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Radical Production in the Radiolysis of Liquid Pyridine

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A combined experimental and theoretical approach has been used to probe the radiolytic decomposition of liquid pyridine. The major single condensed phase product in the γ-radiolysis of pyridine is dipyridyl with a yield of 1.25 molecules/100 eV total energy absorbed. Scavenging studies suggest that most, if not all, dipyridyl has a radical precursor, but only about 10% of that is due to the pyridyl radical. The remainder of the dipyridyl may be due to reaction of the parent radical cation with pyridine. Iodine scavenging and quantum chemical calculations both show that the ortho-pyridyl radical (2-pyridyl) is far more stable than the other two isomers.

Introduction

Pyridine is a heterocyclic aromatic tertiary amine that has been the subject of recent studies on electronic transitions and fragmentation following the absorption of energy.[1−4] These processes have an important role in the decomposition of medium molecules following the passage of ionizing radiation. Little information exists on the nature of the products formed in the radiolytic decomposition of pyridine and the mechanism by which these products are formed. Pyridine is a relatively simple heterocyclic aromatic that should be readily amenable to both experimental and theoretical studies on its radiolytic decomposition. Besides the fundamental interest, pyridine is a very good and thus widely used solvent and a common product in the breakdown of many natural materials that may be exposed to ionizing radiation. A better understanding of its radiolytic properties may help in environmental remediation of waste sites.

A series of studies using iodine scavenging techniques on aliphatic cyclic hydrocarbons led to a relatively simple common scheme describing their radiolytic decomposition.[5] The approach was used to quantify the pathways leading to the major observed products and even led to one of the few successful diffusion-kinetic models of hydrocarbon radiolysis.[6] Cyclic compounds are attractive because the major decomposition process involves the breaking of a carbon−hydrogen bond. The radicals and their products are few and amenable to precise yield measurements and interpretation of their kinetics. A more recent examination of the radiolysis of benzene showed that the radiolytic approach developed with the aliphatic compounds also well represented the radiation chemistry of this fundamental aromatic hydrocarbon.[7,8] A further increase in complexity is to examine a heteroatomic cyclic compound such as pyridine. The asymmetric ring allows one to directly measure the relative yields of the isomeric parent molecular radicals for comparison with theoretical predictions of pyridine decomposition. An examination of the absolute yields from pyridine in conjunction with those of benzene can be used to determine the effect of the nitrogen atom on the energetics of the aromatic ring.

Few experimental studies have been performed on the radiolytic decomposition of liquid pyridine. Some of the major products such as molecular hydrogen and dipyridyl were quantified in the γ-radiolysis of pyridine; however, no information on the mechanism was presented.[9] The yields of free ions and excited states produced by electron pulse radiolysis were also determined.[10] By analogy with studies on other cyclic compounds, one would expect pyridyl radicals and H atoms to be the primary decomposition products. The thermal decomposition of pyridine has been predicted to be initiated by C−H bond cleavage with the production of pyridyl radicals.[11] A number of radicals have been previously observed in the pulse radiolysis of aqueous solutions of pyridine, but the chemistry of that system is dominated by interactions with the radicals produced in the decomposition of water with results of limited applicability to neat liquid pyridine.[12] ESR studies on the radiolysis of solid pyridine revealed a radical initially identified as the radical cation as a major product.[13] Iodine was found to increase the yield of this radical, possibly through the interaction of a charge-transfer complex. However, this spectrum was later reassigned to the 2-pyridyl radical and the ESR spectrum of the authentic radical cation was first reported by Shida and Kato.[14] The role of the radical cation in the radiolysis of the liquid remains uncertain.

This work presents the results of accurate measurements on the major products in the radiolysis of neat liquid pyridine. These species include molecular hydrogen and the dipyridyl isomers. Iodine is used as a scavenger to measure absolute radical yields from formation of the stable iodides. Since iodine is a good radical scavenger, it can also give information on all products with radical precursors. Changes in the dipyridyl and iodopyridine yields with iodine concentration are used to examine the contribution of the pyridyl radicals to total product formation and its temporal variation. Electronic structure calculations are used to characterize the structure and properties of the pyridyl radicals and to suggest the main decomposition pathways of the excited or ionized parent molecule. Comparison of the computed thermochemical parameters with experimental observations further reinforces identification of the transient species.

Experimental Section

Irradiations were made using a Shepherd 109-68 ^{60}Co-γ source having a dose rate of 124 Gy/min. The sample cell for the determination of condensed phase products was made from a quartz cuvette and contained 4 mL of sample. The sample was purged with ultra-high-purity helium and the cell sealed with a rubber septum. Dosimetry was made in the same sample cell using the Fricke dosimeter.[15] The absorbed dose in the

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pyridine was assumed to be proportional to its electron density relative to that of the Fricke dosimeter. Except where otherwise stated, the yields reported here were performed at total doses of 500 Gy. Dose-dependent studies were performed with 0.1–5.0 kGy.

Condensed phase products were analyzed with a Thermo Finnigan Trace gas chromatograph–mass spectrometer operating in the selective ion monitoring mode. Iodopyridines were detected at mass 205, while dipyridyl isomers were detected at mass 156. Chromatographic separations were made with a 25 m Chrompack CP-Sil-8-CB capillary column of 0.32 mm i.d. Splitless mode injection of 1.0 μL solution was used. The initial column temperature was maintained at 90 °C for 13 min. Pyridine and iodopyridines were eluted in this time. The temperature was then raised to 280 °C at a rate of 15 °C/min and held 10 min at this temperature for dipyridyl isomers to elute. Complete separation of 2-, 3-, and 4-iodopyridines was obtained, but the dipyridyl isomers could not be separated completely and the sum of the yields is reported. Calibrations with standards confirmed the relative retention times and showed similar sensitivity for each of the isomers.

Molecular hydrogen was determined using an inline technique as previously reported.[16] The sample was purged with ultra-high-purity argon and the cell was sealed with a four-way valve during the radiolysis. Gas analysis was carried out with an SRI 8610 gas chromatograph. Following the irradiation, the sample cell was opened to the column gas stream using the four-way valve. The column was a 6.4 mm diameter 13X molecular sieve 3 m long. The column temperature was maintained at 40 °C. Calibration was performed by injection of pure hydrogen gas, and dosimetry was made in the same sample cell using the Fricke dosimeter.

Pyridine from Aldrich with purity above 99.9% was used as received. The concentration of dipyridyl in each sample prior to irradiation was always less than 1% of that following irradiation and was ignored.

Computational Details

A survey of the radicals and radical ions likely to be formed during the radiolysis of pyridine was conducted by locating a number of the relevant stationary points on the appropriate $C_5H_{(4-6)}N^{(\bullet + -)}$ energy hypersurfaces using a density functional theory (DFT) approach. The customary B3LYP hybrid functional was used in the DFT calculations,[17] along with a modest polarized split-valence basis set, denoted 6-31G*, to compute analytic energy derivatives for these preliminary geometry optimizations.[18] The nature of each stationary point obtained was checked by further computing analytic derivatives of the energy gradients, from which harmonic vibrational frequencies were obtained in the standard fashion. Rather than adopting the usual scaling factors, a more reliable description of the molecular force field was obtained from an anharmonic vibration–rotation, perturbation-theory-based treatment which provides predictions for the vibrational fundamentals directly.[19] Calculated structures and vibrational spectra for important minima were improved by adopting a more flexible (heavy-atom) diffuse-function-augmented polarized double-ζ basis denoted 6-311+G(d,p).[20] Calculations were performed with a modified version of the Gaussian98[21] and the Gaussian03[22] suites of electronic structure programs. Estimates of the relative energies separating the local minima were refined by recourse to a sophisticated composite electronic structure method, G3B3.[23]

Solvation effects were modeled by a self-consistent reaction field approach using the integral equation formalism of the polarized cavity model (IEFPCM)[24] with a dielectric constant appropriate for pyridine and other default parameters taken from Gaussian03.

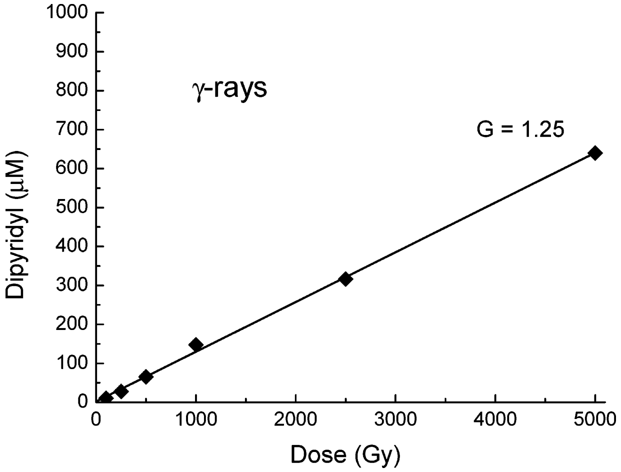

Figure 1. Production of dipyridyl as a function of dose in the γ-radiolysis of neat pyridine.

Results and Discussion

Radiolysis of Neat Pyridine. A previous study identified dipyridyl as the major single product in the γ-radiolysis of liquid pyridine with a yield of 1.1 molecules/100 eV.[9,25] The dipyridyl yield was determined using spectrophotometric techniques, but detailed information on the procedure was not given. Product buildup in the radiolysis of organic materials often leads to erroneous results due to secondary scavenging of transient species. Low doses require sensitive detection techniques that were not generally available 40 years ago. Gas chromatography–mass spectrometry using selective ion monitoring is one of the most sensitive techniques for determining products in the radiolysis of organic liquids. The results of the present work on the formation of dipyridyl as a function of dose are given in Figure 1. It can be seen that the response is linear up to 500 Gy. The slope of the fitted line in Figure 1 leads to a *G*-value of 1.25 molecules/100 eV for dipyridyl, which compares well with the previous determination of 1.1.[9] This value is considerably larger than the yield of 0.08 molecule/100 eV for biphenyl from the radiolysis of benzene, suggesting that the addition of a heteroatom decreases the radiolytic stability of cyclic aromatics.[7] Attempts to separate and identify the different isomers of dipyridyl were unsuccessful, so the reported yield is the sum of all isomers. Isomeric information would be useful for elucidation of the mechanism and comparison with theoretical predictions, but a different analytical technique such as liquid chromatography will probably be required.

The molecular hydrogen yield was found to be 0.027 molecule/100 eV, which agrees with the previously determined value of 0.025.[9] Molecular hydrogen formation is thought to be due to decomposition of the singlet excited state in the radiolysis of benzene.[8] A similar process may be occurring in pyridine, but there is no proof. No fluorescence was observed in the radiolysis of pyridine using a technique identical to that used successfully on benzene.[26] The fluorescence may be weak or too fast for the single photon counting technique to detect. Decay of the singlet excite state of pyridine to the singlet ground state and intersystem crossing to the triplet state are known to be fast and efficient processes both in the vapor[4] and in solution.[27] Further studies with heavy particles similar to those reported previously with benzene may give more information

TABLE 1: Relative Energies[a] of Radicals and Radical Cations Derived from Pyridine

isomer	pyridyl	pyridiniumyl
1-		21
2-	0	12
3-	26	10
4-	21	0

[a] Energies in kJ mol^{-1} from G3B3 calculations (see text).

on the kinetics and identity of the precursor to molecular hydrogen from pyridine.[8,26]

Free radical scavengers are often used to measure total radical yields in the radiolysis of organics. This technique does not identify the types of radicals, but it does allow an estimate of the contribution of radicals to the total product yield. Radical scavengers such as I_2, DPPH (2,2-diphenyl-1-picrylhydrazyl), and $FeCl_3$ are typically used.[28] Antoine used two radical scavengers (4-oxo-TEMPO and di-*tert*-butyl nitroxide) and found total radical yields of 3.45 and 3.15 in pyridine, respectively.[9] An attempt was made to use the spectrometric decay of I_2 as a probe of total radical yield in pyridine, but an unstable complex is formed, as discussed below. A 50 μM solution of DPPH was monitored at 525 nm to give a *G*-value of 2.8 molecules/100 eV. This value is somewhat lower than Antoine's determination. The two most likely radicals in the radiolysis of pyridine are the H atom and the pyridyl radical and its daughters. The yield of dipyridyl is 1.25 molecules/100 eV, and an equivalent product yield due to H atoms is expected. The total value of 2.5 radicals/100 eV agrees reasonably well with the measured loss of 2.8 for DPPH. Slightly higher total radical yields are expected in the use of these radical traps because of instability in the systems and reactions with excited or ionic states.

The initial steps in pyridine radiolysis involve molecular ionization, electron−ion recombination, excited state formation and decay, and, presumably, direct fragmentation of pyridine. The initially formed radical cation, pyridiniumyl, is the least stable of the four $C_5H_5N^{\bullet+}$ isomers as seen from Table 1, and also noted by others from in vacuo calculations.[29] The trends displayed in Table 1 are in accord with the results of previous calculations at both the Hartree−Fock[30] and MP2[11] levels of theory. Pyridiniumyl reacts exothermically with pyridine to give the pyridinium ion and pyridyl radicals. Since 2-pyridyl is the most stable species, the reaction is exothermic by 66 kJ mol^{-1} (free energy change modeled in solution); this pathway is presumably a major source of the neutral radical. The reaction of the 4-pyridyl radical with the pyridinium ion to give the 4-pyridiniumyl radical cation (and pyridine) is computed to be only 9 kJ mol^{-1} endothermic. The overall transformation into 4-pyridiniumyl is then exothermic by about 30 kJ mol^{-1}. Some computed structural parameters for pyridine and the derived radicals and radical ions are collected in Table 2. Table 3 lists the calculated vibrational fundamentals, highlighting those which should be prominent in infrared and Raman vibrational spectra. The infrared bands around 700 cm^{-1} arise from in-phase out-of-plane bends of CH (and NH) bonds; unsymmetrical intra-ring distortions also are IR active (1230−1650 cm^{-1}). Apart from the CH and NH stretches, the most intense Raman activity is found in the ring breathing modes around 1000 cm^{-1}. Knowledge of these frequencies may assist in later identification of these species in further studies of the radiolytic process.

Radiolysis of Iodine Solutions. Iodine is well known to complex with pyridine.[31−33] This association should pose little interference in these studies since iodine is being used as a scavenger and its reactivity toward free radicals should be much greater than its attraction to pyridine. The iodine complex could be observed by its absorption spectra, but it is very slow to form and probably weak compared to other radiolytic processes. For instance, the absorption intensity will vary for hours following irradiation as the complex relaxes. This variation interfered with the use of I_2 loss as a probe of total radical yields. The iodine−pyridine complex is relatively weak, but iodide formation is observed in solutions not irradiated. Figure 2 shows the concentration of the iodides on the addition of different concentrations of iodine to liquid pyridine. The systems are stable, apparently in equilibrium at higher iodine concentrations, and the yields are extremely small, approaching nanomolar concentrations with small amounts of iodine. The most likely source is photolytic (or thermolytic) formation of I_3^-, followed by a nucleophilic attack on the pyridine ring. Only sophisticated analytical techniques can measure concentrations at these levels. With one major exception in the case of 3-iodopyridine, to be discussed below, the background levels of these products have no effect on the radiolytic yields.

Linear dependences of yields as a function of dose show the lack of interference from secondary reactions. Such relationships are found throughout this work. The radiolytic yields of dipyridyl, 2-iodopyridine, 3-iodopyridine, and 4-iodopyridine from 1 mM I_2 solutions are shown in Figure 3 as a function of dose. In this case, the data are presented on a logarithmic scale to better observe the relative yields since the absolute values vary by about 3 orders of magnitude. The solid lines in Figure 3 were obtained by first-order fits to linear plots of the product concentrations as a function of dose (not shown). All the products show good linear responses to the absorbed dose. The exception is for the measured yields of 3-iodopyridine. The yield of 3-iodopyridine at zero dose is equivalent to the measured background of 3-iodopyridine formed on the addition of I_2, as discussed above. Subtraction of this background gives the solid points, which show a linear dependence on dose. Subtraction of background yields has no effect on any of the other products

TABLE 2: Computed[a] Structural Parameters[b] in Pyridine, Pyridyl Radicals, and Pyridiniumyl Radical Cations

	pyridine	2-pyr$^{\bullet}$	3-pyr$^{\bullet}$	4-pyr$^{\bullet}$	pyr$^{\bullet+}$	2-pyr$^{\bullet+}$	3-pyr$^{\bullet+}$	4-pyr$^{\bullet+}$
$r(NC_2)$	133.7	128.2	134.6	133.3	131.0	132.6	135.9	135.3
$r(C_2C_3)$	139.4	139.2	137.8	140.6	140.3	136.7	136.4	138.6
$r(C_3C_4)$	139.2	139.4	137.3	137.1	139.4	140.2	137.5	137.6
$r(C_4C_5)$		140.0	140.0			140.1	140.3	
$r(C_5C_6)$		138.9	139.5			137.8	138.4	
$r(C_6N)$		135.0	133.5			136.5	135.1	
$\vartheta(C_6NC_2)$	117.3	118.8	118.4	118.2	132.4	120.7	122.9	124.0
$\vartheta(NC_2C_3)$	123.6	126.5	119.5	123.7	114.4	124.8	116.2	119.3
$\vartheta(C_2C_3C_4)$	118.5	115.2	123.9	115.3	118.8	115.4	124.9	115.4
$\vartheta(C_3C_4C_5)$	118.5	119.6	116.0	124.0	121.1	120.7	116.5	126.4
$\vartheta(C_4C_5C_6)$		119.0	118.2			119.9	119.4	

[a] From B3LYP/6-311+G(d,p) unconstrained optimizations. [b] Bond lengths in pm, bond angles in degrees.

TABLE 3: Computed[a] Select Vibrational Fundamentals in Pyridine, Pyridyl Radicals, and Pyridiniumyl Radical Cations

pyridine	2-pyr•	3-pyr•	4-pyr•	pyr•$^+$	2-pyr•$^+$	3-pyr•$^+$	4-pyr•$^+$
1579	**1612**	1564	1574	1553	**1653**	1658	**1642**
1575	1526	1495	**1491**	1477	1573	**1614**	1617
1480	1464	1434	1436	1433	**1529**	1512	1552
1441	1389	1407	1377	1411	1472	1477	**1469**
1354	1305	1294	1291	1295	1366	1379	1355
1234	1228	1222	1217	**1231**	1335	1309	1320
1224	1150	1177	1209	1164	1230	1271	1276
1156	1093	1087	1056	1162	1188	1198	1205
1073	1047	1036	1045	1058	1091	1095	1100
1051	*1016*	*1025*	*1020*	1053	1060	1066	1063
1030				*1005*	1031	*1035*	*1030*
998	988	973	963	996	*1030*	1011	1005
994	950	972	961	959	*1014*	1010	985
987	939	925	940	955	987	973	985
939	871	902	810	908	890	908	869
878				**727**	805	843	845
751	**739**	**770**	**754**	654	**730**	**760**	**736**
705	700	**674**	697	607	664	**645**	680
662	655	654	636	571	639	640	626
609	572	572	612	540	607	606	618
411	417	414	436	395	421	409	414
375	377	381	370	324	379	375	386

[a] Fundamental frequencies in cm^{-1} from B3LYP/6-311+G(d,p) calculations. Prominent IR peaks in bold, Raman in italics.

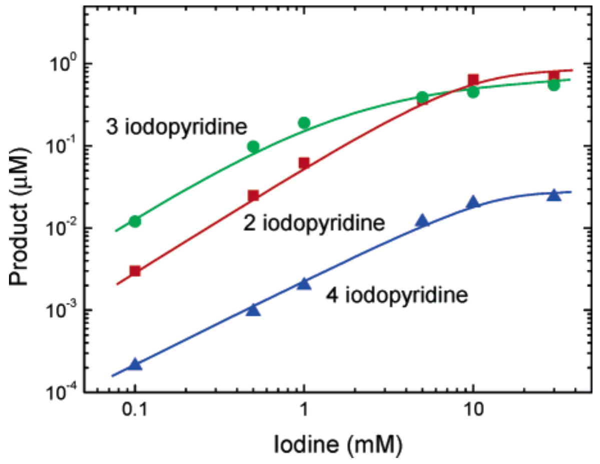

Figure 2. Steady-state concentration of stable products as a function of added iodine without radiolysis: (■) 2-iodopyridine; (●) 3-iodopyridine; (▲) 4-iodopyridine.

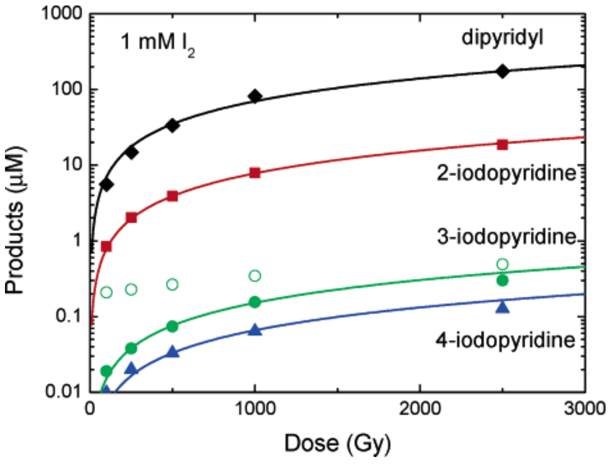

Figure 3. Production of products as a function of dose in the γ-radiolysis of pyridine with 1 mM iodine: (◆) dipyridyl; (■) 2-iodopyridine; (●) 3-iodopyridine; (▲) 4-iodopyridine.

presented in Figure 3. The slopes of the lines in Figure 3 give *G*-values of 0.42, 0.094, 0.0024, and 0.0011 molecule/100 eV for dipyridyl, 2-iodopyridine, 3-iodopyridine, and 4-iodopyridine, respectively. These results suggest that the relative stability of 2-iodopyridine:3-iodopyridine:4-iodopyridine is about 85:2:1. Clearly, 2-iodopyridine comes from the most stable pyridyl radical. Note, however, that while the relative stabilities of the isomeric iodopyridines match that of the corresponding pyridyl radicals, the bulkier iodo substituent leads to a more even isomeric energy distribution. 2-Iodopyridine is calculated to be about 5 kJ mol^{-1} more stable than the meta isomer, which is in turn about 1.5 kJ mol^{-1} more stable than 4-iodopyridine.

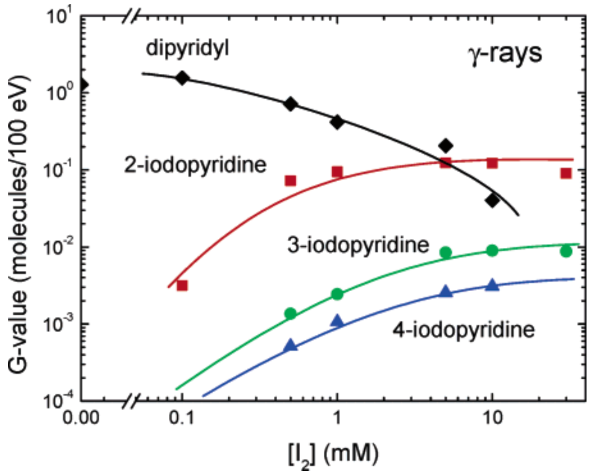

Figure 4. Yields in the γ-radiolysis of pyridine as a function of iodine concentration at a dose of 500 Gy: (◆) dipyridyl; (■) 2-iodopyridine; (●) 3-iodopyridine; (▲) 4-iodopyridine.

The addition of I_2 positively identifies the pyridyl radical isomers by the iodides and gives information on the role of radicals in the production of other products by their decreased yield. Dipyridyl is the major single condensed phase product in the radiolysis of pyridine. Polymer yields are reported to be 3.8 molecules/100 eV, but this group of compounds will have to be ignored until they can be better characterized.[9] Figure 4 shows the variation in product yields as a function of iodine concentration. All three iodopyridines increase in yield with increasing iodine concentration because of the increased scavenging of the pyridyl radical in competition with its other reactions. The relative ratios of the iodopyridines are approximately the same at all iodine concentrations, suggesting they have a common source. All the iodopyridine yields appear to reach limiting values at the highest iodine concentrations. This finding suggests that all pyridyl radicals are scavenged at iodine concentrations above about 30 mM.

The addition of iodine should decrease the yields of those products that have radical precursors. Figure 4 shows a significant decrease in dipyridyl with increasing iodine concentration, suggesting that radicals are the sole source of this product. However, 2-iodopyridine, the major iodide, has a limiting *G*-value of only about 0.1 molecule/100 eV. The initial, no iodine, yield of dipyridyl is 1.25 molecules/100 eV, so only about 10% of its formation is due to scavengable pyridyl radicals. The other portion of dipyridyl involves a radical, but not necessarily the pyridyl radical. One possible explanation is that the decomposition of pyridine produces pyridyl radicals, which rapidly react with pyridine to give a pyridyl–pyridine radical. This reaction is too fast for the iodine to completely scavenge the pyridyl radicals at 10–30 mM I_2. The pyridyl–pyridine radical can itself be scavenged by iodine, leading to a decrease in dipyridyl with increasing I_2 concentration. However, the plateau observed at the highest I_2 concentration for the iodopyridines suggest that all pyridyl radicals have been scavenged. Another possibility for the dipyridyl is an ion molecule reaction of the radical cation with pyridine, followed by neutralization to give the pyridyl–pyridine radical. The radical cation is observed in γ-irradiated rigid matrixes[14] and in the gas phase by neutralization–reionization mass spectrometry.[29] Calculations presented in this work suggest its formation in the liquid will be followed by proton transfer to produce the pyridinium ion and predominantly the 4-pyridiniumyl radical. This latter radical cation can then react with pyridine to give, after deprotonation, a pyridyl–pyridine radical.

Conclusions

The major single condensed phase product in the γ-radiolysis of pyridine is dipyridyl with a yield of 1.25 molecules/100 eV total energy absorbed. This result agrees well with an earlier study by Antoine.[9] A radical trap, DPPH, found that the total radical yield is about 2.8, which matches the measured yield of dipyridyl. Scavenging studies suggest most of the dipyridyl has a radical precursor, but only about 10% of that is due to the pyridyl radical. The remainder of the dipyridyl may be due to reaction of the parent radical cation with pyridine followed by neutralization. Iodine scavenging and quantum chemical calculations both show that the ortho-pyridyl radical (2-pyridyl) is far more stable than the other two isomers.

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