Investigations of Reactions of Selected Azaarenes with Radicals in Water. 1. Hydroxyl and Sulfate Radicals

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The oxidative degradation of binuclear azaarenes is studied in a number of environmentally relevant radical reactions. The comparison between oxidation mechanisms of hydroxyl and sulfate radicals, as well as between dark and photoreactions, is done. Most of the products formed are identified. With the change from dark to photoreactions of quinoline and isoquinoline, a shift of the oxidation center from the benzene to the pyridine rings is observed. The reaction behavior of the benzodiazines can be derived from the reaction patterns of quinoline and isoquinoline. The rate constants of second order are determined for the reactions of the azaarenes with carbonate radicals. The rate constants and the differences in the products formed conformably prove the importance of the inclusion of excited states in the reaction mechanism. The application of the frontier orbital concept allows an easy interpretation. Electron transfer reactions resulting in radical oxygen species are shown to be product determining in direct photolysis, too.

Introduction

PAH and the analogous azaarenes ubiquitously occur in nature. Many of these compounds and of their oxidation products are toxic and carcinogenic, respectively.[1] Chemical oxidation and photooxidation are the main abiotic degradation reactions for azaarenes in nature. Compared with PAH, abiotic degradation of dissolved substances or microbiological transformations in water are of higher importance for azaarenes because of their higher water solubility (3−4 orders of magnitude).[2,3] Despite many papers on oxidative degradation reactions of environmentally relevant compounds, many questions on the mechanisms and the oxidizing species have not yet been answered. Concerning the advanced oxidation process (AOP) in photocatalysis, for example, there is still a controversial discussion on the role of hydroxyl radicals, positive holes on the surface of a semiconductor or on the role of other reactive oxygen species in electron-transfer reactions.[4−6] For many reactions in nature, the formation, significance, and the combined action of the oxidizing species are not yet understood.[7−9]

To study differences in the reaction mechanism of different radicals, binuclear azaarenes are suitable reactants because of the difference in the electron density within and between the two nuclei, which therefore causes the azaarenes to differ in the oxidation behavior. Substituted benzene derivatives are limited in their validity because often identical products (via intermediately formed cyclohexadienyl radicals) are formed independent of the oxidation mechanism.[4] In this paper the oxidation mechanisms of quinoline and isoquinoline and the benzodiazines quinoxaline, quinazoline, phthalazine, and cinnoline are studied.

The azaarenes react in environmentally relevant radical reactions, photoreactions, and combinations of both. As dark reactions the Fenton reactions with hydrogen peroxide and peroxodisulfate, respectively, are studied. The Fenton reaction with hydrogen peroxide occurs in nature within the photo-Fenton cycle,[10−14] while the sulfate radicals are intermediate products within the radically driven S^{IV} oxidation in water droplets in the troposphere.[15] There are characteristic differences between these two reactions.[16] The sulfate radicals only react with the aromatics in electron transfer reactions (ETR). The hydroxyl radicals and the aromatics form σ complexes. Addition on a double bond, abstraction of hydrogen atoms, and ETR can follow and result in a much more complex spectrum of products. The dark reactions also serve as reference reactions for the photolysis or for the reactions with photochemically produced radicals.

Compared with the dark reactions irradiation leads to a more complicated situation. The formation of hydroxyl and sulfate radicals by the photolysis of hydrogen peroxide and peroxodisulfate as well as the formation of a steady state concentration of excited aromatic molecules is observed. The radicals can react with the aromatic molecules in the ground state and the excited state (T_1). The molecules in the excited state (S_1) can also perform unimolecular reactions such as the valence isomerization. Energy transfer reactions with the formation of reactive singlet oxygen should be possible as well. All this leads to more products and to more complex reaction mechanisms. Photolysis of hydrogen peroxide has less importance in nature (little absorbance at $\lambda > 290$ nm), but in other environmentally relevant photoreactions, such as the nitrate photolysis, hydroxyl radicals participate. Therefore their reaction mechanism under irradiation is investigated.

The differences in the reactivities of the azaarenes are difficult to study in reactions with hydroxyl and sulfate radicals. Both radicals nearly react controlled by diffusion. The carbonate radical[16−20] is much less reactive and much more selective in its reactions with organic compounds. For example, it reacts with aniline 10^5 times faster than with benzene. The reaction mechanisms of the carbonate and the sulfate radicals are identical. Therefore, we use the carbonate radical to characterize the gradation in the reactivity of the azaarenes by the determination of the reaction rate constants.

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TABLE 1: Concentrations of the Reactants

reactions	azaarene [mM]	radical forming system [mM]
Fenton reaction, H_2O_2	0.01−1.0	$FeSO_4$, $Na_2C_2O_4$, H_2O_2 in 1 and 5 molar excess
Fenton reaction, $S_2O_8^{2-}$	0.01−1.0	$FeSO_4$, $Na_2C_2O_4$, $K_2S_2O_8$ in 1 and 5 molar excess
photoreaction, H_2O_2	0.01−1.0	H_2O_2: 100 molar excess
photoreaction, $S_2O_8^{2-}$	0.01−1.0	$K_2S_2O_8$: 100 molar excess
kinetics, carbonate radical	0.0028	H_2O_2: 280 μM−2.8 mM + K_2CO_3: 84.0 mM

Experimental Section

Materials. All reactants were purchased from Aldrich in maximum purity grade. The identification of most of the reaction products was proved using native samples, which were commercial products of Aldrich and Merck (quinoline-*N*-oxide; 2-, 4-, 5-, 6-, 8-hydroxyquinoline; isoquinoline-*N*-oxide; 1-, 3-, 5-hydroxyisoquinoline; 1-, 2-hydroxynaphthalene; 4-hydroxyquinazoline; 2-hydroxyquinoxaline; 1(2H)-phthalazinone; 1H-, 3H-quinazoline-2,4-dione; 2,3-dihydro-1,4-phthalazinedione; 2,3-dihydroxyquinoxaline; 2,4-, 2,6-dihydroxyquinoline; 8-hydroxyquinoline-*N*-oxide; phthalimide; 2-cumaranone; 1,2-phthaldialdehyde; cumarine; dihydrocumarine; 1,2-dicyanobenzene; 2-cyanobenzaldehyde; pyridine-2-aldehyde; pyridine-3-aldehyde; pyridine-4-aldehyde; and anisole). Ethyl acetate and dichlormethane used for solvent extraction (resi analyzed), hexane (GC grade), acetonitrile, and methanol (HPLC gradient grade) were obtained from Baker. Ultrapure water was prepared in a Milli-Q-plus-apparatus (Millipore).

Procedure. A high-pressure mercury lamp TQ 150 (150 W) and a low-pressure mercury lamp (80 W) from Heraeus are used as immersion lamps in a photo reactor thermostated at 25 °C. The monochromatic radiation at $\lambda = 313$ nm is isolated by a filter solution (aqueous sodium dichromate solution) from the complex line spectrum of the high pressure mercury lamp TQ 150. The low pressure mercury lamp mainly provides light of $\lambda = 254$ nm. The dark reactions are performed in reactors of 100 mL solution, the photo reactions in 400 mL. The reaction mixtures are air saturated (for concentrations, see Table 1).

For extraction experiments, several solvents with different polarity are tested: cyclohexane, toluene, methylene chloride, and ethyl acetate. Additionally the SPME (solid phase microextraction) as a new extraction technique is tested using two different phases (polyacrylate and polydimethylsiloxane). The highest analytical sensitivity has been achieved with the classical liquid−liquid extraction with methylene chloride and ethyl acetate as solvents. Therefore, the aqueous samples (pH = 7) are extracted with ethyl acetate (+NaCl). An aliquot of the solvent extract is evaporated to dryness and dissolved in 500 μL hexane for GC injection. The products are identified by GC/MS (GC HP 5890 series II and MSD HP 5971, Hewlett-Packard). The identification of most of the reaction products was proved using native commercial samples (Aldrich and Merck). The products were determined in SCAN and SIM mode.

The experimental determination of rate constants is carried out directly without any special sample preparation by HPLC (HP 1050 and UV-diode array detector HP 1040M series II, Hewlett-Packard) measuring the disappearance of the azaarenes.

A short column and isocratic mode are sufficient for separation of the reactants. Trimethylamine is added to suppress a possible tailing of azaarenes.

Kinetic Method. The carbonate radicals are prepared in redox reactions of hydroxyl radicals and carbonate anions.[16−20] Hydroxyl radicals are obtained by photolysis of H_2O_2 ($\lambda = 313$ nm). The reaction needs a highly basic milieu (pH = 11). The pK_a value of the radical is between 7.0 and 8.2. Therefore, its conjugated acid, the HCO_3 radical, is of minor importance. The OH radicals quantitatively react with the carbonate ions, which are present in excess (Figure 1).

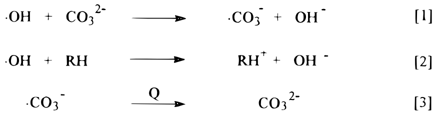

Figure 1. Reaction of formation of carbonate radicals with the according rate constants: reaction 1, $k = 4.2 \times 10^8$ (M s)$^{-1}$; reaction 3 $k = 2 \times 10^7$ (M s)$^{-1}$.

The carbonate radicals quickly react in the self-quenching reaction 3 or in ETRs with electron rich inorganic and organic compounds comparable with reaction 2. The continuous irradiation leads to a steady state concentration of carbonate radicals $[\cdot CO_3^-]_{SS}$. The influence of organic compounds on the lifetime of the radicals is low if the concentration of the organics is low. Then the kinetics follows that of pseudo-first-order reactions (correlation coefficients > 0.99):

$$k = [\cdot CO_3^-]_{SS} k(\cdot CO_3^- + RH)$$

$k(\cdot CO_3^- + RH)$ represents the second-order rate constant for the reaction between the carbonate radical and the organic compound. $k(\cdot CO_3^- + RH)$ is proportional to the rise of the $k/C(H_2O_2)$ plot. The direct determination of $k(\cdot CO_3^- + RH)$ is not possible as the $[\cdot CO_3^-]_{SS}$ is unknown. By means of anisole as a reference substance with $k(\cdot CO_3^- + \text{anisole}) = 2.8 \times 10^5$ L(mol s)$^{-1}$,[16] relative rate constants for the azaarenes are calculated.

Theoretical Calculations. Electrostatic charges and coefficients of the frontier orbitals of the azaarenes are calculated using a workstation RS 6000 (IBM) and the chemical modeling software Sybyl (Tripos).

Results

Dark Reactions of Quinoline and Isoquinoline. Main products in the Fenton reaction of quinoline with peroxodisulfate are quinoline-5,8-dione and three products with a fragment peak at 132, which could not be clearly identified. Pichat et al.[1] also found these three compounds ($M = 161$, CI) during the photocatalysis (TiO_2, $\lambda = 365$ nm) of quinoline, but only one was identified as *N*-formyl-2-aminobenzaldehyde. After several tests, the authors proceed on the assumption that the remaining isomers are the two pyridinealdehydes resulting from the cleavage of the benzene ring. Our investigations on the Fenton reaction with naphthalene support this hypothesis. In the reaction, two products with mass spectra analogously are obtained showing the mass peaks at m/z(naphthalene) = m/z(quinoline) − 1. In the Fenton reaction with isoquinoline, the formation of three products with fragment peaks at 132 and in the reactions with the benzodiazines analogous products with mass peaks at m/z(benzodiazines) = m/z(quinoline) + 1 are also formed. In all cases, the formation of twice oxidized products formed by cleavage of the benzene rings are likely. Beside the traces indicating main products, traces indicating 5-, 8-hydroxyquinoline and indol-2,3-dione are found. The latter compound

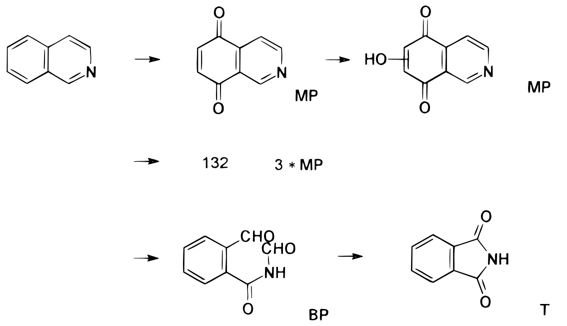

Figure 2. Fenton reaction of isoquinoline with peroxodisulfate and hydrogen peroxide, respectively (MP, main product; BP, byproduct; T trace). Extent of isoquinoline degradation: 30%.

is the only oxidation product of the pyridine ring. The Fenton reaction with hydrogen peroxide follows the same pattern. The side reactions of the OH radicals lead to a slight increase particularly in the oxidation products of the pyridine ring. The double amount of indol-2,3-dione and also *N*-formyl-2-aminobenzaldehyde can be found.

The Fenton reactions with isoquinoline and peroxodisulfate or hydrogen peroxide result in product spectra comparable with quinoline. The existence of the products prove that oxidation mainly occurs at the benzene ring. Oxidations at the pyridine ring produce two byproducts of low concentrations, the isoindol-1,3-dione and a 3-fold oxidized ring cleavage product (Figure 2).

Photoreaction of Quinoline and Isoquinoline ($\lambda = 313$ nm). Both the reactions of quinoline and isoquinoline with photochemically produced sulfate radicals (identification of 9 and 14 products, respectively) result in a distinct shift within the product spectra. Beside the formation of three main products with fragment peaks at 132, a clear decrease in the concentrations of the 5,8-dione compounds and their higher oxidized products is accompanied by a significant increase in the concentrations of the hydroxy compounds, the 5- and 8-quinolinol and the 5-isoquinolinol. Oxidation products of the pyridine ring occur in much higher concentrations particularly for isoquinoline. Therefore, the two oxidation products of the pyridine ring formed in the dark reaction are produced in significantly higher concentrations after irradiation. Furthermore, the 1-isoquinolinol and the 5-isoquinolinol are formed in equal amounts and products resulting from the nitrogen elimination can be detected. Altogether a clear shift of the reactivity from the benzene ring to the pyridine ring can be recognized.

The photoreactions with hydrogen peroxide are even more complex. An increasing number and concentration of hydroxy compounds is observed which arise from the specific addition−elimination mechanism of the OH radicals. The compounds with the fragment peak at 132 are of less importance but their higher oxidized products can be found. The concentrations of the 5,8-dione products further decrease (Figure 3).

Dark Reactions of the Benzodiazines. The Fenton reactions of quinoxaline result in five products, three hydroxy compounds, and two dihydroxy compounds. The 5-hydroxyquinoline is the main product and it is produced more selectively by the sulfate radical than by the OH radical. The ratio between the hydroxy compounds is (sulfate radical):5-OH:6-OH: 2-OH-quinoxaline = 100:5:1. The dihydroxy compounds are of minor importance. Oxidation is performed mainly at the benzene ring.

The reaction of quinazoline and the sulfate radical has a strongly defined reaction course: only the 4(1H)-quinazolinone is formed. In contrast, quinazoline also reacts with hydroxyl radicals to form 2(1H)-quinazolinone and 2,4(1,3H)-quinazolindione as main products but altogether in lower concentrations than with the sulfate radicals. Four compounds resulting from the oxidation of the benzene ring can be identified traces; three with a fragment peak at 133 and as one hydroxyquinazoline.

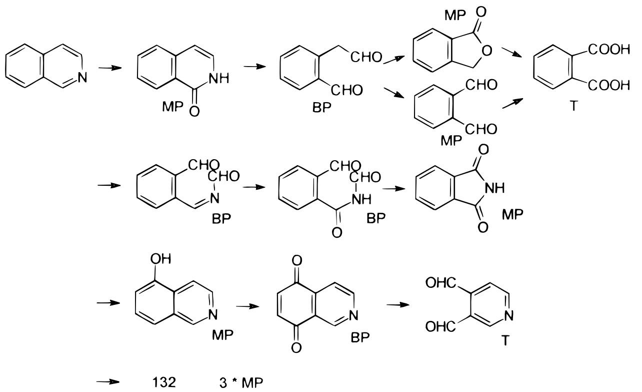

Figure 3. Photoreaction of isoquinoline with hydrogen peroxide ($\lambda = 313$ nm). Extent of isoquinoline degradation: 50%.

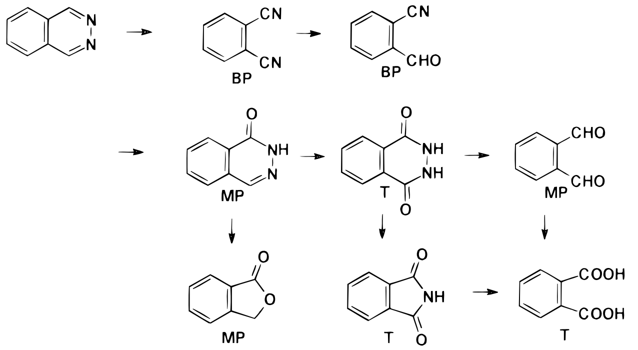

Figure 4. Photoreaction of phthalazine with hydrogen peroxide ($\lambda = 313$ nm). Extent of phthalazine degradation: 50%.

Photoreactions of Benzodiazines ($\lambda = 313$ nm). In the photoreaction with peroxodisulfate and quinoxaline only the hydroxy compounds are formed, but in a ratio different from that of the dark reaction: 5-OH:6-OH:2-OH-quinoxaline = 12: 2:1. The photoreaction with hydrogen peroxide shows the same pattern, and beside two twice oxidized products, one compound, which is formed by elimination of one N atom, is detected. This also proves the thesis of the reactivity shift from the benzene ring to the pyrazine ring.

Oxidation of phthalazine under irradiation proceeds only at the pyridazine ring. It is the opposite reaction to the photochemical oxidation of quinoxaline, which is oxidized mainly at the benzene ring. Oxidation of phthalazine leads to eight products. During the first electron transfer step the reaction splits into a reaction main path and a side path. During the main reaction step, 1-hydroxyphthalazine, 1(3H)-isobenzofurone and benz-1,2-dialdehyde are formed. In the side path 1,2-dicyanobenzene is the oxidation product. The reaction course is nearly independent of the oxidizing radical (Figure 4).

The photoreaction of quinazoline with peroxodisulfate selectively proceeds according to its radical character. Like in the dark reaction 4(1H)-quinazolinone is formed but with a yield of more than 45%. In the reaction with hydrogen peroxide eight substances can be detected. 2(1H)-quinazolinone is the main product, and the 4(1H)-compound exists only in traces. The higher number of products is due to side reactions of the OH radicals. Compared with phthalazine more oxidation products of the benzene ring can be seen.

Photoreactions at 254 nm. The change in the wavelength from $\lambda = 313$ nm to $\lambda = 254$ nm leads to characteristic changes

TABLE 2: Ionization Potential and Rate Constants of second order for the Reactions of Azaarenes with Carbonate Radicals (Reference Rate Constant of Anisole is $k = 2.8 \times 10^5$ L (mol s)$^{-1}$ (Reference 16))

substance	rate constant [L (mol s)$^{-1}$]	absolute (relative) error [10^5 L (mol s)$^{-1}$]	ionization potential [eV]
cinnoline	0.96×10^5	±0.04 (4.60%)	9.77
phthalazine	1.44×10^5	±0.04 (2.71%)	9.73
isoquinoline	3.02×10^5	±0.08 (3.05%)	9.33
quinoxaline	8.20×10^5	±0.74 (9.02%)	9.77
quinazoline	12.60×10^5	±0.31 (2.90%)	9.73
quinoline	35.10×10^5	±0.81 (2.77%)	944

in the product spectra of the photoreactions with hydrogen peroxide. Particularly, higher oxidized products in which the aromatic system is degraded by ring cleavage or by oxygen incorporation are formed. These products show less absorbance and are therefore more stable. Compounds with fragment peaks at 131, 132, and 133, respectively, and the dione products can be found only in traces. The number of simple oxidized compounds increases and in the case of naphthalene and quinoxaline it exceeds the number of possible hydroxy isomers. With high probability photochemical rearrangements occur. At $\lambda = 254$ nm these products are also formed by the direct photolysis of the azaarenes, result from dewar and benzvalene like compounds or they are formed by ring enlargments through oxygen insertion. Photoreactions at $\lambda = 254$ nm with or without oxidizing agent (radical forming agent) show similar products.

Rate Constants in Photoreactions with Carbonate Radicals. The carbonate radicals result from reactions of photochemically prepared hydroxyl radicals with carbonate ions. The carbonate radicals react with the azaarenes in electron transfer reactions, such as in those with sulfate radicals. Because the carbonate radicals are much less reactive, they more selectively react with the azaarenes than hydroxyl or sulfate radicals. Hydroxyl and sulfate radicals react nearly diffusion controlled. Their rate constants exceed that of the carbonate radicals in 3−4 orders of magnitude and differ among each other only by a factor of 4.[21] The values of rate constants of carbonate radicals are measured between 1.1 and $38.1 \times 10^{+5}$ L(mol s)$^{-1}$ (see Table 2).

To assess the steady state concentration of carbonate radicals, reference substances are necessary. Anisole was taken from the literature. No other compounds compatible with the analytical method could be found. Therefore, not so much the absolute values but the graduation in the rate constants reflects the reactivity differences of the azaarenes. For three compounds (quinoline, isoquinoline, and quinoxaline) next to the azaarene concentration of 2.8 μM, two additional concentrations are checked (10 and 30 μM). For these experiments an identical rate constant independent of the azaarene concentration has been found. For the other compounds in the investigated concentration range we generalize this result.

Discussion

Comparison of the Products of the Dark Reactions with Hydroxyl and Sulfate Radicals. The reactions with the two radicals are compared according to differences in the products and to the competition of both rings of the azaarenes in the oxidation reactions. Sulfate radicals react in electron transfer reactions with the heterocycles. Permanganate as a classical oxidizing agent reacts with quinoline in redox reactions oxidizing the benzene ring in a basic milieu and oxidizing the pyridine ring in an acidic milieu. The different reaction paths are due to the protonation of the ring nitrogen in the acidic environment. Our reactions proceed at pH = 7. According to the pK_A values (quinoline, p$K_A = 4.87$; isoquinoline, p$K_A = 5.14$), the nitrogen protonation in the molecules is neglectable. Therefore mainly the benzene ring is oxidized.

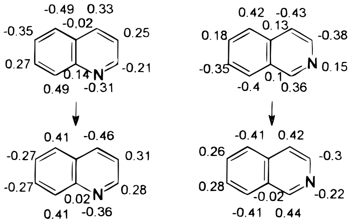

Figure 5. Coefficients of the frontier orbitals, HOMO−LUMO transition.

The hydroxyl radicals show a more complex reaction behavior than the sulfate radicals. Intermediate σ complexes are formed, which lead to addition and electron transfer reactions. As a result, the concentration of quinone compounds formed in redox reactions decreases and the amount of hydroxy compounds formed by electrophilic addition−elimination reactions increases. The hydroxyl radical can be considered as an electrophilic agent. The place for the electrophilic attack can be predicted by calculations of the electrostatic charges or the coefficients of the frontier orbitals. The coefficients of the HOMO of quinoline and isoquinoline, respectively, point to the carbon atoms 5 and 8 as places for an electrophilic attack. Therefore, the oxidation of the benzene ring is no surprise. Oxidation reactions at the pyridine ring occur only as side reactions. According to the coefficents of HOMO, the pyridine ring in isoquinoline is slightly more oxidized (Figure 5).

The benzodiazines more distinctly react in the dark reactions. With quinoxaline, only the benzene ring is oxidized, and with quinazoline, only the pyrimidine ring reacts to form mainly 4(1H)-quinazolinone. Both reactions can be understood by the frontier orbital concept. Redox reactions of the azaarenes and the sulfate radicals lead to the respective cations which are nucleophilicly attacked by water molecules. Including the LUMO coefficients the attack goes to C_4 in quinazoline and to C_5 or C_8 in quinoxaline molecules.

Comparison of the Products in Dark and Photoreactions. The change from the dark to the photoreaction has several consequences. Radicals are no longer produced in a redox reaction with Fe(II) but by photolysis. This leads to another kind of kinetics. In the Fenton reactions the radicals are prepared at once. The reactions are fast. In the photoreactions continuous irradiation leads to a low steady state concentration of radicals over the whole irradiation time. Furthermore, there is an interaction between the azaarene molecules and the radiation resulting in a steady state concentration of excited aromatics (S_1 and T_1), too. The T_1 excited molecules can react with the radicals in competition with the molecules in the ground state. The S_1 excited molecules allow valence isomerization reactions. Both lead to more reaction products.

The changes in the coefficients during the HOMO−LUMO transition easily provide information on changes in the electron density distribution if the molecule is excited. Although the

TABLE 3: Photophysical Data of Selected Azaarenes (Reference 22)

substance	E_{S1} [kJ/mol]	τ_{S1} [ns]	φ_{ISC} (n)[a]	E_{T1} [kJ/mol]	τ_{T1} [μs]	relative absorption
naphthalene	385	105	0.75	255	1800	1
quinoline	381		0.31	261		30
isoquinoline	374	0.25	0.21	254		23.5
quinazoline	327	0.079 (n)	0.70	262		23.5
quinoxaline	319	0.023 (n)	0.99	254	29.4	60
phthalazine	309	0.19 (n)	0.29	275	21.3	2.5
cinnoline	270	0.24				

[a] (n): constants were determined in nonpolar solvents.

trends obtained are only rough approximations, they are very useful in the interpretation of the observed phenomena and correlate well with the experimentally found increase in the basic strength of the nitrogen atoms of azaarenes in the excited state (both S_1 and T_1). According to the frontier orbital concept, which predicts a shift in the electron density in direction to the pyridine ring during irradiation, more oxidation products of the pyridine ring are observed. The trend must be stronger for isoquinoline than that for quinoline (Figure 5).

Quinoxaline resembles quinoline in its reaction behavior. The kind of superposition in the structure of quinoxaline is also reflected in the reaction behavior. In the dark reaction, only the benzene ring is oxidized, and in the photoreaction, more oxidation products of the pyrazine ring are formed than with quinoline, a fact which correlates with the stronger shift of the electron density. In the photooxidation of phthalazine, only the pyridazine ring is oxidized. Phthalazine shows a kind of superposition of the reaction behavior of isoquinoline. Quinazoline shows a reaction behavior somewhere between phthalazine and quinoxaline according to its structure. Oxidation mainly proceeds at the pyrimidine ring, but higher amounts of products formed by oxidation of the benzene ring are found as well.

Direct photolysis and photoreaction of quinoline and isoquinoline with radicals result in similar products. This leads to the conclusion that photooxidation in direct photolysis also runs in radical reactions caused by electron transfer processes from excited aromatics to the molecular oxygen in aqueous solution. A steady state concentration of reactive radicals is formed. Energy transfer processes and the following formation of singlet oxygen should be of minor importance. Oxidation products of the benzodiazines are extremely similar in both direct photolysis and photoreactions with radicals. The formation of 1,2-dicyanobenzene in the direct photolysis of phthalazine is another clear hint on ETR. Furthermore, an interaction between singlet oxygen and the electron deficient benzodiazines is very unlikely. Compared with the photoreaction with radicals in direct photolysis the ratio of the steady state concentration of excited aromatics to radicals is increased. This leads to an increase in the oxidation products of the pyridine and diazine rings, respectively.

In irradiation experiments with light of $\lambda = 254$ nm special photochemical reactions such as valence isomerizations and photochemical rearrangements occur.

Kinetic Investigation of the Reactions of Azaarenes with Carbonate Radicals. The carbonate radicals react in ETR with azaarenes. Because of their lower reactivity, compared with sulfate and hydroxyl radicals, they have rate constants which are 3−4 orders of magnitude lower. Therefore they are more suitable to detect differences in the reactivity of the azaarenes. A possible parameter to compare the azaarenes in ETR is their ionization potential. The lower the ionization potential of the reactants, the more easily oxidation occurs and the rate constants increase. The ionization potentials increase with increasing number of nitrogen atoms. This is also due to the experimentally observed higher stability of the benzodiazines compared with quinoline. Anyhow, the rate constant of isoquinoline cannot be understood considering its ionization potential.

The already discussed interaction of the aromatics with radiation and the formation of excited molecules give reason for the inclusion of photophysical data in the argumentation. Bimolecular reactions of excited molecules (T_1) are of particular interest because of the lifetime of T_1. It is 10^4-10^6 times longer than that of S_1. Electron transfer and energy transfer processes are possible and also bimolecular reactions with the radicals. The high energy of the T_1 molecules also allows reactions which would not proceed in the ground state. The energy of T_1 and S_1 also clearly exceeds the activation energy necessary for the reaction of the azaarenes with the radicals.

The half-lives of the T_1 states remarkably differ for the single azaarenes. It is 1800 μs for naphthalene but only 21.3 μs for phthalazine. Because only a few values are available, it is difficult to assess the importance of half-life, but a low relaxation rate of the T_1 states will result in a high steady state concentration of excited molecules.

Absorption coefficient and quantum efficiency for the ISC (inter state crossing), the S_1 to T_1 transition, mainly determine the steady state concentration of excited molecules (T_1). In Table 3 photophysical data and absorption values (relative to naphthalene) are listed.

By examining the data of the quinoline/isoquinoline product pair, the higher reactivity of quinoline can easily be explained with the absorption and ISC quantum efficiency values. Both the relative absorption and the φ_{ISC} are higher for quinoline. This leads to a higher steady state concentration of excited molecules and to a higher rate constant. In the same way, the differences in the rate constants of the benzodiazines can be discussed:

$$\{\epsilon(\text{phthalazine}) = 2.3\} < \{\epsilon(\text{quinazoline}) = 23.5\} < \{\epsilon(\text{quinoxaline}) = 60\}$$

$$\{\varphi(\text{phthalazine}) = 0.29\} < \{\varphi(\text{quinazoline}) = 0.7\} < \{\varphi(\text{quinoxaline}) = 0.99\}$$

Therefore the rate constant of phthalazine is lower than the rate constants of the two other compounds. From this discussion, the anomaly of isoquinoline with respect to the more stable benzodiazines can be understood. The rate constants also underline the participation of excited molecules in the photoreactions with radicals resulting in another product spectrum than the dark reactions.

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