State Scavenging. The pyridine triplet excited state was previously determined to be 1.30 molecules/100 eV, which is very similar to dipyridyl yields.[21] Figure 2 shows the yields of dipyridyl with γ-rays and the absorption of the pyridine triplet excited state, monitored at 310 nm and 5 ns in pulse radiolysis,[21] as a function of anthracene concentration, [Q]. The scavenging reaction proceeds by energy transfer from the pyridine triplet excited state to Q giving pyridine in its ground state, S_0, and the triplet excited state of the quencher, Q*(T), as follows.

$$C_5H_5N^*(T) + Q \rightarrow C_5H_5N(S_0) + Q^*(T) \qquad (3)$$

An increase in the anthracene concentrations leads to a decrease in the absorption of pyridine triplet excited state at 310 nm with a concurrent decrease in the dipyridyl. The rate coefficient for the reaction of the pyridine triplet excited state with anthracene is estimated to be 9.5×10^8 M^{-1} s^{-1}.[21] Scavenging capacities for the pyridine triplet excited state by anthracene are defined as the product of the anthracene concentration and the scavenging rate coefficient and are shown on the upper axis of Figure 2. The inverse of the scavenging capacity is equal to the lifetime of the reactive species. Direct measurements show the pyridine triplet excited state has a lifetime of 72 ns.[21] The corresponding half-life agrees well with the inverse of the scavenging capacity at one-half of the original dipyridyl yield. The results strongly suggest that a pyridine triplet excited state is the predominant precursor of dipyridyl.

Dipyridyl Production. The scavenging experiments suggest that most of the dipyridyl production is due to a triplet excited-state decay process. Of course, the pyridine triplet excited state is expected to decay to the pyridyl radical. Pyridyl radicals may react with the parent pyridine giving a pyridyl radical−pyridine complex. Dehydrogenation of this species then gives dipyridyl. The scavenging results of Figure 1 comparing the formation of iodopyridine with the decay of dipyridyl suggest that this mechanism accounts for only 10% of dipyridyl formation. Pyridiniumyl radical cation ($C_5H_5N^{\bullet+}$) can react with parent pyridine to give a charge-transfer complex, $(C_5H_5N)_2^{\bullet+}$. Deprotonation of this species also may give the pyridyl radical−pyridine complex. This mechanism was investigated at length elsewhere and was found to have a negligible contribution to dipyridyl formation.[21] Another possible mechanism for the production of dipyridyl is the formation of an excimer by coupling of the pyridine triplet excited state with a ground state pyridine molecule, reaction 4. Dehydrogenation of the triplet excimer then gives dipyridyl, reaction 5.

$$C_5H_5N^*(T) + C_5H_5N \rightarrow (C_5H_5N)_2^*(T) \qquad (4)$$

$$(C_5H_5N)_2^*(T) \rightarrow (C_5H_4N)_2 + 2H^\bullet \qquad (5)$$

The data of Figure 1 suggests that the excimer can be scavenged by iodine or that reaction 5 is a two-step process with a pyridyl radical−pyridine complex being formed by the excimer decay. H atom production is assigned to reaction 5, because the LET effects discussed below show that the dipyridyl yields decreases with increasing LET while the H_2 yields increase. Measurements of HI may resolve this mechanism, but attempts to quantitatively determine HI have not been successful.

The yields of dipyridyl in neat liquid pyridine were determined at high LET to help elucidate the mechanism. Figure 3 shows the yields of dipyridyl in pyridine (and of biphenyl in benzene[16]) as a function of track average LET. Dipyridyl yields in the radiolysis of neat liquid pyridine using γ-rays (LET =

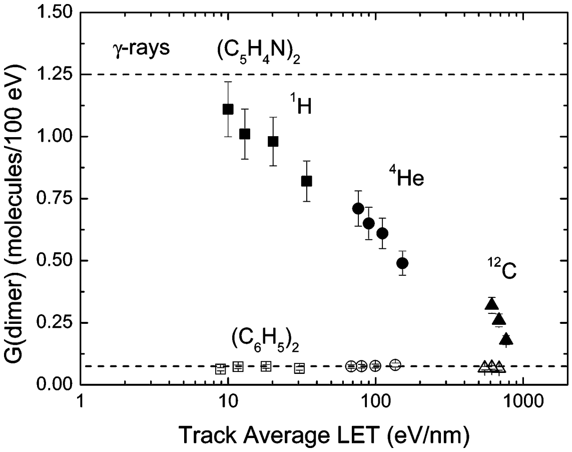


Figure 3. The yields of dipyridyl in pyridine and of biphenyl in benzene (ref 16) as a function of track average LET with γ-rays, ^1H ions, ^4He ions, and ^{12}C ions.

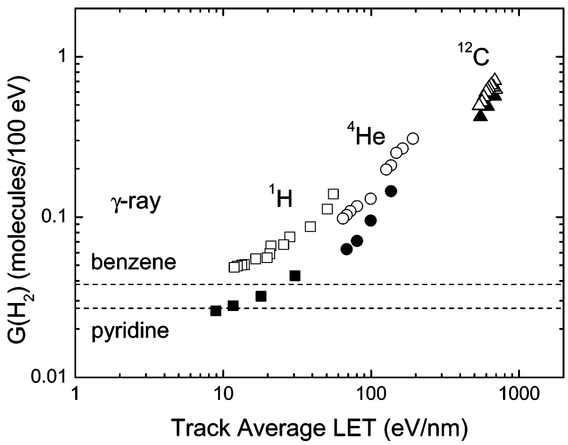


Figure 4. The yields of molecular hydrogen in pyridine and in benzene (ref 16) as a function of track average LET with γ-rays, ^1H ions, ^4He ions, and ^{12}C ions.

0.2 eV/nm), 10 MeV ^4He ions (LET = 99 eV/nm), and 10 MeV ^{12}C ions (LET = 686 eV/nm) are 1.25, 1.15, 0.62, and 0.20 molecues/100 eV, respectively. Dipyridyl is formed by the decay of a triplet excited state as described above. An overall singlet to triplet excited state transition due to random recombination of spin states in high LET tracks is expected to result in an increase in dipyridyl yields with increasing LET.[28] A decrease in dipyridyl yields with increasing LET suggests that the yield of the triplet excited state decreases with increasing LET. On the other hand, biphenyl yields are 0.075 molecues/100 eV with γ-rays as shown by the dash line in Figure 3, and they are independent of LET suggesting its formation by a first-order process.[16] Different order processes for dimer production must be occurring in pyridine and in benzene.

Molecular Hydrogen Production. The molecular hydrogen yield in the γ-radiolysis of liquid pyridine is 0.027 molecues/100 eV,[19,20] which is on the same order as the determination of 0.038 molecues/100 eV for molecular hydrogen in the γ-radiolysis of liquid benzene.[29] Figure 4 shows the yields of molecular hydrogen in pyridine and in benzene[16] as a function of track average LET using γ-rays, ^1H ions, ^4He ions, and ^{12}C ions. An increase in the yield of molecular hydrogen with increasing LET for pyridine is observed. Molecular hydrogen yields in the radiolysis of neat liquid pyridine using γ-rays, 10 MeV ^1H ions, 10 MeV ^4He ions, and 10 MeV ^{12}C ions are 0.027, 0.12, and 0.72 molecues/100 eV, respectively. The increase is very similar to the heavy ion radiolysis of liquid benzene. A possible source of molecular hydrogen is the H atom−H atom reaction, which is a second-order process that is dependent on LET. However, scavenger experiments show no dependence of molecular hydrogen yields on the addition of iodine suggesting that the H atom is not a major precursor to H_2.[30] H atom combination reactions are expected to be negligible considering the high-scavenging capacity of the molecular pyridine for H atom addition reactions. Molecular hydrogen has been shown to be due to the decay of the singlet excited state in the radiolysis of liquid benzene.[15−17] Singlet excited states of pyridine also could be the precursor of molecular hydrogen. No fluorescence was observed in the radiolysis of pyridine employing a technique identical to that used successfully on benzene.[15] Pyridine exhibits a very low fluorescence quantum yield, followed by an ultrafast nonradiative deactivation process[31−36] when excited in higher energy singlet states above the S_1 state.[29] This phenomenon is termed the "channel three" process.[37] The fluorescence decay lifetime is estimated to be 20 ps[38,39] and intersystem crossing for singlet state, $S_1 \rightarrow T$, occurs with a relatively high yield.[33,34]

Bimolecular Deactivation of the Triplet Excited State. Since the pyridine triplet excited states are long-lived (72 ns),[21] there is a high probability of two lowest triplet states (T_1) reacting to form a higher energy singlet excited state and the ground state. This T−T annihilation process is allowed by the Dexter mechanism, reaction 6.[31,40]

$$C_5H_5N^*(T_1) + C_5H_5N^*(T_1) \rightarrow C_5H_5N^*(S_{n\geq 1}) + C_5H_5N(S_0) \tag{6}$$

Reaction 6 will exhibit a strong LET dependence due to the increase in local pyridine triplet excited state concentrations in heavy ion tracks leading to a decrease in pyridine triplet excited state yields and dipyridyl yields. A higher energy singlet excited-state produced in this process may be the precursor to molecular hydrogen yields, which increase with increasing LET. Callomon et al.[37] report the formation of molecular hydrogen in benzene when given an excitation of ~3000 cm^{-1} of excess vibrational energy in the excited singlet state. LaVerne[15] has shown that the yield of molecular hydrogen increases with a concomitant drop in the fluorescence yield with increasing LET for the heavy ion radiolysis of liquid benzene. This phenomenon could be due to the channel three process. For pyridine, the same process may be responsible for the observed increase in molecular hydrogen yields with increasing LET. No attempt was made to determine other products from the decay of the pyridine singlet excited state.

On the addition of anthracene and biphenyl as triplet excited-state quenchers, the formation of the higher energy singlet state by T−T annihilation occurs in competition with the quenching of the pyridine triplet excited state, reaction 3. The quenching rate coefficients (k_q) were estimated to be 9.5×10^8 and 1.0×10^9 M^{-1} s^{-1} for anthracene and biphenyl, respectively.[21] The yield of molecular hydrogen in the γ-radiolysis of solid biphenyl is 4.4×10^{-3} molecules/100 eV, so its direct radiolysis is not expected to contribute significantly to the production of molecular hydrogen at high biphenyl concentrations.[41] Figure 5 shows the yields of molecular hydrogen in pyridine as a function of triplet excited-state quencher concentration for γ-rays and 5 MeV helium ions. The dashed lines are the predicted molecular hydrogen yields when there is no scavenging of the pyridine triplet excited state by the quenchers. The data show that the molecular hydrogen yields for γ-rays and helium ions are independent of the triplet excited-state quencher concentration up to 500 mM biphenyl at which the lifetime of pyridine triplet excited state is about 2 ns. At 3 M biphenyl, the molecular

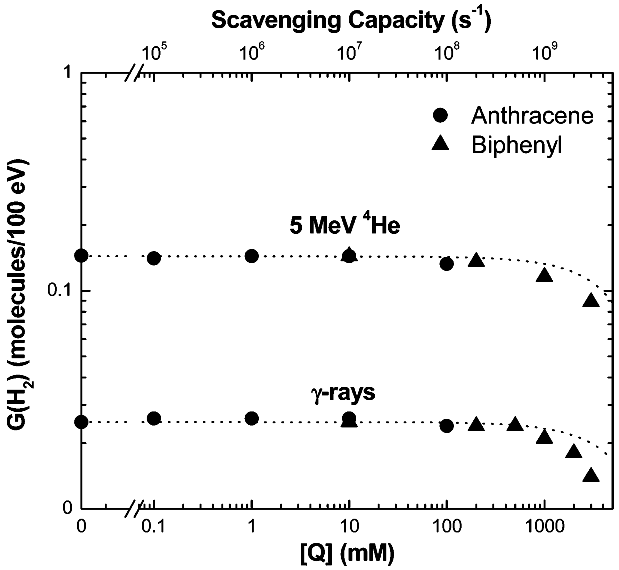


Figure 5. The yields of molecular hydrogen in pyridine as a function of triplet excited-state quencher concentration for γ-rays and 5 MeV helium ions: (●) anthracene and (▲) biphenyl. The dashed lines are the predicted molecular hydrogen yields when no scavenging of pyridine triplet excited state occurs.

hydrogen yields for γ-rays and helium ions are 0.014 and 0.089 molecules/100 eV, which are 70 and 80%, respectively, of the yields expected with no quenching (dashed lines). The need for high quencher concentrations to have an observable effect on hydrogen production for both γ-rays and helium ions suggests that the T−T annihilation reactions induced by helium ions are not readily quenched. Further work is required to understand the appropriate kinetics.

Polymer Production. Pyridyl radicals and H atoms are thought to be consumed in "polymer" formation, which generally refers to the formation of trimers and higher order compounds (>$C_{15}N_3$).[27,42] Polymer yields in liquid pyridine radiolysis were determined by direct measurements using GPC techniques.[17] Figure 6 shows the GPC time profiles of polymer production obtained by the radiolysis of neat pyridine for γ-rays. Irradiation doses were varied from 10 to 50 kGy (1−5 Mrad). GPC gives a very good estimation of mass for a given class of compounds, and the molecular weights of pyridine radiolysis products are shown on the upper axis of Figure 6. Two major peaks in the chromatograph are observed at elution times of 28.0 and 27.0 min, which are assigned to trimers and tetramers, respectively, by comparison with the elution times of authentic compounds. The peaks in the molecular weight region higher than tetramers are attributable to higher order compounds consisting of multiples of C_5N units. The peaks of biphenyl and pyridine are observed at elution times of 29.8 and 30.8 min, respectively.

Polymer yields were determined by scaling the relative GPC responses to that for the dipyridyl found in γ-radiolysis for which the absolute yield is known from previous studies.[19] The yields of trimers and polymer in the γ-radiolysis of helium saturated neat liquid pyridine (Figure 6A) are 0.16 and 0.33 molecules/100 eV, respectively, as shown in Table 1. The sum of all the condensed phase products in liquid pyridine is 1.6 molecules/100 eV and the triplet excited-state yield is 3.2 molecules/100 eV, so 50% of the pyridine triplet excited states decay to product formation instead of undergoing intersystem crossing to the ground state. On the other hand, the sum of all the condensed phase products in liquid benzene is 0.65 molecules/100 eV, which is only 14% of the benzene triplet excited-state yield (4.8 molecules/100 eV). The lack of significant radiolytic products in benzene suggests that there is an efficient pathway for relaxation of the benzene triplet excited state to the ground state.[17] Pulse radiolysis studies show that the transient triplet excited state of liquid pyridine has a longer lifetime as compared to that for liquid benzene.[21] This lifetime difference probably is responsible for the observed variations in final product yields.

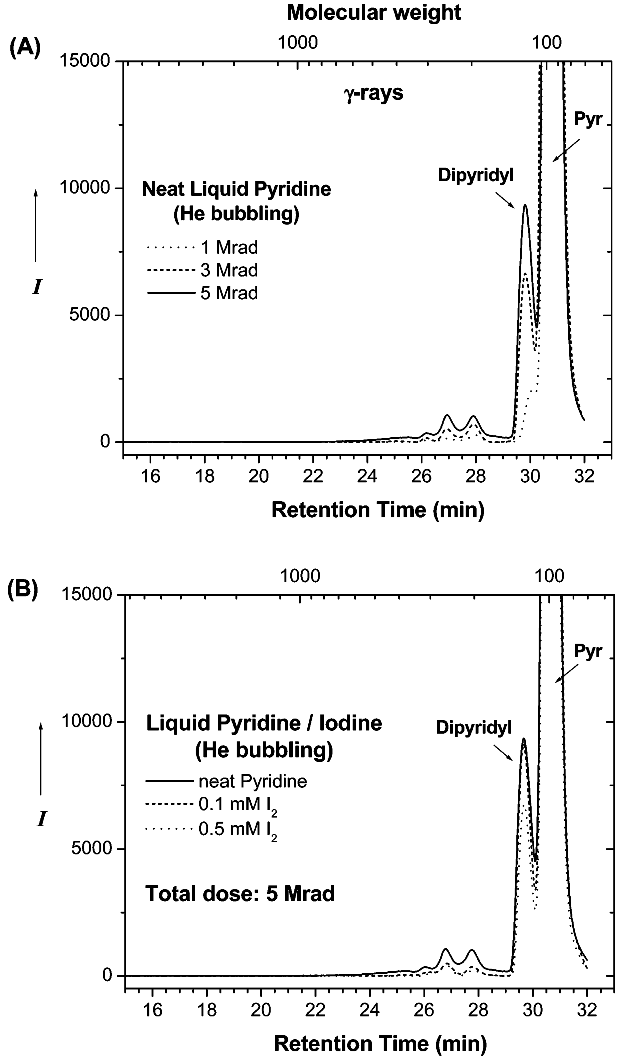


Figure 6. GPC chromatograph of polymer production obtained by the radiolysis of deaerated pyridine for γ-rays: (A) neat solution and (B) iodine solution.

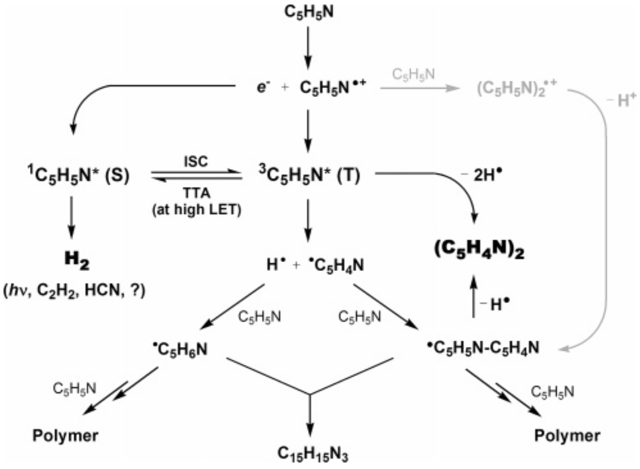
TABLE 1: Polymer Yields in the γ-Radiolysis of Liquid Pyridine[a]

product	neat solution	0.1 mM I_2	0.5 mM I_2	1.0 mM I_2
bipyridyl	1.2$_5$[b]	1.2	0.81	0.55
trimer	0.16	0.047	0.029	0.032
>$C_{15}N_3$	0.17	0.064	0.043	0.025
polymer[c]	0.33	0.11	0.072	0.057

[a] Dose of 50 kGy (5Mrad). [b] Ref 19. [c] Sum of trimer and >$C_{15}N_3$.

Iodine scavenging has been used to probe pathways to polymer formation in pyridine irradiated with γ-rays. Pyridyl radicals can be scavenged by iodine and their role or that of other radical precursors to polymer can be affected by the addition of iodine. As shown in Figure 6B, polymer yields are found to decrease markedly with increasing iodine concentration indicating the predominance of radical precursors. The yield of polymer is 0.33, 0.11, and 0.057 molecules/100 eV at 0 (neat),

SCHEME 1: Low LET Radiolytic Decomposition of Liquid Pyridine



0.1, and 1.0 mM iodine, respectively (Table 1). Pyridyl radicals and H atoms produced by the decomposition of the pyridine triplet excited state appear to be the main precursor radicals leading to polymer formation. The resultant yields of dipyridyl are given in Table 1 and are in good agreement with previous results (Figure 1).[19]

FTIR spectra of the polymers were obtained following the radiolysis of liquid pyridine to a dose of 30 kGy (3 Mrad). Irradiation led to new peaks at 2932 and 2834 cm^{-1}, which are assigned to asymmetric and symmetric methylene stretching vibrations, respectively. Furthermore, the GC/MS spectrum of the dimer shows fragment signals at $m/z = 158$, 130, 80, and 78 that are assigned to the partly saturated dimer of dihydrodipyridyl ($C_5H_4N-C_5H_6N$). The formation of methylene strongly suggests that the structure of the polymer possesses a partly saturated ring.

Pyridine Decomposition Scheme. The energy deposited by the passage of ionizing radiation in liquid pyridine leads to ionization giving an electron and the parent cation ($C_5H_5N^{\bullet+}$). For fast electrons, combination reactions of ion pairs generated in liquid benzene occur with a lifetime of 1.2 ps and a similar time scale is expected for liquid pyridine since the dielectric constant of pyridine ($\epsilon_r = 13.3$) is comparable to that of benzene ($\epsilon_r = 2.28$).[43,44] Neutralization reactions then produce the singlet and triplet excited states. The formation of the pyridine triplet excited state is enhanced in the tracks of high LET ions because of random recombination of spin states within them leading to the statistical maximum of 75%. A total mechanism of the formation and decay of the excited states in liquid pyridine and the products from them are shown in Scheme 1.

The chemistry of the singlet excited state in liquid pyridine radiolysis is not very well known because pyridine exhibits a very low fluorescence yield as described above. Nevertheless, there is sufficient evidence to suggest that the pyridine singlet excited state is the precursor of molecular hydrogen. The yield of molecular hydrogen is very dependent on LET and is 0.027 and 0.72 molecues/100 eV for γ-rays and 10 MeV ^{12}C ions, respectively. In addition, the pyridine singlet undergoes ring opening to form acetylene (C_2H_2), cyclobutadiene (C_4H_4), and HCN in the gas-phase photolysis.[45−49] These products have not been identified in the liquid and future studies will focus in this area.

The total yield of pyridine triplet excited state, including intersystem crossing from singlet to the triplet excited state, is 1.30 molecules/100 eV for fast electrons, and its lifetime is 72 ns.[21] Most of the triplet excited state seems to form an excimer by coupling with a ground state pyridine molecule. Dehydrogenation of the triplet excimer then gives dipyridyl and two H atoms. About 10% of the triplet excited states decay to pyridyl radicals and H atoms. The pyridyl radicals react with parent pyridine giving a pyridyl radical−pyridine complex and dehydrogenation of this species then gives dipyridyl. The H atoms will react with parent pyridine to give dihydropyridyl radicals ($C_5H_6N^\bullet$) without leading to the production of molecular hydrogen. The total yield of dipyridyl is 1.25 molecules/100 eV for γ-rays, and the yield of H atoms, thereby, is about 2.5 radicals/100 eV. The total radical yields agree reasonable well with a measured radical yield of 2.8 from scavenging studies using DPPH (2,2-diphenyl-1-picrylhydrazyl).[27] These radicals add to pyridine and lead to polymer formation until radical termination occurs. Similar processes are observed in liquid benzene radiolysis.[16,17]

A decrease in the yield of dipyridyl with increasing LET is observed due to the enhancement of the intratrack second-order T−T annihilation, reaction 6, over the first-order decomposition, reaction 4, at high LET. Energy transfer following T−T annihilation leads to formation of high-energy singlet excited states above the S_1 state, reaction 6. These higher energy singlet states in pyridine are thought to decay to molecular hydrogen through channel three processes. The yield of molecular hydrogen increases with increasing LET suggesting that the dominating primary process responsible for its formation is the singlet excited state created by T−T annihilation. Thus, singlet and triplet excited-state interactions due to the T−T annihilation at high LET are a significant factor in liquid pyridine.

Conclusions

The radiation chemical yields of the main products produced in liquid pyridine radiolysis (molecular hydrogen and dipyridyl) have been studied as a function of linear energy transfer (LET) with protons, helium ions, and carbon ions of a few to 30 MeV and γ-radiolysis. Anthracene and biphenyl scavenging techniques have been used to clarify the role of the triplet excited state produced in the heavy ion radiolysis of liquid pyridine at high LET. An increase in the yield of molecular hydrogen produced because of the decay of the pyridine singlet with increasing track average LET is observed. Its yield decreases with increasing scavenger concentration at high LET. Dipyridyl seems to have a pyridine triplet excited-state precursor because an increase in anthracene concentration leads to a decrease in pyridine triplet excited-state yields with a concurrent decrease in the dipyridyl. A decrease in the yield of dipyridyl with increasing track average LET is observed. Its yield with 10 MeV carbon ions is 0.20 molecules/100 eV, which is only 16% of that of observed with γ-rays. The lower yield for dipyridyl with carbon ions can be attributed to T−T annihilation processes due to the increase in local concentrations of triplet excited states with increasing LET. This process leads to a higher molecular hydrogen yield by channel three processes involving the resultant singlet excited states. A complete mechanism for the radiolysis of liquid pyridine is presented.

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