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Formation and Decay of the Triplet Excited State of Pyridine

Kazuyuki Enomoto,[†] Jay A. LaVerne,*,[†,‡] Shu Seki,[§] and Seiichi Tagawa*,[§]

Radiation Laboratory and Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556,
and The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki,
Osaka 567-0047, Japan

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A pulse radiolysis study of the formation and decay of the triplet excited state of liquid pyridine has been performed using quenching techniques. The pyridine triplet excited state is observed with an absorption band at $\lambda = 310$ nm and has a first-order decay with a lifetime of 72 ns. Stern−Volmer plots of the quenching of the pyridine triplet excited state with anthracene, naphthalene, and biphenyl give its yield to be 1.3 molecules/100 eV. This value is very similar to the previously determined yield of 1.25 molecules/100 eV for dipyridyl, the predominant condensed-phase product in the γ-radiolysis of liquid pyridine. The rate coefficient for pyridine triplet excited-state scavenging by oxygen is estimated to be 6.6×10^9 M^{-1} s^{-1}. Oxygen may also scavenge the electron precursor to the pyridine triplet excited state, whereas nitrous oxide is observed to have little effect. A pyridyl radical−pyridine (dimer) complex produced in the pulse radiolysis of neat liquid pyridine is detected at $\lambda = 390$ nm and is consistent with iodine scavenging effects. Formation of the pyridiniumyl radical cation−pyridine charge-transfer complex is proposed to be insignificant in liquid pyridine.

Introduction

Pyridine is a simple aromatic compound used extensively in photochemistry and yet the yields and kinetics of the excited states produced by the radiolytic decomposition of neat pyridine have never been examined. Although the chemistry of transient species derived from the pulse radiolysis of aqueous solutions of pyridine has been extensively studied, that knowledge is not applicable to neat liquid pyridine.[1] Pyridine carries an unshared electron pair on the tertiary amine nitrogen of the aromatic ring and the transition states of pyridiniumyl radical cations, pyridine excited molecules, and pyridyl radicals are stabilized at the carbon center adjacent to the nitrogen atom.[2,3] These transient states should exhibit different lifetimes and yields as compared to those for liquid benzene, which has been more thoroughly studied.[4,5] Product yields from the radiolysis of pyridine are found to be very different from that of benzene, which again suggests that there are differences in the chemistry of the transient excited-state species.[3,6] The purpose of this work is to use pulse radiolysis techniques to examine the transient species, particularly the triplet excited state, produced in the radiolytic decomposition of liquid pyridine.

The initial product in neat liquid pyridine radiolysis is the pyridiniumyl radical cation, which was identified by ESR studies.[7] Free ion and triplet excited-state yields in the pulse radiolysis of liquid pyridine were determined to be 0.40 ions/100 eV and 0.54 molecules/100 eV, respectively.[8] However, that study did not determine the lifetime of the triplet excited state and the reported yield is not the total yield because scavenger concentration was not varied. Triplet excited states are generally assumed to be the predominant precursors to radical formation.[4,5] Radicals can be formed by dissociative electron capture, but there is little evidence for such a process in liquid organic compounds. Several different radical traps have been used to estimate the total radical yield in the radiolysis of liquid pyridine.[3,6,9] Scavenging studies using DPPH (2,2-diphenyl-1-picrylhydrazyl) found that the total radical yield is about 2.8 radicals/100 eV, suggesting that the yield of the precursor triplet excited state is at least half this large.[3] On the other hand, the yield of the triplet excited state produced in liquid benzene radiolysis has been estimated using the steady-state γ-ray induced cis−trans isomerization of *cis*-butene by the benzene triplet and the pulse radiolysis examination of the quenching of the benzene triplet by a solute such as anthracene.[10−14] The latter technique gives the yield of the benzene triplet excited state to be about 4.2 molecules/100 eV with a lifetime of about 3.3 ns.[14] Similar techniques applied to pyridine radiolysis give vital information on the yield and lifetime of its triplet excited state.

In this work, a pulse radiolysis study of the formation and decay of the triplet excited state in liquid pyridine has been performed. The transient absorption spectrum of the pyridine triplet excited state produced in the pulse radiolysis of neat liquid pyridine was observed directly and the decay rate gave information on its lifetime. The yield of the pyridine triplet excited state was estimated from the Stern−Volmer plots for its quenching using anthracene, naphthalene, and biphenyl. Because oxygen is an effective electron and triplet excited-state scavenger, oxygen saturated solutions were used to give more information on the kinetics of pyridine decomposition. Nitrous oxide saturated solutions were also examined. A radical produced in the pulse radiolysis of neat liquid pyridine was assigned using iodine scavenging techniques.

Experimental Section

Pyridine (HPLC grade), anthracene, naphthalene, biphenyl, *n*-butyl chloride and iodine (99.999%) were purchased from Aldrich and used without further purification.

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* Authors for correspondence. E-mail: (J.A.L.) laverne.1@nd.edu, (S.T.) tagawa@sanken.osaka-u.ac.jp.

[†] Radiation Laboratory, University of Notre Dame.

[‡] Department of Physics, University of Notre Dame.

[§] Osaka University.

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Pulse radiolysis experiments were performed using the fast electron linear accelerators at Osaka University and at the University of Notre Dame. Preliminary qualitative radiolysis measurements were performed with 8 ns pulses from the L-band electron linear accelerator at the Radiation Laboratory of the Institute of Scientific and Industrial Research, Osaka University. The details of the apparatus have been described elsewhere.[15] Quantitative analysis was performed using 5 and 14 ns pulses of 8 MeV electrons from the Notre Dame Radiation Laboratory Q-band 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.[16] 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 used as received. The pulsed electron beam width was 5 and 14 ns with a dose of 12 and 26 Gy per pulse, respectively, 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 ultrahigh-purity Ar, O_2 or N_2O, which flowed through the cell continuously throughout the experiment. Transient absorption data and kinetic traces were averaged over 6 shots. Analysis of the optical absorption time dependence was done using ORIGIN (Microcal Software, Inc.) software.

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

Results and Discussion

The initial products in the radiolysis of liquid pyridine are the electron (e^-) and the pyridiniumyl radical cation ($C_5H_5N^{\bullet+}$), which combine to give pyridine singlet and triplet excited states as shown in reactions 1−3.[2] Excited states may also be formed

$$C_5H_5N \rightarrow C_5H_5N^{\bullet+} + e^- \tag{1}$$

$$C_5H_5N^{\bullet+} + e^- \rightarrow C_5H_5N^*(S) \tag{2}$$

$$C_5H_5N^{\bullet+} + e^- \rightarrow C_5H_5N^*(T) \tag{3}$$

by direct excitation of the medium. Formation of the triplet excited state is followed by its decay to give pyridyl radical and an H atom.

$$C_5H_5N^*(T) \rightarrow C_5H_4N^{\bullet} + H^{\bullet} \tag{4}$$

Combination reactions of pyridyl radicals or their addition to pyridine followed by H atom elimination lead to dipyridyl 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.[5,6] The corresponding product in liquid benzene is biphenyl with a yield of 0.075 molecules/100 eV.[4] Iodine scavenging techniques in the γ-radiolysis of liquid pyridine suggest that most of the dipyridyl can be scavenged, but only about 10% of the dipyridyl is due to the pyridyl radical.[6] The additional source of dipyridyl may be due to ion−molecule reactions or due to an undefined decay channel of the pyridyl radical precursor, possibly a “hot” triplet excited state.

Pyridine Triplet Excited-State Formation. Formation and decay of the triplet excited state in liquid pyridine radiolysis is observed in the pulse radiolysis experiments shown in Figure 1. The pulse radiolysis of Ar-saturated neat liquid pyridine gives a transient absorption band at $\lambda_{max} = 310$ nm due to the triplet excited state of pyridine, which has a rise time shorter than the pulse width.[17] Another slower forming absorption peak is observed at $\lambda_{max} = 390$ nm and is probably due to a pyridyl radical−pyridine complex (discussed below). The pyridine triplet excited state exhibits first-order decay with a lifetime of 72 ns (inset of Figure 1). This value is much slower than the lifetime of 3.3 ns reported for the benzene triplet excited state, suggesting the pyridine triplet excited state is more stable.[14] The pyridine singlet excited state is estimated to have a lifetime of 20 ps, which is too short to be observed in these experiments.[18,19]

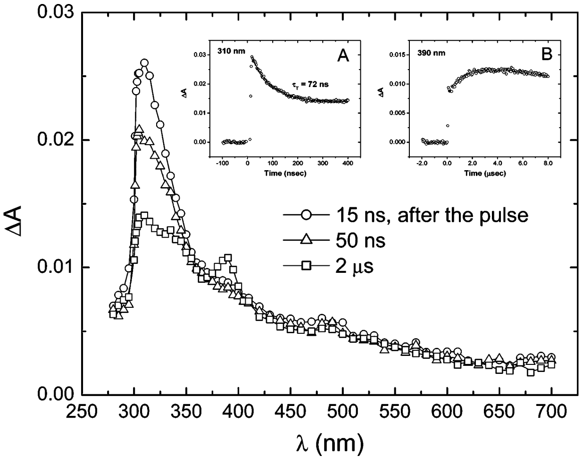

Figure 1. Transient absorption spectra obtained in the pulse radiolysis of Ar-saturated pyridine at 15 ns (○), 50 ns (△), and 2.0 μs (□) after the pulse. The insets show the time profiles at (A) 310 and (B) 390 nm.

Pyridine Triplet Excited-State Yields. The yield of the pyridine triplet excited state in the pulse radiolysis of liquid pyridine was determined by its quenching with the molecular aromatics, Q, anthracene, naphthalene, and biphenyl. The quenching 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.

$$C_5H_5N^*(T) + Q \rightarrow C_5H_5N(S_0) + Q^*(T) \tag{5}$$

Absorption spectra of the triplet excited states of the quenchers were obtained by pulse radiolysis of Ar-saturated pyridine solutions with corresponding quenchers. Absorption peaks are observed at 435, 425, and 360 nm, characteristic of the absorption maxima of anthracene, naphthalene, and biphenyl triplet excited states, respectively.[14,20] The yield of Q*(T) increases with increasing concentration of Q in pyridine solutions reaching a limiting value equivalent to the yield of the pyridine triplet excited state. Quencher concentrations were varied from 0.1 to 100 mM. Figure 2A shows the formation time profile of the absorption peak at 435 nm in the pulse radiolysis of Ar-saturated pyridine solutions of anthracene (5 ns pulse width). Formation of the anthracene triplet excite state occurs within the pulse width and remains fairly constant over hundreds of nanoseconds. Self-quenching of the anthracene triplet excited state may be occurring at the highest concentrations, as suggested by the decay in the 100−200 time range, but the decrease within 5 ns of the pulse is negligible for the purposes of this study.[14] The rate of change in the absorption maximum decreases with increasing quencher concentration, approaching saturation with anthracene concentrations of 100 mM, Figure 2B. Furthermore, the absorption of the pyridine triplet excited state, monitored at 310 nm, decays with increasing

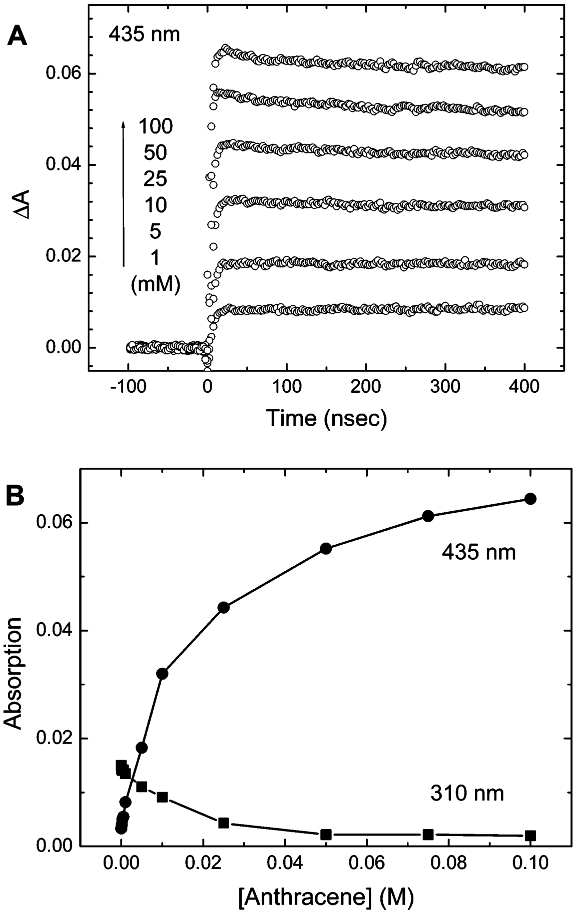

Figure 2. (A) Time profiles of the absorption at 435 nm observed in the pulse radiolysis of Ar-saturated pyridine with various amounts of anthracene. (B) Absorbance of the anthracene triplet excited state at 435 nm and the pyridine triplet excited state at 310 nm 5 ns after the pulse as a function of anthracene concentration.

absorption of the quencher excited state. Formation of the anthracene triplet excited sate is unequivocally associated with the decay of the pyridine triplet excited state at 310 nm. Similar results are found for the formation of quencher triplet excited states in naphthalene and biphenyl solutions. The pyridine triplet excited-state decay was not monitored at 310 nm when quenched by biphenyl because the triplet excited-state absorptions of biphenyl and of pyridine overlap each other at this wavelength.

Determination of the pyridine triplet excited-state yield is straightforward from the absorption measurements of the quencher excited states. The singlet excited state of pyridine has a lifetime of 20 ps, which is too short to contribute significantly to quencher excited-state formation.[18,19] In the presence of quenchers, the decay of the pyridine triplet excited state occurs by reactions 4 or 5. The lifetime of reaction 4, τ_4, is equal to the inverse of the rate coefficient for reaction 4 ($1/k_4$) and was determined to be 72 ns from the direct measurements discussed above. Quencher excited-state yields, $G(\mathrm{Q^*(T)})$, are related to the pyridine excited-state yields, $G(\mathrm{C_5H_5N^*(T)})$, by the following equation,

$$G(\mathrm{Q^*(T)}) = G(\mathrm{C_5H_5N^*(T)}) \times k_5[\mathrm{Q}]/(k_5[\mathrm{Q}] + \tau_4) \quad (6)$$

where [Q] is the quencher concentration and k_5 is the rate coefficient for the quenching reaction 5. Inversion of this equation gives the classical Stern−Volmer formalism.[21]

$$G(\mathrm{Q^*(T)})^{-1} = G(\mathrm{C_5H_5N^*(T)})^{-1} + \tau_4/(k_5[\mathrm{Q}] \times G(\mathrm{C_5H_5N^*(T)})) \quad (7)$$

A plot of the inverse yield of the quencher excited state as a function of the inverse concentration of quencher gives the inverse of the pyridine triplet excited-state yield as the intercept. Extinction coefficients used for the conversion of quencher triplet excited-state absorptions to G-values were the same as reported for these quenchers in benzene and given in Table 1.[20] The Stern−Volmer plots of the results in Figure 3 show a linear correlation for all quenchers with an average intercept of 0.77 ± 0.01, which gives the yield of pyridine triplet excited state to be 1.3 molecules/100 eV. The agreement of the results for the different quenchers suggests that the extinction coefficients of the quencher triplet excited states are similar for benzene and pyridine. Benzene is reported to have a triplet excited-state yield of 4.2 molecules/100 eV, which is about 3 times greater than the results found here for pyridine.[14] Dipyridyl is the predominant condensed-phase product in the γ-radiolysis of liquid pyridine with a yield of 1.25 molecules/100 eV.[3] The good agreement between the yield of the pyridine triplet excited state and dipyridyl suggests the former is the predominant precursor to the latter.

Rate coefficients for the reaction of each quencher with the pyridine triplet excited state, k_5, can be obtained from the slopes of the Stern−Volmer plots in Figure 3. The quenching rate coefficients are estimated to be 9.5×10^8, 1.5×10^9, and 1.0×10^9 $\mathrm{M^{-1}\ s^{-1}}$ for anthracene, naphthalene, and biphenyl, respectively (Table 1). The Dexter energy-transfer model is often used for the analysis of the triplet-energy-transfer rate constant (k) between the excited triplet-state molecule and the quencher as follows:

$$k = A \exp\left(-\frac{2r}{L}\right)\int f_{\mathrm{M}}(\nu)\, \epsilon_{\mathrm{Q}}(\nu)\, \mathrm{d}\nu \quad (8)$$

where A is a constant, r is the distance between the excited molecule and the quencher, and L is the effective Bohr radius. The terms f_{M} and ϵ_{Q} represent the phosphorescence spectrum from the triplet excited molecule and absorption spectrum of the quencher, respectively. The last term represents the degree of dipole−dipole interaction between the molecule and quencher. The broad phosphorescence spectrum of pyridine was reported to range from 350 to 550 nm with the peak at 470 nm.[22] The steady-state absorption spectrum of biphenyl shows no overlap with the phosphorescence spectra of pyridine; however, a high value of k was observed. In the case of energy-transfer processes limited by free diffusion in the media, the following empirical formulation was suggested,

$$\frac{k}{k_{\mathrm{dif}}} = \left[1 + \exp\left(-\frac{\Delta E}{RT}\right)\right]^{-1} \quad (9)$$

where k_{dif} is the rate constant of the diffusion controlled reaction and ΔE is the difference in energy between the triplet excited states of the molecule and the quencher.[23] The value of k_{dif} in pyridine is estimated as 1.0×10^{10} $\mathrm{M^{-1}\ s^{-1}}$ based on the viscosity index of pyridine as 0.879 mPa s at 297 K. Triplet excited-state energies of pyridine, anthracene, naphthalene, and biphenyl were reported as 332, 178, 253, and 274 kJ/mol, respectively. The calculated values of k are not consistent with the values determined in the present study. Formation of an exciplex between pyridine and electron-donating aromatics was suggested to contribute to the quenching of pyridine triplet

TABLE 1: Triplet Yields in the Pulse Radiolysis of Liquid Pyridine

quencher	extinction coefficient,[a] M^{-1} cm^{-1} (λ_{max}, nm)	limiting $G(Q^*(T))$ (molecules/100 eV)	$10^{-9}k_5$, M^{-1} s^{-1}
anthracene	45 500 (435)	1.3_2	0.95
naphthalene	13 200 (425)	1.2_8	1.5
biphenyl	27 100 (360)	1.3_1	1.0

[a] Reference 20.

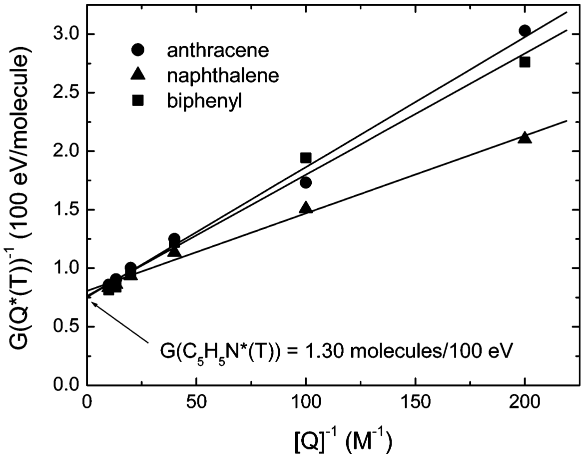

Figure 3. Stern−Volmer plots for the formation of quencher triplet excited states as a function of inverse quencher concentrations: anthracene (●), naphthalene (▲), and biphenyl (■).

excited states and this process may account for the different rate coefficients observed.[24]

These rate coefficients determined here for pyridine are much lower than the corresponding values of 3.8 × 10^{10}, 3.8 × 10^{10}, and 2.8 × 10^{10} M^{-1} s^{-1} for anthracene, naphthalene, and biphenyl, respectively, in benzene. However, the ratios of k_5/k_4 are very nearly the same for each of the quenchers in pyridine and in benzene.

The absorbance of the pyridine triplet excited state at 310 nm is 0.014 when triplet quenchers are absent and decreases gradually with increasing quencher concentration; see Figure 2B. Because the yield of pyridine triplet excited state was estimated to be 1.3 molecules/100 eV, the absorbance at 310 nm in the absence of triplet quenchers corresponds to an extinction coefficient of the pyridine triplet excited state in pyridine of 8800 M^{-1} cm^{-1}.

Oxygen Scavenging. The pyridine triplet excited state can be identified kinetically by its decay being concurrent with the formation of the triplet excited state of the quencher, as shown in the previous section. Oxygen is expected to be a good quencher of the pyridine triplet excited state and it can also scavenge the electron precursors to that state.[25]

$$e^- + O_2 \rightarrow O_2^{\bullet -} \tag{10}$$

Figure 4 shows the observed decay profiles of the pyridine triplet excited-state absorption at 310 nm obtained by the pulse radiolysis of liquid pyridine with various concentrations of oxygen. Considerable increase in the rate of decay of the pyridine triplet excited state is observed from deaerated to O_2 saturated (4.9 mM at 1 atm and room temperature)[26] solutions. A plot of the measured rate coefficients as a function of O_2 concentration is shown in the inset of Figure 4. The results show a linear correlation with a slope corresponding to a rate coefficient of 6.6 × 10^9 M^{-1} s^{-1} for the O_2 reaction with the pyridine triplet excited state, which is in agreement with the rate coefficient of 3.9 × 10^9 M^{-1} s^{-1} for the oxygen quenching reaction in the vapor phase of pyridine.[27] The intercept of 1.3 × 10^7 s^{-1} corresponds to a lifetime of 77 ns for the pyridine triplet excited state in the absence of oxygen, in agreement with the results discussed above. An initial decrease in the absorption at 310 nm is observed with increasing O_2 concentration. This result suggests that the electrons generated by the initial pyridine decomposition, reaction 1, are scavenged by O_2.

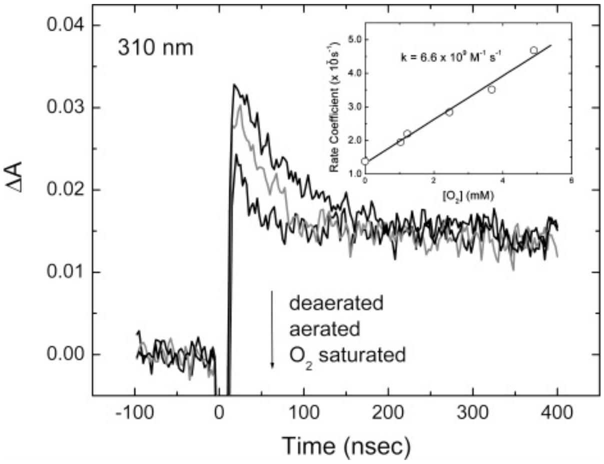

Figure 4. Decay profiles of pyridine triple excited-state absorption at 310 nm in liquid pyridine with different concentrations of O_2. The inset shows a plot of the rate coefficients as a function of O_2 concentration.

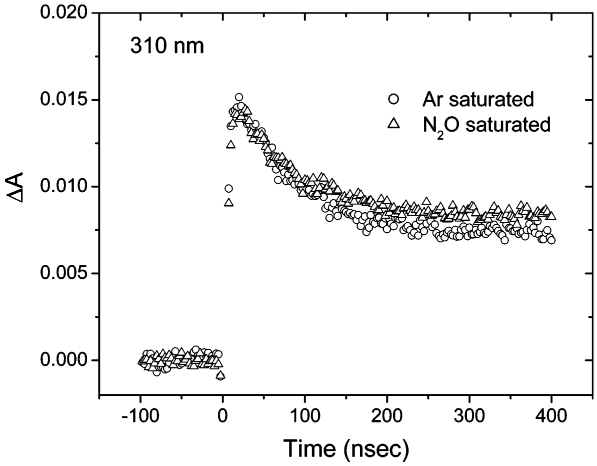

Figure 5. Decay profiles of the pyridine triplet excited-state absorption at 310 nm in liquid pyridine saturated with Ar or N_2O.

Nitrous Oxide Scavenging. Nitrous oxide, N_2O, is a well-known scavenger of solvated electrons in water.[8] Scavenging of thermal electrons may occur in liquid pyridine.

$$e^- + N_2O \rightarrow N_2 + O^{\bullet -} \tag{11}$$

Figure 5 shows the decay profiles of the pyridine triplet excited-state absorption at 310 nm observed in the pulse radiolysis of Ar and N_2O-saturated liquid pyridine. Very little difference is observed in the two decay traces. Either nitrous oxide is a poor scavenger of electrons in liquid pyridine or its concentration in saturated solutions is too low to compete with the fast neutralization reaction 1. Nitrous oxide also does not appear to scavenge the pyridine triplet excited state. These results agree with those of a previous study, suggesting that nitrous oxide has little effect on the formation or decay of triplet excited states in pyridine.[8]

Iodine Scavenging of Radicals. The pulse radiolysis of Ar-saturated liquid pyridine produces a transient absorption band

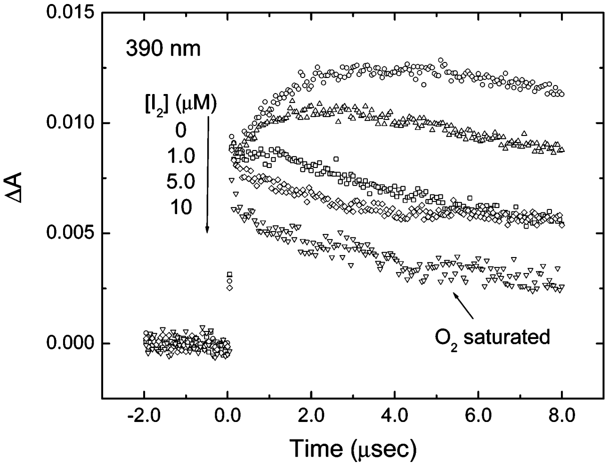

Figure 6. Time profiles of the pyridine triplet excited-state absorption at 390 nm in liquid pyridine: saturated with Ar (○), 1 μM I_2 (△), 5 μM I_2 (□), 10 μM I_2 (◇), and saturated with O_2 (▽).

at $\lambda_{\max} = 310$ nm due to pyridine triplet excited state as discussed above. Another peak at $\lambda_{\max} = 390$ nm as shown in Figure 1 is observed to be formed on the microsecond time scale. The latter peak exhibits a formation rate of 0.88 μs and decays with a lifetime of 49 μs. This absorption decreases rapidly on addition of O_2 (cf. Figure 6, inverse triangles) and, therefore, is probably due to a transient radical species. Iodine is a very efficient radical scavenger, but it is not expected to react with electrons.[3,28] More detailed information on the transient species at 390 nm was obtained by pulse radiolysis of Ar-saturated liquid pyridine in the presence of increasing iodine concentration from 1 to 10 μM, as shown in Figure 6. The level of formation of the peak at 390 nm is observed to decrease with increasing iodine concentration, indicating that this peak is probably due to a radical.

The rate coefficient for the iodine scavenging of the absorption peak at 390 nm is estimated to be 9.0×10^9 M^{-1} s^{-1}, which is similar to the diffusion-controlled rate coefficient for iodine reaction with alkyl radicals.[29] However, the absorption at 390 nm is probably not due to (monomer) pyridyl radicals. The decay of the pyridine triplet excited state occurs with a lifetime of 72 ns to give the pyridyl radicals in reaction 4. This rate of formation for pyridyl radicals is much too fast to correspond to the microsecond rise time of the radical at 390 nm. Pyridine is a good radical scavenger, and pyridyl radicals may add to it, giving a pyridyl radical−pyridine complex. Dehydrogenation of this species gives dipyridyl.[3] A similar process is thought to occur in benzene giving biphenyl.[5] Because the pyridyl radical−pyridine complex is expected to be formed and react on the microsecond time scale, the absorption peak at 390 nm has been assigned to it.

Quantum chemical calculations suggest the pyridiniumyl radical cation ($C_5H_5N^{\bullet+}$) can react with pyridine to give a charge-transfer complex (dimer).[6] Deprotonation of this species may also give the pyridyl radical−pyridine complex.

$$C_5H_5N^{\bullet+} + C_5H_5N \rightarrow (C_5H_5N)_2^{\bullet+} \qquad (12)$$

$$(C_5H_5N)_2^{\bullet+} \rightarrow {}^{\bullet}C_5H_5N - C_5H_4N + H^+ \qquad (13)$$

Maroz et al. have reported that radical cations of primary amines absorb near 400 nm.[30] However, those studies were performed in *n*-chlorobutane solutions where the formation was also on the microsecond time scale. *n*-Chlorobutane is an efficient electron scavenger and when used as a solvent it can substantially decrease the amount of neutralization by reaction 1, thereby increasing the probability of formation of a charge-transfer complex by reaction 12. The lifetime of the pyridine triplet excited state is 72 ns so the neutralization reaction 1 must occur on a faster time scale. The observed formation rate of 0.88 μs for the peak at 390 nm suggests that at most only a few percent of pyridiniumyl radical cations can compete in reaction 12 with the neutralization reaction 1. Pulse radiolysis studies of pyridine in *n*-chlorobutane show a decreased absorption at 390 nm compared to neat pyridine instead of an increase expected by scavenging of the electrons. The conclusion is that the peak at 390 nm is due to the pyridyl radical−pyridine complex and that pyridiniumyl radical cation reaction with pyridine is not significant.

The pulse radiolysis studies show that the transient triplet excited state of liquid pyridine has a different lifetime and yield as compared to those for liquid benzene. These differences are responsible for the observed variations in final product yields because of their effect on radical formation. These studies show the importance of the connection between transient excited states and final product formation in the radiation chemistry of organic liquids.

Conclusions

A pulse radiolysis study of the formation and decay of the triplet excited state in liquid pyridine has been carried out using quenching techniques. The pyridine triplet excited state is observed with an absorption band at $\lambda_{\max} = 310$ nm and has a first-order decay with a lifetime of 72 ns. The yield of pyridine triplet excited state is estimated to be 1.3 molecules/100 eV from the Stern−Volmer plots for its quenching using anthracene, naphthalene, and biphenyl. Dipyridyl is the predominant single condensed-phase product in the γ-radiolysis of liquid pyridine with a yield of 1.25 molecules/100 eV, suggesting that the pyridine triplet excited state is its precursor. The rate coefficient for scavenging the pyridine triplet excited state by O_2 is estimated to be 6.6×10^9 M^{-1} s^{-1}. Oxygen may also scavenge the electron precursor to the pyridine triplet excited state, whereas nitrous oxide is a poor scavenger of the electron and the pyridine triplet excited state. A pyridyl radical−pyridine (dimer) complex produced in the pulse radiolysis of neat liquid pyridine is detected at $\lambda = 390$ nm, as suggested by iodine scavenging studies.

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