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ABSTRACT: The contribution of the low-energy excited states to the overall product formation in the radiolysis of simple aromatic liquidsbenzene, pyridine, toluene, and aniline—has been examined by comparison of product yields obtained in UV-photolysis and in γ -radiolysis. In photolysis, these electronic excited states were selectively populated using UV-light excitation sources with various energies. Yields of molecular hydrogen and of "dimers" (biphenyl, bibenzyl, dipyridyl for benzene, toluene, pyridine, respectively, and of ammonia and diphenylamine for aniline) have been determined, since they are the most abundant radiolytic products. Negligibly small production of molecular hydrogen in the UVphotolysis of aromatic liquids with excitation to energies of 4.88, 5.41, 5.79, and 6.70 eV and the lack of a scavenger effect suggest that this product originates from short-lived high-energy singlet states. A significant reduc-



tion in "dimer" radiation-chemical yields in the presence of scavengers such as anthracene or naphthalene indicates that the triplet excited states are important precursors to these products. The results for toluene and aniline suggest that efficient dissociation from the lowest-energy excited triplet state leads to noticeable "dimer" production. For benzene and pyridine, the lowest-energy triplet excited states are not likely to fragment into radicals because of the relatively large energy gap between the excited state level and corresponding bond dissociation energy. The "dimer" formation in the radiolysis of benzene and pyridine is likely to involve shortlived high-energy triplet states.

INTRODUCTION

Selective excitation to a specific molecular state and monitoring its subsequent decay is of obvious importance in typical photochemical studies of hydrocarbon liquids, but ionizing radiation can lead to the population of a wide variety of energetic molecular states whose role in the overall radiolytic process is not very well understood. The passage of high-energy radiation in simple aromatic liquids is known to result in the formation of excited states and ionized species.^{1,2} For example, the average energy required to produce an ion pair (W value) of benzene is 26.9 eV per ion pair, whereas its ionization potential is only 9.2 eV.^{3,4} In other words, for every ion pair produced in benzene, 17.7 eV or more than 65% percent of the energy ends up in electronic, vibrational, and rotational modes of excitation that do not lead to ionization. Neutralization reactions in media of low relative static permittivity (dielectric constant) are very efficient. The radiation-chemical yield (*G* value) for free ion pair production in the γ -radiolysis of liquid benzene is only 5.5 nmol/J (0.053 ions per 100 eV).⁴ The extremely fast ion-recombination reactions populate molecular excited states with energies ranging from the lowest-energy excited state all the way to the ionization continuum. Each of these molecular states can initiate a chemical pathway for the decomposition of the medium.

Excited states are known to play an important role in the radiolysis of aromatic compounds. Both molecular products and radicals are thought to originate from excited states.^{1,5-7} For

example, a singlet excited state of benzene is believed to be the precursor to molecular hydrogen and acetylene,^{8,9} while a triplet excited state has been shown to give rise to a phenyl radical and hydrogen atom.¹⁰ Scavenging studies conclude that most of the dipyridyl production in the γ -radiolysis of pyridine is due to the decay of a pyridine triplet excited state.¹¹ However, little is known about which singlet or triplet excited state leads to product formation. Photochemical studies of aromatic hydrocarbons have shown that internal conversion from the higher to lower-energy excited states is very fast.¹² The generally accepted concept is that higher energy states initiate little chemistry.¹ Early studies on the relaxation of benzene suggested that, in addition to fluorescence and intersystem crossing, a third pathway exists for the decay of higher-energy excited states.¹⁴ This process has been proposed to occur in pyridine to account for radiationless decay and for the production of H_2 .^{15,16} A similar phenomenon has also been proposed for the dissociation of the higher-energy singlet excited states of benzene and similar compounds,¹⁷ but the overall significance of higher-energy excited states in the general scheme for decomposition of aromatic liquids has not been established.

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The purpose of the present study is to determine the role of selected excited states in the formation of some of the observed products in the radiolysis and photolysis of simple aromatic liquids. The response of these media to specific UV excitation energies are compared to that observed with γ -radiolysis. Benzene, pyridine, aniline, and toluene were chosen as representative of simple aromatic liquids. The molecules have sufficient variation that the effects due to heteroatom substitution and the addition of side chains can be evaluated.

EXPERIMENTAL SECTION

Benzene, pyridine, toluene and aniline in the highest purity available were obtained from Sigma Aldrich and used as received, with the exception of aniline. Rapid oxidation of aniline required it to be distilled under vacuum immediately prior to irradiations. A spinning band distillation apparatus from B/R Instrument Corporation was used for this purpose. Biphenyl, bibenzyl, and 2,2'-dipyridyl were also obtained from Sigma Aldrich and used without further purification. Diphenylamine from Fisher Scientific Company was recrystallized twice from isopropanol before use. Napthalene and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) used as triple state scavengers in aniline were obtained from Aldrich. The ferrioxalate actinometer was synthesized using potassium oxalate monohydride and anhydrous ferric chloride, both from Alfa Aesar with purity of at least 98%. 1,10phenanthroline used for coloring the ferrioxalate actinometer was of 99+% purity from Sigma Aldrich.

Irradiations were carried out using a Shepherd 109 – 68 ⁶⁰Co γ -source in the Radiation Laboratory at the University of Notre Dame. Radiolysis of all compounds was performed under inert atmosphere (ultrahigh purity argon or helium). The dose rate was 67.4 Gy/min as measured by the Fricke dosimeter.¹⁸ The absorbed dose in irradiated aromatics was assumed to be proportional to its electron density relative to that of the dosimeter. Samples for H₂ analysis were irradiated in a cell made from a quartz cuvette containing an entrance and exit port for inline connection to the gas chromatograph. Samples for analysis of other products were purged and flame-sealed in Pyrex tubes of 1 cm diameter by about 10 cm long.

Excitation with UV was obtained by using several different discharge lamps. A low pressure mercury lamp was used at 254 nm (4.88 eV) and a similar lamp with a high purity quartz window was used at 185 nm (6.70 eV). Both lamps were from Atlantic Ultraviolet. Cadmium and zinc lamps of 229 nm (5.41 eV) and 214 nm (5.79 eV), respectively, from Ealing were also used. The sample cell was a modified quartz cuvette containing a four way valve for connection to the gas chromatograph. The 3.5 mL sample was purged with ultrahigh purity argon before irradiation and continuously stirred throughout the irradiation. Actinometry was performed in the same configuration as used with the aromatics. The actinometer used at 185 nm was an aqueous solution of ethanol.¹⁹ The actinometer used for the other lamps was the ferrioxolate.^{20,21} At 254 nm, the actinometry based on [Co(NH₃)₅Br]Br₂ complex was used as well.²² The actinometer solutions were stirred during irradiation in the same fashion as the aromatic samples. Absorbance spectra of the aromatics as presented in Figure 1 show that virtually all of the incident photons are absorbed by the sample. Photolytic quantum yields were determined by dividing the amount of products formed by the number of photons absorbed. Since all photon energy is absorbed by the media the absolute photolytic yields



Figure 1. UV-visible absorption spectra of benzene, toluene, pyridine, and aniline.

were determined by dividing the quantum yields by the energy per photon and conversion to the radiation chemical unit of nanomoles per Joule (nmol/J).

Molecular hydrogen was determined using an inline technique as previously described.¹⁵ Gas chromatographic analysis was performed with a SRI 8610 apparatus equipped with a thermal conductivity detector. The chromatographic column was a 6.4 mm diameter 13X molecular sieve 3 m long, maintained at 40 °C. Calibration was performed by injection of pure H_2 at normal conditions.

Biphenyl, dipyridyl isomers, bibenzyl, and diphenylamine were analyzed with a Thermo Finnigan Trace gas chromatograph-mass spectrometer functioning in the selective ion monitoring mode. Biphenyl was detected at mass 154, dipyridyl isomers at mass 156, diphenylamine at mass 169, and bibenzyl at mass 182. A 25 m Chrompack CP-Sil-8-CB capillary column (0.32 mm i.d.) was used for these separations. A 1.0 μ L aliquot of the studied samples was analyzed in a splitless injection mode. Chromatographic analysis of bibenzyl and dipyridyl isomers consisted of maintaining an initial column temperature at 145 °C for 30 min. The temperature was then raised to 250 °C at a rate of 30 °C/min and held for 10 min. The separation of the dipyridyl isomers could not be fully achieved, and the sum of their yields is given. Experimental conditions of diphenylamine detection included maintaining of initial column temperature at 160 °C for 30 min and subsequently heating to 250 °C at a rate of 30 °C/min and then held for 10 min. Biphenyl analysis was performed with an initial column temperature held at 100 °C for 15 min and then increased to 145 $^{\circ}\mathrm{C}$ at a rate of 30 $^{\circ}\mathrm{C}/\mathrm{min}$ and held for 14 min followed by heating to 250 at 30 $^{\circ}\mathrm{C/min}$ and held for 10 min. The relative retention times of the compounds of interest were confirmed by comparison with corresponding standards and their fragmentation patterns. Sets of standard solutions were also used for concentration calibration.

The production of ammonia was determined using an analytic AMMONIA CHEMets kit from CHEMetrics, Inc., which employs the salicylate method of ammonia determination. Following irradiation, aniline was purged with a stream of helium gas, which then passed through two traps. Aniline vapors were captured in the first trap that was filled with toluene. The resulting helium—ammonia



Figure 2. Energies of the three lowest-energy singlet excited states of benzene, pyridine, toluene, and aniline and the corresponding energies of the UV excitation sources.

mixture was bubbled through a water trap where the ammonia was captured and analyzed according to the AMMONIA CHEMets procedure. A cross check of this procedure was made using a UV–visible spectrometer to get accurate absorbance values at $\lambda_{max} =$ 700 nm. The concentration of ammonia was calculated on the basis of calibration performed with ammonia standard solutions in the concentration range between 0.5 ppm and 2.0 ppm of NH₃ nitrogen. Stock standard solutions of ammonia (50 ppm NH₃ nitrogen) were obtained from the Hach Company.

RESULTS AND DISCUSSION

Two γ -rays of 1.17 and 1.33 MeV energy are emitted by the decay of 60 Co.² These γ -rays lose energy by interactions with electrons of the medium in Compton processes to produce secondary electrons with hundreds of kiloelectron volts. The mean energy loss by high-energy electrons is on the order of tens of electron volts, which is much higher than the energy required for most common transitions of a molecule and leads to ionization of the medium molecules with unit efficiency.²³ In aromatic liquids, the initially formed radical cations and electrons undergo an extremely fast recombination. For instance, in liquid benzene, the combination reaction in ion pairs happens within 1.2 ps.²⁴ Similarly fast recombination is known to occur in toluene and pyridine. Only the aniline radical cation has a lifetime long enough to be easily observed by nanosecond pulse radiolysis.²⁵ Neutralization reactions in γ -radiolysis produces excited states of the medium ranging in energy from the lowest to superexcited states lying above the ionization continuum.²

In contrast, low-energy photons of the few electron volts used here are completely absorbed (cf. Figure 1) to excite the medium to the corresponding molecular excited states. The compounds examined in this study are in the liquid phase so the energy levels are not discrete, but broad bands. Figure 2 depicts the lowest three energy levels of excited singlet states for the aromatic compounds chosen for this study and the corresponding energies of the excitation sources. Excitation with a mercury vapor lamp at 254 nm (4.88 eV) will excite all of the compounds to at least the lowest-energy singlet excited state. The other mercury vapor line at 185 nm (6.70 eV) is capable of exciting the S₃ level of all four aromatic compounds. Various energy levels can be reached by the cadmium 229 nm (5.41 eV) and zinc 214 nm (5.79) lamps. These latter two lamps were only used for H_2 determination and were found to give identical results as with the 254 nm lamp.

The high-energy singlet excited states of aromatic compounds generated in γ -radiolysis are rather short-lived species. In general, they are expected to undergo internal conversion to the lower levels within about 10^{-11} s.⁴ In UV-photolysis, internal conversion often brings the aromatic system into a highly vibrationally excited ground electronic state, which is commonly called a "hot molecule". The rate of internal conversion increases rapidly as the energy of the excited state increases. For instance, the S₂ state of benzene and its analogues are found to undergo internal conversion in the subpicosecond time scale.^{12,17} The energy possessed by the "hot molecule" is high enough to cause the bond rupture. However, the dissociation process is rather slow and may take several microseconds to occur.²⁷

Photoexcitation of benzene and its derivatives results in variety of reactions.²⁸ Part of the excited state molecules undergoes photoisomerization reactions forming the fulvenes, benzvalenes, Dewar-isomers, prismanes, as well as isomerization of the alkyl substituent in the aromatic ring and fragmentation reactions.²⁹ These photochemical processes account for the reduced internal conversion efficiency from the S₂ and S₃ to S₁ state of benzene and its derivatives.³⁰ Isomerization products are not observed in the γ -radiolysis of aromatics. The bulk of the primary excitations in γ -radiolysis is to the higher energy range of 20–40 eV, i.e., much higher levels than S_2 or S_3 are initially excited.31 These high-energy excited states undergo internal conversion directly to the lowest energy singlet level, which is manifested by the increased fluorescence efficiency in γ -radiolysis compared to UV-excitation.³² On another hand, the reaction pathways originating from the high-energy excited states are accessible only in γ -radiolysis. This variation in the accessible excited states must be kept in mind while contemplating the molecular product patterns observed in the continuous UV-photolysis experiments with those found in γ -radiolysis.

All electronically excited states may dissociate when the excitation energy exceeds the energy of the weakest chemical bond. However, in the liquid phase, the excess energy of the excited state is promptly dissipated if the dissociation constants are less than typical vibrational relaxation rates in fluids, i.e., $10^{12}-10^{13}$ s^{-1.26} Taking into account very high rates of internal conversion processes between excitation levels in aromatics, it follows that the major part of high-energy excited states eventually dissipate their energy and populate the lowest-energy excited state. The lowest energy singlet and triplet states (more precisely, their excimers, which is a dimer of the excited molecule with a ground state molecule) of aromatic liquids are formed in high yields in γ -radiolysis. For instance, radiation-chemical yields of the lowest-energy excited states in γ -radiolysis of benzene equal to $G(S_1) = 0.17 \ \mu \text{mol J}^{-1}$ and $G(T_1) = 0.44 \ \mu \text{mol J}^{-1.1}$

The lowest energy singlet and triplet states of aromatics are relatively long-lived species with lifetimes on the nanosecond time scale. So, if allowed thermodynamically, they can initiate chemical reactions. Dissociation processes such as $ArH^* \rightarrow Ar \bullet + H \bullet$ are the dominant primary sources of radicals formed in radiolysis. In turn, the formation of "dimer" products in the γ -radiolysis of aromatics is related to a larger or lesser extent to radical combination reactions. The energetics of the process must be analyzed to establish the feasibility of the direct dissociation from the lowest-energy excited state. Thus, the energies of the lowest singlet and triplet states and the bond dissociation energies for the dissociation process $ArH^* \rightarrow Ar \bullet + H \bullet$

	Table 1. Energies of	of the Low	est S1 and T	¹ States and	Bond	Dissociation	Energy
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	benzene	pyridine	toluene	aniline
bond dissociation energy [*] , kJ mol ⁻¹	475 ^{33,34}	439 ^{33,35}	378 ³⁶	370 ³⁷
vertical energy of the lowest singlet excited state S_1 , kJ mol ⁻¹	473 ³⁸	457 ³⁹	448 ³⁸	418 ³⁸
vertical energy of the lowest triplet excited state T ₁ , kJ mol ⁻¹	354 ³⁸	396 ³⁹	371 ³⁸	361 ³⁸
* For benzene PhH* \rightarrow Ph• + H•; pyridine PyrH* \rightarrow 2-Pyr• + H	•; toluene PhCH ₂ H	$* \rightarrow PhCH_2 \bullet + H \bullet;$ anilin	ne $PhNH_2^* \rightarrow PhNH_2$	I● + H●.

Table 2. Experimental Yields of Some Products Formed in Photolysis and γ -Radiolysis of Aromatics

		product yield, nmol J^{-1}			quantum yield		
aromatic compound	product	254 nm (4.88 eV)	185 nm (6.70 eV)	γ-Co ⁶⁰	254 nm (4.88 eV)	185 nm (6.70 eV)	
benzene	hydrogen	0.21	1.4	3.9	$9.1 imes 10^{-5}$	$9.4 imes 10^{-4}$	
	biphenyl	0.039	0.25	7.8	$2.2 imes 10^{-5}$	$1.7 imes 10^{-4}$	
pyridine	hydrogen	~ 0	0.22	2.8	~ 0	$8.5 imes 10^{-5}$	
	dipyridyl	0.069	1.5	130	$3.3 imes 10^{-5}$	$9.9 imes 10^{-4}$	
toluene	hydrogen	0.098	0.82	14.5	$9.1 imes 10^{-5}$	$4.8 imes 10^{-4}$	
	bibenzyl	0.65	7.1	6.8	$3.2 imes 10^{-4}$	$4.0 imes 10^{-3}$	
aniline	hydrogen	0.17	1.9	12.4	$8.3 imes 10^{-5}$	$1.2 imes 10^{-3}$	
	diphenylamine	22	61	4.15	$9.1 imes 10^{-3}$	4.0×10^{-2}	
	ammonia	31	40	52	1.5×10^{-2}	3.6×10^{-2}	

are presented in Table 1 for the molecules examined here.^{33–39} On the basis of the data presented in Table 1, the thermodynamic feasibility of C–H bond dissociation exists for the lowest-energy singlet excited state of the studied aromatics. The excess energy is especially large for toluene and aniline. In the case of toluene and aniline, even the lowest-energy triplet excited state possesses enough energy to allow for C–H bond dissociation. In contrast, the dissociation from the T₁ state of benzene and pyridine has a low probability based on energetic reasons.

In this work, the measured yields of H_2 and of "dimers" of the parent molecules are used as probes of the effects caused by the primary excitation to the different energy levels. The molecular products investigated here are typically the most abundant and should give a good representation of the overall medium decay. The results of the γ -radiolysis and UV-photolysis of benzene, pyridine, toluene, and aniline with various excitation energies are presented in Table 2. The yields are expressed in the radiation chemical unit of nanomoles per joule (104 nmol $J^{-1} = 1$ molecule/100 eV). The equivalent unit can be obtained from the photolytic quantum yields by the number of photons absorbed and the energy per photon.

H₂ **Production.** The H₂ yields for the UV-photolysis at 254 and 185 nm and for γ -radiolysis are arranged in graphic form in Figure 3. Higher yields of H₂ are observed in the γ -radiolysis of all the studied aromatics compared to those values obtained in photolysis. The γ -radiolysis of toluene and aniline produces considerably more H₂ compared to benzene and pyridine due to the presence of the H• atom containing substituents ($-CH_3$ and $-NH_2$, respectively), which are expected to be actively involved in fragmentation processes. Radiolysis of aliphatic compounds is well-known to produce H₂ in much larger quantities than found with aromatic compounds.¹

Molecular hydrogen yields obtained in the UV-photolysis are negligibly small in all cases compared to the γ -radiolysis results. Nevertheless, H₂ yields increase when the photon excitation energy is increased. This observation suggests that high-energy excited states are the main precursors of H₂. The formation of H₂ from the high-energy excited states must be due to very rapid processes since they have to compete with internal conversion, which typically occurs on the picosecond time scales.

The yield of H_2 in the radiolysis of liquid benzene and pyridine varies significantly with the type of radiation and on the linear energy transfer (LET = -dE/dx).^{15,40} In general, $G(H_2)$ increases with LET due to the increased significance of the intratrack bimolecular processes. Burns has suggested that H_2 is produced in the radiolysis of benzene as a result of the reaction between two singlet excited state molecules.^{8,41} The implied intermediate in this process is a high-energy singlet state that is more likely to decompose to H₂ than the S₁ excited state. A study of the fluorescence intensity dependence on LET in the heavy ion radiolysis of benzene has provided strong support for the role of the excited singlet state in H₂ production.^{9,40} A logical assumption of this observation is that reaction between singlet excited states is facilitated in the radiolysis of all the aromatic compounds studied here because of the nonhomogeneous nature of energy deposition in radiolysis as compared to the homogeneous deposition of energy in photolysis. Excited states produced by the latter are generated homogeneously in the bulk of the solution, and the chances of their encounter are rather small.

One more experimental evidence corroborating the importance of the bimolecular mechanism of molecular hydrogen formation comes from isotopic composition studies. Total hydrogen yield $G(H_2 + HD + D_2)$ generated from benzene-benzene-d₆ equimolar mixtures clearly shows a large contribution of HD, which is the product of bimolecular reaction.⁴² Identical isotopic composition of molecular hydrogen is observed for the different types of radiation, although the total yield changes markedly.⁴³ Again, this result is evidence for the bimolecular mechanism of molecular hydrogen formation. Only a small number of H• atoms contribute to the H₂ yield in the case of benzene and its derivatives, since H• atoms readily add to the aromatic ring.⁴⁴ Irradiation of toluene and its deuterated analogues demonstrates that the H₂ is formed from the H• atoms of



Figure 3. Molecular hydrogen production in photoexcitation at 254 and 185 nm and in the γ -radiolysis of benzene, pyridine, toluene, and aniline: left to right in each panel.

both the side-chain and the aromatic ring.⁴⁵ However, the contribution of the toluene methyl group to H_2 formation is greater than that of the aromatic moiety. Unimolecular processes account for about 38% of H_2 formed from the ring, while 62% is due to bimolecular reactions.

Experimental efforts to elucidate the precursor of H₂ produced in the radiolysis of liquid aromatics have used quenchers to selectively scavenge radicals, electrons, radical cations or excited states. The addition of typical radical scavengers, like iodine, shows no effect on the formation of H₂ in the radiolysis of benzene,⁴⁶ pyridine,⁴⁷ and toluene.¹ Unfortunately, radical scavengers I2 and 1,1-diphenyl-2-picrylhydrazyl (DPPH) cannot be used with aniline because of their direct chemical interaction.⁴⁸ One can conclude from the available information that radical processes do not contribute noticeably to the radiolytic formation of H₂. Experiments on benzene solutions with electron scavengers (COS, N2O) demonstrate that there is significant formation of electrons in the system as reflected by the production of CO and N2, respectively, but the H2 yields are not affected.49 In this work, similar results were observed with saturated solution of N₂O in toluene; that is, no effect on H₂ yields was noticed with added quencher. C2H5OH and C2H5Br have been used as radical cation and electron scavengers, respectively, in the radiolysis of toluene, and no influence on H₂ yield is noticed.⁵⁰ Finally, the H₂ yields show no dependence on the addition of the excited state scavengers anthracene and biphenyl in the radiolysis of pyridine and aniline.47,51 The formation of H_2 in the γ -radiolysis of aniline is not affected by the addition of naphthalene and TMPD either.⁵¹ Apparently, none of the conventional quenchers are capable of scavenging any appreciable fraction of H₂ formed in the radiolysis of liquid aromatics. The only possible precursor to H₂ remaining are the high-energy excited states of these aromatics. These high-energy excited states must be very short-lived, since they can not be scavenged by the quenchers even at high concentration.

There are reports in the literature that the addition of chloroform leads to the reduction of the relative fluorescence efficiency of the high-energy excited states.^{52–54} These excited states can be viewed as charge-transfer (CT) complexes.³² Chloroform acts as an extremely efficient electron acceptor and quenches such CT complexes. An attempt was made to observe whether the presence of chloroform would affect the H₂ formation in the γ -radiolysis of aromatic hydrocarbons. For this purpose, the





Dimer

Figure 4. Biphenyl, dipyridyl, and bibenzyl production in photoexcitation at 254 and 185 nm and in the γ -radiolysis of benzene, pyridine, and toluene, respectively: left to right in each panel.

solutions of 0.5 M chloroform in benzene, toluene, and aniline were irradiated, and H₂ yields were determined. The yields of H₂ were reduced by 10–15% compared to the neat aromatics. However, a more detailed study of a wide range of chloroform concentrations in toluene revealed that the reduction in H₂ yield is proportional to the molar fraction of the scavenging additive. The result indicates that the decrease in the amount of H₂ comes simply from a dilution effect since the radiolysis of chloroform itself is not known to produce H₂.⁵⁵

The conclusion based on the presented data is that H_2 formed in the radiolysis of these aromatic liquids originates from shortlived high-energy excited states. Available literature data also strongly suggest that molecular hydrogen comes from a bimolecular process. These excited states are formed and decompose at the earliest stages after irradiation in the subpicosecond time range. Higher levels of excitation than used in this work (>6.7 eV) would be necessary to identify the excitation energy limit required to achieve H_2 yields comparable with those in γ -radiolysis.

Biphenyl Formation from Benzene. The main simple hydrocarbon product observed in the γ -radiolysis of neat liquid benzene is biphenyl with a small yield of 7.8 nmol $J^{-1.7}$. The initial decomposition of benzene following the absorption of energy from ionizing radiation results in the generation of the phenyl radical, C₆H₅•, and a H• atom. One might assume that biphenyl is formed by the recombination of phenyl radicals by analogy to the dimer formation in the radiolysis of cyclic alkanes.⁴⁷ However, aromatic compounds are good radical scavengers, and studies with I₂ have shown that both C₆H₅• and the H• atom combine with parent benzene molecules to initiate formation of phenylcyclohexadienyl and cyclohexadienyl radicals, respectively.⁷ Subsequent reactions of the phenylcyclohexadienyl radical result in biphenyl formation, but most radicals generated in radiolysis contribute to polymer production.⁵⁶

The total radiation-chemical yield of biphenyl in neat benzene is due to several contributing processes. Even at the highest concentrations of I_2 , when virtually all phenyl radicals are scavenged, the yield of biphenyl does not drop to zero.⁴⁰ The fact that biphenyl yield does not depend on LET further suggests that precursors of this dimer do not participate in bimolecular reactions of reactive species, and part of this product is formed due to a nonradical mechanism.⁴⁰ Biphenyl may be formed by the dissociation of high-energy excited states. These excited states are short-lived, so their decomposition may account for minor processes such as the formation of biphenyl.

The yield of biphenyl in the 254 and 185 nm photolysis of benzene corresponds only to 0.5% and 3.2% of the radiation chemical yield obtained in γ -radiolysis (cf. Table 2 and Figure 4). Excitation at 254 nm produces the lowest energy singlet state S₁ of benzene, while 185 nm excitation generates the S₃ excited state. Subsequently, the S3 state undergoes internal conversion to the S₁ level with an efficiency of 0.45.⁵⁷ The lowest-energy triplet excited state T₁ is formed from S₁ with an intersystem crossing efficiency equal to 0.56.¹ The formation of phenyl radical due to the dissociation of the excited molecule of benzene in the T_1 state is improbable due to the unfavorable energetics of the process (cf. Table 1). The remaining alternative for biphenyl production in photolysis is a direct dissociation process. Such dissociation is thought to take place not from the S₃ state directly, but from the ground state via a "hot" benzene mechanism.⁵⁸ Very small yields of biphenyl obtained in UV-photolysis, as shown in Figure 4, seem to reflect this low probability of the excited molecule dissociation.

Radiation-chemical yield of biphenyl in the radiolysis of benzene is strongly reduced in the presence of naphthalene or anthracene, well-known scavengers of the triplet excited states.^{1,10,59} The reduction of biphenyl yield in their presence suggests that a high-energy triplet state of benzene is a precursor to the phenyl radical and H• atom. Nevertheless, both naphthalene and anthracene were shown not only to quench the triplet states of benzene, but also to add readily to phenyl radicals.⁵⁹ Biphenyl production is obviously affected by additives at different stages of its formation: quenching of high-energy triplet excited states of benzene and reactions of already formed phenyl radical. In other words, the triplet scavenger effect on the "dimer" formation in the radiolysis of benzene is complex. This observation must be borne in mind when considering the scavenger effect on the production of "dimers" of other studied aromatics as well.

Dipyridyl Formation from Pyridine. The photolytic yields of dipyridyl are negligibly small (<1%) in comparison to its radiation chemical yield (cf. Figure 4 and Table 2). These results suggest the lower-energy excited states of pyridine give only a very minor contribution to the dimer formation. Iodine scavenging studies demonstrate that most of dipyridyl has a radical precursor, but only about 10% of it is due to the pyridyl radical.¹⁵ In close analogy to the biphenyl formation in benzene radiolysis, the dipyridyl yield is the result of several processes: direct recombination of the pyridyl radicals, dehydrogenation of the "pyridyl radical-pyridine" (analogous to the phenylcyclohexadienyl radical), deprotonation of the charge-transfer complex of pyridiniumyl radical cation and neutral pyridine (minor channel, only a few percent).¹⁵ The production of dipyridyl can almost completely be thwarted by the presence of scavengers of the triplet excited states like anthracene.¹¹ As in the case of benzene, the quencher effect may be complex too, that is, the high-energy triplet excited states can be scavenged as well as the low-energy states or pyridyl radicals may add to the quencher molecules.

In contrast to biphenyl, the value of G(dipyridyl) is LET dependent. The dimer yield decreases with increasing track average LET.¹⁵ This result is attributed to intratrack triplet—triplet annihilation processes that gain importance at high LET

with the increased concentrations of triplet excited states. The result of the annihilation is a repopulation of high-energy singlet excited states. Photolysis measurements show that the lowest T_1 state is unlikely to produce pyridyl radical. This dissociation is also not favored energetically (cf. Table 1). The high observed yield of dipyridyl in the radiolysis of pyridine suggests that the high-energy excited states might be responsible for "dimer" formation.

Bibenzyl Formation from Toluene. Analysis of the published data shows that most of the photolytic studies on toluene were conducted in the vapor phase.^{58,60-64} Collision-free conditions are created in the gaseous state and the dissipation of energy by the excited state molecules through interaction with medium can be prevented. Hence, the formation of various photoproducts is expected in such conditions. The photolytical research on toluene performed in the liquid phase reveals only the importance of photophysical relaxation processes and of photoisomerization reactions. 17,65-67 Nevertheless, the formation of bibenzyl in the Hg-sensitized photolysis of toluene vapor has been reported. Bibenzyl is formed in relatively high yield compared to other stable molecular products.⁶⁸ In this work, bibenzyl is also detected as a dominant "simple" product among other condensed-phase products generated both in steady-state photolysis and γ -radiolysis. Another contemporary work corroborates our observation.69

The yield of bibenzyl in the γ -radiolysis of liquid toluene is reduced to 5% of the initial value in the presence of radical scavengers.⁷⁰ Hence, bibenzyl produced upon irradiation of toluene derives almost entirely from a radical precursor, the benzyl radical. Benzyl radical, in turn, is thought to be formed due to the decay of excited state molecules of toluene.⁷¹ Irradiation of toluene under collision-free conditions at 193 nm showed that α -H• atom elimination and CH₃ elimination are the major dissociation channels (cf. reactions 1–2):

$$C_6H_5CH_3^* \to C_6H_5CH_2 \bullet + H \bullet \tag{1}$$

$$C_6H_5CH_3^* \rightarrow C_6H_5 \bullet + CH_3 \bullet$$
 (2)

The dissociation rate for process (1) was found to be $2 \times 10^6 \text{ s}^{-1}$. Direct C-H and C-C bond cleavage is believed to be the dissociation mechanism, proceeding through the vibrationally excited ground electronic state of toluene ("hot toluene").72 Rapid internal conversion to S₀ and S₁ states was observed for the S₂ state of toluene produced by 200 nm excitation. This state has a lifetime of \sim 50 fs.⁷³ The "hot molecule" reaction mechanism is justified by the fast internal conversion from initial high-energy excited states to lower-energy excited states and the slow dissociation rate of toluene. These considerations are based on the gas phase studies, whereas in liquid solutions the dissociation process was shown to be rather inefficient due to the fast dissipation of excess energy through intermolecular collisions. Indeed, the quantum yields of bibenzyl, the product of benzyl radical combination reactions, obtained in this work are small: 3.2×10^{-4} for 254 nm irradiation and 4.0×10^{-3} for 185 nm. However, as can be seen from Figure 4 and Table 2, the yield of bibenzyl at 185 nm photolysis is about the same as in γ -radiolysis. This result gives clear evidence that even 6.70 eV excitation of liquid toluene leads to results similar to that in γ -radiolysis where a large range of excitation is accessible.

There was a distinct difference in temperature regimes while performing 185 nm photolysis and γ -radiolysis of toluene. The exposure of the toluene sample to the 185 nm source heats it to



Figure 5. Four possible dissociation channels of the aniline excited state 80 (254 nm = 4.88 eV and 185 nm =6.70 eV).

40–45 °C during long-time irradiations, whereas γ -radiolytic samples were at room temperature. Radiolysis studies have shown that the yield of bibenzyl exhibits complex temperature dependence.⁷⁴ For example, *G*(bibenzyl) at 25 °C is reported to be 4.1 nmol J⁻¹, whereas at 50 °C it is almost doubled to 7.3 nmol J⁻¹. In this work, the radiation-chemical yield of bibenzyl in γ -radiolysis was repeatedly found to be 6.8 nmol J⁻¹ at room temperature. A temperature effect in photolysis would suggest a slightly lower yield at room temperature than the observed value of 7.1 nmol J⁻¹ at 185 nm. Nevertheless, the results show that the 185 nm excitation of toluene generates excited states that are capable of photodissociation in the liquid phase with yields approaching or equal to that in γ -radiolysis.

Iodine scavenging studies in toluene show that about 95% of bibenzyl has benzyl radical as a precursor.⁷⁰ The energy of the lowest triplet excited state T_1 of toluene is comparable to the bond dissociation energy for the process: PhCH₃* \rightarrow PhCH₂• + H• (cf. Table 1). Therefore, even the 254 nm excitation source employed in this work provides the toluene molecule with enough energy for dissociation either from S_1 or from T_1 state.

An excitation energy of 6.4 eV is sufficient for direct C–C bond and C–H bond dissociation in toluene.⁷² Therefore, the 185 nm (6.70 eV) excitation of toluene can lead directly to the production of benzyl radicals. This bond rupture occurs through the vibrationally excited ground electronic state ("hot toluene" mechanism).

Diphenylamine and Ammonia Formation from Aniline. The γ -radiolysis of aniline is known to generate a large variety of products including the isomeric aminobiphenyls, aminodiphenylamines, and diaminobiphenyls with ammonia, H₂, benzene, and diphenylamine having the greater yields.⁵¹ UV photochemistry of aniline has been studied in detail with special emphasis given to the photoionization and photodissociation processes and how the medium influences them.^{75–77} Polar solvents such as water were shown to facilitate the photoionization from aniline singlet excited states. Fluorescence spectroscopy of the first singlet excited state of aniline S₁ has delivered information on the fluorescence lifetime and quantum yield of each vibronic



Figure 6. Production of diphenylamine and ammonia (left to right in each panel) in photoexcitation at 254 and 185 nm and in the γ -radiolysis of aniline.

level.⁷⁸ The fluorescence lifetime was found to be about a few nanoseconds. Among the nonradiative processes, the intersystem crossing from the S_1 state appears to be the major one. The triplet excited state decays rapidly, so that no phosphorescence is observed. The rate of the triplet excited state decay increases as the energy of the state increases.⁷⁹

Photolysis of aniline with high energy excitation, such as the 6.7 eV photons employed in this work, involves excitation of the electrons of the aromatic ring $(\pi \rightarrow \pi^*)$. Internal conversion of these excited states occurs very fast and dissociation of the molecule proceeds from the ground state through the channels with low dissociation barriers (N – H and C – N bond rupture). Nevertheless, about 75% of H• atom elimination occurs in the electronic excited state.⁸⁰ Four major dissociation channels are presented in Figure 5.⁸⁰ As a peculiarity of aniline photolysis, the release of closed shell molecules (H₂ and NH₃) in the primary dissociation processes is observed. Even the lowest excitation energy of 254 nm photons used in this study is sufficient enough to overcome the activation energies of all four channels (cf. Figure 5).

Experimental yields of ammonia and diphenylamine in the photolysis and γ -radiolysis of aniline are shown in Figure 6. According to the scheme in Figure 5, ammonia can be formed by the direct dissociation of aniline (branch 4) or by the NH₂ radical intermediate (branch 3). Formation of ammonia increases with increasing photon energy and the highest yield of NH₃ is achieved with γ -rays. Nevertheless, even 254 nm irradiation generates NH₃ in significant amounts. This result is not surprising since the decomposition branch 4 (cf. Figure 5) giving ammonia directly has the lowest dissociation barrier, which is below all the excitation energies applied in this work.

Diphenylamine is most likely to be formed in radical combination reactions. Unfortunately, the typical radical scavenger I_2 was found to directly react with aniline and could not be used to identify specific radical precursors to diphenylamine. Two possible pathways for diphenylamine formation are shown in Figure 7: the first one is the recombination of aminyl and phenyl radical, and the second one is the reaction between 1,2-dehydrobenzene and aniline. Dehydrobenzene has been reported to react readily with amines,⁸¹ and it could be formed in quantities similar to that for ammonia by the decomposition of low-energy excited states (branch 4 of Figure 5). At least 3 out of 4 initial



Figure 7. Diphenylamine formation from aniline.



Figure 8. Yield of diphenylamine in the γ -radiolysis of aniline as a function of added (\blacksquare) naphthalene and (\bigcirc) TMPD.

dissociation channels of excited aniline (Figure 5) generate precursors of diphenylamine. These diverse sources make it quite difficult to track down the origin of diphenylamine to any particular excited state.

Diphenylamine yields as shown in Figure 6 are significantly higher in photolysis than in radiolysis. The γ -radiolysis studies of liquid aniline revealed that H₂ production is not quenched in the presence of various scavengers of excited states, whereas the yield of ammonia and diphenylamine is reduced approximately by half.⁵¹ Hence, H₂ is produced in very fast processes that are most probably due to the direct decay of the higher-energy excited singlet states, which have lifetimes in the picosecond time domain. In contrast, at least half of the yield of ammonia and diphenylamine is derived from a precursor that can be scavenged by quenchers of triplet excited states, like naphthalene, in a diffusion-controlled reaction (cf. Figure 8). The conclusion is that the triplet excited state is a precursor to at least part of the ammonia and diphenylamine. Work elucidating the role of the lower-energy excited states in photoreactions of aromatic amines has suggested that the photodissociation $(RNH_2 \rightarrow RNH \bullet + H \bullet)$ reaction takes place from both lowest-energy singlet and triplet excited states of aniline, but the process occurs more efficiently from the triplet excited state.⁸² This photodissociation reaction creates the aminyl radical, which is one of diphenylamine precursors.

Time-resolved photoacoustic and multiphoton ionization spectroscopic studies of aniline show that the energy deposited into aniline can be selectively directed either into ionization or dissociation.⁸³ The initial yield of the first singlet excited state in the pulse radiolysis of aniline is very low. This state is populated through the internal conversion from the higher-energy singlet excited states over a period of ~10 ns.²⁵ Part of these higher

energy singlet states decompose to give H₂. Population of the higher-energy singlet excited states can occur only for γ -radiolysis in our studies, which justifies the big difference in H_2 yield between radiolysis and photolysis of aniline (cf. Figure 3). Once the higher-energy excited state fragments, it is not capable of populating the lower-energy excited states through internal conversion. However, photolysis directly populates the lowerenergy excited states, which tend to dissociate into radical fragments that are the precursors of diphenylamine. Dissociation is especially efficient from the triplet excited state of aniline.⁸² Taking into account the high yield of intersystem crossing $(\Phi_{\rm ISC}$ = 0.68)⁷⁶ for the process $S_1 \rightarrow T_1$ in aniline, the 254 and 185 nm excitation used in this work should populate well the lowest-energy triplet excited state of aniline with some additional vibrational excitation, which would lead to efficient dissociation and eventually to the formation of diphenylamine in high yields.

Aniline has high viscosity (3.71 cP), which is 4-6 times greater than the viscosity of other aromatic liquids studied here. Such high viscosity of the medium could influence the efficiency of solvent stirring and, therefore, the homogeneity of the products in the photolysis of aniline. High local concentrations of products could lead to new reactive pathways with the more transient species, or those products themselves could be photolytically degraded.

CONCLUSIONS

The role of the lower-energy excited states in the radiolysis of simple aromatics-benzene, toluene, pyridine, and aniline-has been examined using UV-light excitation sources with various energies. The contribution of the excited states to the overall product formation has been evaluated by comparison of product yields obtained in UV-photolysis and in γ -radiolysis. Yields of H₂ and of "dimers" (biphenyl, bibenzyl, dipyridyl, and diphenylamine for benzene, toluene, pyridine, and aniline, respectively) have been determined since they are the most abundant radiolytic products. Ammonia production in aniline has also been determined. Negligibly small H₂ production in the UV-photolysis of aromatic liquids (4.9, 5.4, 5.8, and 6.7 eV excitation energies) and the lack of any scavenger effect suggests that H₂ originates from very short-lived higher-energy excited states. A significant reduction in "dimer" radiation-chemical yield in the presence of anthracene or naphthalene demonstrates that triplet excited states are important precursors in "dimer" formation of the studied aromatics. Triplet excited state molecules dissociate to give radical fragments: H• atom and the corresponding phenyl, benzyl, pyridyl, or aniline radical. However, attachment of the radical to the parent molecule is strongly favored, and the resulting product does not always lead to "dimer" formations, such as in the case of benzene. The probability of dissociation into radical fragments is governed by the energetic proximity of the lowestenergy excited state level and corresponding bond dissociation energy. In case of benzene, the energetic gap between the lowest triplet state and C-H bond dissociation energy is large, and phenyl radicals are formed in low yields. In contrast, for toluene and aniline, the energies of the lowest triplet states lie very close to the respective bond dissociation energies, which results in effective radical production. The recombination of radicals subsequently leads to the dimeric molecular products. For this reason, even low excitation energies of 4.9 and 6.7 eV give yields

of "dimers", bibenzyl and diphenylamine, that are comparable or even higher than those observed in γ -radiolysis.

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