Investigations of Reactions of Selected Azaarenes with Radicals in Water. 2. Chlorine and Bromine Radicals

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The halogen radicals that react with azaarenes are produced by the photooxidation of halogenide anions with hydroxyl and sulfate radicals and exist as complexes of the radical and the respective halogenide anion in the aqueous phase. The main reaction products of the reactions are identified, and in the case of the bromine radicals, the second order rate constants are determined. Oxidation takes place according to the different redox potentials of the two reactants and is especially observed for chlorine radicals. A typical product spectrum comparable with that in reactions with hydroxyl and sulfate radicals has been found. The formation of some oxidation products in reactions of bromine radicals is in contradistinction to the oxidation potentials of the azaarenes and can be understood only by the reaction of their excited states. The halogenation is the main reaction of the azaarenes. Halogenation products of both, the benzene and the pyridine/diazine rings, have been found. The halogenation of the pyridine/diazine ring again requires the reaction of excited states. The majority of derivatives is halogenated in substitution reactions, but in the reaction of benzo[*h*]quinoline, addition is also observed. The resonance energy per electron is responsible for the change in the halogenation mechanism from substitution to addition.

Introduction

Halogenated aromatics show properties such as high persistence, ecotoxicity, humantoxicity, and bioaccumulability. [1] The introduction of one or several chlorine atoms into the molecule increases the toxicological and pharmacological effect by several orders of magnitude.[2] Nature used this principle long before mankind did. The chemical and metabolic stability of halogenated aromatics and the bioaccumulation of the compounds in the fatty tissue with the following chronic effects increases with an increasing number of halogen atoms.[3]

Many halogenated compounds detected in the environment can be assigned to anthropogenic sources, such as products of chemical industry and products formed unintentionally (e.g., in combustion events or during the disinfection of water). Today, between 700 and 2000 natural chlorine containing compounds are known, primitive as well as highly complex ones, synthesized by about 270 species of organisms.[3,4] The majority of the more complex compounds represents active substances in lower concentrations. However, low molecular compounds,[5] such as methylene chloride, biogenically produced in about five million tons annually, are very important for the geochemical global chlorine cycle.[3]

While several papers[5−7] deal with the mechanism and the proof of the formation of halogenated organics by biotic and abiotic sources, in this study the reaction of chlorine and bromine radicals with aromatics is reported. Both radicals are produced by the reaction of strong oxidizing agents such as hydroxyl[8−10] and sulfate radicals with the halogenide anions. For bromine the reaction goes via the intermediate [$\bullet BrOH^-$] complex and the following combination with bromide to form $\bullet Br_2^-$[11] (Figure 1).

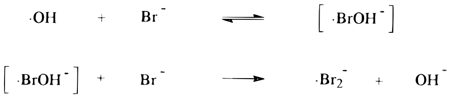

Figure 1. Formation of bromine radicals

If available in excess, chloride ions can compete with bromide to form $\cdot BrCl^-$. In the oceans, about 80% of the hydroxyl radicals[12,13] are likely to be trapped in reactions producing bromine radicals. The chlorine radical can be formed by hydroxyl radicals only in a strong acidic solution.[11] Therefore, the formation of chlorine radicals should be possible by hydroxyl radicals in the acidic aerosol droplets of the troposphere and also through sulfate radicals formed as intermediates[14] within the S^{IV} oxidation mechanism in acidic and neutral media. A problem is the stability of the chlorine radicals in aqueous solution in dependence on the pH. Jacobi et al.[18] confirmed that chlorine radicals are very unstable in alkaline solutions ($k(\bullet Cl_2^- + OH^-) = (4.0 \pm 0.6) \times 10^6\ (M\ s)^{-1}$. The decay of chlorine radicals results in the formation of OH radicals. But the authors also show that the rate constant with water ($k(\bullet Cl_2^- + H_2O) < 610\ s^{-1}$) is very small. We assume that the decay of chlorine radicals to OH radicals under our reaction conditions ($pH = 7$) is not essential. This assumption is supported by our observations for the reaction of chlorine radicals with quinoline discussed later. The bromine radicals are stable until a $pH = 11$.

Halogene radicals mainly react with organic compounds in electron-transfer reactions (ETR). Other reactions, such as the H-abstraction by the chlorine radical, are of lesser importance. The reactivity of both reactants depends on the difference of their redox potentials. For the radicals, the redox potentials $E(\bullet Cl_2^-/2Cl^-) = 2.0$ V and $E(\bullet Br_2^-/2Br^-) = 1.63$ V[11] are given. The chlorine radical is the stronger oxidizing agent while the bromine radical can only react with compounds with high electron density. The addition of halogen radicals on double bonds is also reported.

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TABLE 1: Composition of the Reaction Mixture

reaction type	azaarene [mM]	radical forming system
identification of products		
photoreaction, chlorine radical	0.01−1.0	$m(K_2S_2O_8) = 1.0$ mM + $m(NaCl) = 1$ M
photoreaction, bromine radical	0.01−1.0	$m(K_2S_2O_8) = 1.0$ mM + $m(KBr) = 1$ M
kinetic experiments		
photoreaction, bromine radical	0.0028	$m(H_2O_2) = 280\ \mu$M − 2.8 mM $m(KBr) = 84.0$ mM

This paper presents studies of the results reactions of binuclear and trinuclear azaarenes with halogen radicals. Their reactions in the aqueous phase are of interest because of the 3−4 orders of magnitude higher solubility of the azaarenes[15] compared with PAH. The other mechanistic reason[16] for the use of the azaarenes are strong gradients of the electron density in the aromatic ring system, an electron rich benzene and an electron poor pyridine/diazine ring. From the products formed, conclusions on the reaction mechanism are drawn. In the product studies both halogen radicals are produced by sulfate radicals (photolysis of peroxydisulfate). In the kinetic studies, the bromine radicals are produced by OH radicals (photolysis of hydrogen peroxide) and the second-order rate constants for the reactions of the azaarenes with bromine radicals are determined.

Experimental Section

Materials. Naphthalene, quinoline, isoquinoline, cinnoline, quinoxaline, quinazoline, and phthalazine as well as the trinuclear azaarenes phenazine, acridine, benzo[*c*]cinnoline (BcC), phenanthridine, and benzo[*h*]quinoline (BhQ) were purchased from Aldrich. 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; benzene-1,2-diacide; cumarine; dihydrocumarine; 1,2-dicyanobenzene; 2-cyanobenzaldehyde; pyridine-2-aldehyde; pyridine-3-aldehyde; pyridine-4-aldehyde; anisole; 1-, 2-bromonaphthalene; 1-chloronaphthalene; 3-, 8-bromoquinoline; 4-bromoisoquinoline; 2-, 4-, 6-chloroquinoline; 9(10H)-acridinone; 6(5H)-phenanthridinone). The extractants ethyl acetate and methylene chloride as well as the solvents hexane (GC grade), acetonitrile and methanol (HPLC grade) were obtained from Baker. Sodium peroxodisulfate, hydrogen peroxide, sodium bromide, and trimethylamine were obtained from Aldrich.

Procedure. A high-pressure mercury lamp of 150 W (TQ 150, Heraeus) is used for irradiation as an immersion lamp in a photoreactor thermostated at 25 °C. For $\lambda = 313$ nm the respective emission line of the complex line spectrum is isolated by a filter solution (aqueous sodium dichromate solution). The reaction vessel has a volume of 400 mL. The reaction mixtures are air saturated.

For extraction experiments several solvents of different polarity are tested: cyclohexane, toluene, methylene chloride, and ethyl acetate. Additionally, the SPME (solid-phase microextraction) as a new extraction technique is tested with two different polar phases (polyacrylate and polydimethylsiloxane). The highest analytical sensitivity is 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 or acetonitrile for GC injection. The products are identified by GC/MSD (GC HP 5890 series II and MSD HP 5971, Hewlett-Packard). The products are determined in SCAN and SIM mode and compared with native samples (see Table 1).

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 the separation of the reactants. Trimethylamine is added to suppress a possible tailing of the azaarenes.

Kinetic Method. The bromine radicals are produced by the redox reaction of bromide with hydroxyl radicals, which are formed by the photolysis of hydrogen peroxide ($\lambda = 313$ nm). The hydroxyl radicals are trapped quantitatively by the surplus of bromide. The bromine radicals formed react with the azaarenes by ETR. Continuous irradiation leads to a steady-state concentration of bromine radicals $[\bullet Br_2^-]_{ss}$. Sufficiently small concentrations of organic substances only have a small influence on the half-life of the radicals. Then the kinetics can be described as first-order reaction

$$k = [\bullet Br_2^-]_{ss} k(\bullet Br_2^- + RH)$$

with $k(\bullet Br_2^- + RH)$ as the second-order rate constant (correlation coefficients > 0.99). The first-order rate constants are determined as a function of the hydrogen peroxide concentration. The slope of the $k/c(H_2O_2)$ plot is proportional to the second-order rate constant. Its direct determination is not possible as the steady-state concentration of the bromine radicals is unknown in this method. A calibration with hydroquinone for which the reaction data are known ($k(\text{hydroquinone} + \bullet Br_2^-) = 1 \times 10^8$ L(mol s)$^{-1}$) gives the absolute values of the second-order rate constants.

Results

Photoreactions of Naphthalene, Quinoline and Isoquinoline with Halogen Radicals. The addition of peroxodisulfate to a solution containing bromide and naphthalene leads to the selective formation of 1-bromonaphthalene. The yield is increased from 30% to 80% by irradiation. The oxidation potentials of both reactants have similar values $E(\bullet Br_2^-) = 1.63$ V and $E(\text{Naph}) = 1.67$ V. Although an oxidation cannot be expected, traces of five oxidation products are observed.

The large difference between the oxidation potentials of both reactants, isoquinoline (1.98 V) or quinoline (2.06 V) and the bromine radical (1.63 V) should not allow the oxidation of the aromatic system but in the reactions oxidation products are observed. With isoquinoline a relatively high concentration of isoindole-1,3-dione (Figure 2) and with quinoline traces of indole-2,3-dione are identified. In both cases only the pyridine ring is oxidized.

Halogenated derivatives of azaarenes are of higher importance for the product spectrum than the oxidation products. Five and six brominated derivatives of isoquinoline and quinoline are

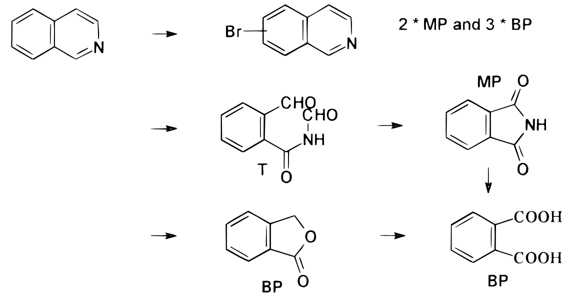

Figure 2. Photoreaction of isoquinoline with bromine radicals (MP, main product; BP, byproduct; T, trace) (extent of reaction of isoquinoline is 0.2).

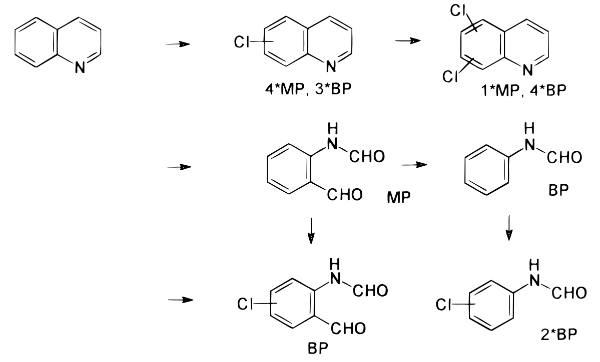

Figure 3. Photoreaction of quinoline with chlorine radicals (extent of reaction of quinoline is 0.3).

found, among them the main products; products with one (isoquinoline) or two (quinoline) substitutions at the pyridine ring with its low electron density attract attention. Considerations of the frontier orbitals show a preferred formation of the brominated isomers on positions 5 and 8.

The oxidation potentials of the azaarenes and chlorine radicals have similar values. The analysis of the reaction mixture shows a parallel formation of oxidized and chlorinated compounds with a different extent of chlorination. It was observed that both the naphthalene reaction paths produced similar yields. The analysis of the product mixture of isoquinoline shows a more complex pattern. Oxidation products of the pyridine ring (higher concentration) are found but also traces of 5-isoquinolinol. Because the oxidation potential of quinoline is somewhat higher, the chlorination reaction dominates and only oxidation products of the pyridine ring can be observed (Figure 3). This supports our assumption that the decay of chlorine radicals to OH radicals under the given reaction conditions is not essential. The presence of OH radicals (formed in the decay of chlorine radicals) should lead to oxidation products of the benzene ring.

The chlorinated derivatives are the main products. With isoquinoline six monochlorine and six dichlorine compounds and with quinoline seven monochlorine and five dichlorine compounds are observed. The proof of all seven possible mono chlorine isomeres gives evidence for the high reactivity of chlorine radicals. On the other hand, the strong differentiation of the isomer concentrations corresponds to the variation of the electron density in the molecule.

Photoreaction of Benzodiazines with Halogen Radicals. The oxidation potentials of quinazoline (2.7 V) and quinoxaline (2.3 V) are significantly higher than that of the chlorine radical (2.0 V). Therefore an oxidation of both compounds is not observed. The oxidative degradation of phthalazine is possible (1.95 V). Four oxidation products are found corresponding to the pattern of the reaction with hydroxyl and sulfate radicals.

The photochemical reaction of chlorine radicals with quinoxaline leads to the formation of five chlorinated products (three monochlorine and two dichlorine derivatives) in high yield. They are produced in the ratio 5-Cl^-:6-Cl^-:2-Cl^-: dichlorine isomers = 8:2:1:0.25. Calculations of frontier orbitals also favor a substitution on the atom C_5. There is a relatively high halogenation of the pyrazine ring with its low electron density. In the reaction with bromine radicals, the formation of only two brominated derivatives on the C_5 and C_6 positions is observed in a ratio of 4:1.

Two (ratio of 40:1) and four chlorinated derivatives are found in the photoreaction of phthalazine and quinazoline with chlorine radicals, all substituted at the benzene ring. Brominated products of phthalazine are not proved. Oxidation and chlorination reactions of phthalazine have similar yields. In the reaction of quinazoline with bromine radicals, two brominated isomers in significant concentrations are formed.

Photoreaction of Selected Trinuclear Azaarenes with Halogen Radicals. The experimentally determined oxidation potentials are given for the linear anellated azaarenes phenazine (1.98 V), acridine (1.66 V), and for the angular anellated azaarenes BcC (1.86 V), phenanthridine (1.92 V), and BhQ (1.79 V). Therefore redox reactions of phenazine are not observed. The analysis of the reaction of acridine with chlorine radicals shows three competitive reactions. Four chlorinated derivatives were produced at all possible positions of the terminal benzene ring. The oxidation leads to the formation of acridone as the main reaction product but also to the oxidative degradation of the terminal benzene rings, producing the quinoline-2-aldehyde. For phenazine the selective formation of 1-Cl-phenazine as main product, 2-Cl-phenazine as a trace and a dichlorinated compound is observed. The selectivity of the bromination of phenazine is even higher (1- and 2-bromophenazine with a ratio of about 40:1). In the analysis of the bromination of acridine 12 brominated products were found, 3 monobromine (ratio 1:2:3), and 9 dibromine derivatives. The concentration of monobrominated compounds is significantly higher than that of the dibrominated ones. The trend of a significantly higher product yield of bromination compared with the chlorination was also confirmed for phenazine and acridine.

The BcC should be oxidized as well as chlorinated by chlorine radicals and will only be brominated by bromine radicals. This forecast has been experimentally confirmed. The yield of chlorination is higher than that of the oxidation. Three chlorinated derivatives in similar concentrations have been found and also traces of oxidation products. Only traces of four monobromine isomers were formed in the reaction of BcC with the bromine radicals.

The chlorine radicals and phenanthridine form seven monochlorine and fourteen dichlorine isomers. Their concentrations vary by a factor of 6 for the monochlorinated (ratio 1:1.5:1.5:2:4:4:6) and 8 for the dichlorinated compounds. The oxidation leads to the gradual degradation of the terminal ring A and the pyridine ring but the yield is significantly lower than in the chlorination reaction. Highly oxidized products, such as the 2H-isoindole-1,3-dione and phthalic acid, are found. For phenanthridine the yield of bromination again exceeds that of the chlorination. Seven monobromine and eight dibromine isomers are found. The higher specificity of the electrophilic attack on the individual C atoms results in a variation of the monobromine and dibromine isomers by a factor of about 900 (1:1:10:10:40:300:900) and 140 (1:1:5:6:7:16:140), respectively.

For BhQ with its lower oxidation potential, three reaction ways exist in the reaction with chlorine radicals. Beside the

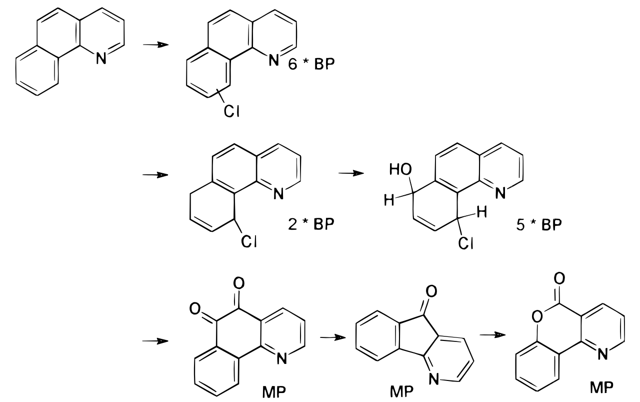

Figure 4. Photoreaction of BhQ with chlorine radicals (extent of reaction of BhQ is 0.3).

TABLE 2: Second Order Rate Constants of the Photoreaction of Bi- and Trinuclear Azaarenes with Bromine Radicals

substance	rate constant [10^5 L(mol s)$^{-1}$]	absolute (relative) error [10^4 L(mol s)$^{-1}$]
cinnoline	0.48	± 0.032 (6.68%)
phthalazine	5.69	± 0.34 (7.19%)
isoquinoline	14.39	± 0.40 (2.33%)
quinoxaline	43.95	± 0.87 (2.04%)
quinazoline	48.93	± 1.11 (2.20%)
quinoline	105.34	± 3.31 (3.01%)
benzo[*c*]cinnoline	reaction too slow	
phenazine	0.167	± 0.016 (10.60%)
acridine	1.01	± 0.084 (8.81%)
benzo[*h*]quinoline	28.32	± 1.41 (5.11%)
phenanthridine	70.91	± 6.75 (6.75%)

expected oxidation and substitution reactions addition reactions, until now not observed, have led to the formation of chlorine adducts and chlorine−hydroxy adducts. Due to the electrophilic substitution five chlorinated isomers of BhQ are found. Their concentrations vary by a factor of 5 (ratio: 1:1:1.5:2:5). The addition products, two monochlorine adducts and five chlorine-hydroxy-adducts, are observed in a yield similar to the substitution products. The oxidation is the main reaction and leads to the formation of degradation products of the central benzene ring (Figure 4).

In the reaction of BhQ with bromine radicals, oxidation and bromination products are found in similar content; although on the basis of the redox potential of BhQ, an oxidation was not expected. Compared with the addition, the substitution is the main reaction. Three monobromine (ratio: 1:2:7.5) and two dibromine products are found but only one bromine adduct and one bromine−hydroxy adduct.

Kinetics. The rate constants show a significantly lower reactivity and higher selectivity of the bromine radicals in comparison to the hydroxyl and sulfate radicals and can be used to study the gradation in the reactivity of azaarenes. The rate constants of the reactions of bromine radicals with the azaarenes vary in a factor of 200. Because of its low value it is not determined for BcC. Thus the bromine radicals have an even higher selectivity against the azaarenes than the carbonate radicals.[17] The absolute errors were determined close to 2−3% and increases for substances with very low rate constants (Table 2).

In the literature, the number of substances studied in reactions with the bromine radical is very small. From the reported substances, only hydroquinone could be used as reference compound ($k = 1 \times 10^8$ L(mol s)$^{-1}$).[10] This compound reacts very fast under the used measuring conditions and is nearly incompatible as reference compound. Thus the constants should not be taken as absolute values but are very suitable for an illustration of the reactivity gradation of the azaarenes. For three compounds (quinoline, isoquinoline, and quinoxaline) next to the azaarene concentration of 2.8 μM two further concentrations are taken (10 and 30 μM). For a given azaarene in these experiments identical rate constants are found.

Discussion

The results show a different reaction behavior of halogen radicals with aromatics. The competition of two reactions will be observed (i.e., the oxidative degradation and the formation of halogenated derivatives). The oxidation of aromatics occurs in dependence on the relation of redox potentials of halogen radicals and azaarenes. High oxidation potentials shifts the relation of both parallel reactions in favor of the halogenation. The reactivity of the different C atoms with halogen radicals follows the charge gradient resulting from substitution of a CH group by a nitrogen atom. While 50% oxidation products were observed for the reaction of chlorine radicals with naphthalene, the oxidation decreases according to the difference of redox potentials for quinoline, isoquinoline, and phthalazine, respectively, and does not occur for quinoxaline and quinazoline. In reactions with bromine radicals the oxidation has a minor importance and oxidation products can only be observed in traces for naphthalene and for isoquinoline. The trinuclear azaarenes follow the same trend. The oxidation of phenazine is proved only by traces of products. For BcC and phenanthridine with redox potentials close to that of the chlorine radicals, the chlorinated products dominate and the oxidation products are of small yield. The oxidative degradation is important for acridine and BhQ with their significantly lower oxidation potentials. The oxidation of trinuclear azaarenes follows the π sextett concept of Clar. According to the concept, the maximum number of sextetts is formed. Therefore the oxidation of the central ring will be preferred, resulting in the selective formation of acridone (acridine) and the specific oxidation of BhQ on the positions 5 and 6. The good correlation with the oxidation potentials indicates that as a first step in the mechanism only an electron transfer from the aromatics to the halogen radical and the following nucleophilic attachment of water is possible.

In a former study the oxidation of quinoline and isoquinoline by hydroxyl and sulfate radicals is investigated in dark reactions and photoreactions. In the dark reactions, the molecules are oxidized on the benzene ring, while in the photoreactions the transition to the oxidative attack on the pyridine ring occurs. The shift of the reaction center to the pyridine ring correlates with the shift of the electron density. The shift can be described by HOMO−LUMO calculations and experimentally measured as higher pK_a values in the excited states S_1 and T_1. Oxidation products of the benzene ring are also proved. The cause is the parallel reaction from the ground and the excited states, because the hydroxyl as well as the sulfate radicals are able to oxidize the molecule in the ground state as well ($E_{Ox} > 2.5$ V). The oxidation by the chlorine radical should only occur according to the redox potentials for a few azaarenes in the ground state, and the oxidation by the bromine radical should not occur. The proof of oxidation products in the reaction of isoquinoline with bromine radicals and quinoline with chlorine radicals contradicts this forecast and points to a participation of excited states in the oxidation. The proof of oxidation products of the pyridine ring instead of the benzene ring is an additional indication. The observed formation of 1-bromonaphthalene in a dark reaction and the missing bromination products in the dark reaction with azaarenes point to a thermal formation of bromine radicals. The kinetic experiments confirm a further reaction with strongly different reaction rates. The reactions with azaarenes start only after the activation of azaarenes by light. This is another piece of evidence for the participation of excited states in the bromination of azaarenes.

The represented results document the significance of the halogenation in the reactions. Many halogenated isomeric products are observed. The reaction with bromine radicals leads to several monobromine isomers and with chlorine radicals to a higher number of monochlorine and dichlorine isomers. The absence of the dibrominated derivatives for binuclear azaarenes is due to the lower reactivity of bromine radicals. The differences in the concentrations of brominated isomers are larger than those of the chlorinated isomers, which points to a higher selectivity of bromine radicals. The stronger electrophilic chlorine radicals have a higher reactivity. This leads to a chlorination of individual C atoms of the pyridine and diazine rings and the formation of dichlorinated aromatics. Despite their high reactivity, strong differences in concentrations of chlorinated isomers can be observed. Altogether, a higher yield of brominated than chlorinated products is found. This can be explained by the 1 order of magnitude higher rate constant for the formation of bromine radicals at pH = 7 ($k(\bullet Br_2z^- + \bullet SO_4^-) = 3.5 \times 10^9\ (M\ s)^{-1}$; $k(\bullet Cl_2^- + \bullet SO_4\text{-}) = 3.1 \times 10^8\ (M\ s)^{-1}$).[10] An exception are azaarenes with low electron densities that only form brominated products in a very low yield.

The halogenation of the pyridine/diazine ring, which is nonreactive against S_EAr reactions, is observed for quinoline, isoquinoline and quinoxaline, respectively. Analogous to the explanation of the oxidation, this halogenation is explained by the participation of excited states.

An interpretation of the halogenation mechanism only on the basis of the described results is difficult. We prefer an explanation that includes the mechanism of the electrophilic substitution. While the electrophilic substitution occurs in nonpolar solvents by a positive polarization of the molecular halogen by a metal catalyst, the halogen radicals are negatively charged complexes. An electrophilic attack will only be probable if the halogen complex decays starting with the interaction of the halogen species with the aromatics [Ar ... ·Br Br$^-$]. We believe that the halogenide leaves the complex at the beginning of the interaction with the aromatics. An intermediate σ complex is formed by the halogen radical and the aromatics. The high energy of the aromatic resonance stabilization enables the restoration of the π sextett under release of hydrogen. Another possibility, the radicalic H abstraction and the following addition of halogen radicals, is energetically not possible for aromatic compounds in the ground state (C_6H_5–H, $H_D = 456$ kJ/mol; H–Br, $H_D = 363$ kJ/mol). In the excited state S_1, the C–H bonding energy seems even to increase as the experimentally observed decrease of the C–H and the increase of the C–C bond lengths show.

The halogenation of all binuclear and the most trinuclear azaarenes leads to halogenated substitution products. Chlorinated addition products and chlorine–hydroxyl products were found in the reaction of BhQ with chlorine radicals. Substitution and addition products are formed in similar concentrations. These products prove the formation of an intermediate σ complex. That is the starting point for the parallel formation of aromatic substitution products under abstraction of hydrogen (rebuild of aromaticity), the chlorinated addition products, and the chlorine–hydroxyl–products by addition of water or reactive oxygen species and the following formation of oxidation products by ETR. The concentration of chlorinated substitution and addition products are explained by similar reaction rates of consecutive reactions. The addition reactions seem to prefer the central C_5–C_6 bond and the terminal benzene ring. In phenanthrene this bond shows pure double bond character decreasing in direction to BhQ. Compared with benzene or naphthalene, the terminal ring has a lower REPE (resonance energy per electron). The absence of the addition reactions for BcC, phenanthridine, the linear anellated trinuclear, and the binuclear azaarenes supports this assumption.

It seems that a threshold value of REPE exists for a change in the halogenation mechanism. The Dewar resonance energy becomes too low for the restoration of aromaticity after formation of the σ complex. Addition and addition–oxidation products are formed.

The selectivity of bromine radicals is significantly high with a variation of rate constants by a factor of 200 compared with a factor of 4 for the hydroxyl radicals and a factor of 40 for the carbonate radicals. This is due to the lower oxidation potential (1.63 V) of the bromine radicals. The observed oxidation products could only be explained by the interaction of azaarenes with the radiation and the following reaction out of the excited state. The analysis documents the formation of brominated substitution and oxidation products. The bromination on the pyridine and the diazine ring will also be facilitated by the reaction out of the excited states. The observed rate constants contain the sum of all parallel reactions, that means the halogenation out of the ground and excited states and the oxidation out of the excited states.

The rate constants of the bromine radicals are not suitable for a discussion of structure–reactivity relations because of the parallel reactions and because of the changing ratio of bromination to oxidation in dependence on the photophysical data of the azaarenes. In the experiment an excellent agreement with the gradation of reactivities of carbonate radicals (which reacts only by ETR) was found. The gradation of rate constants for the carbonate radicals follows the ionization energies and considers corrections according to the photophysical data (absorbance and quantuum yield of ISC). The similar gradation of rate constants of carbonate and bromine radicals (i.e., the parallel reactions of bromination and ETR points to a common rate determining reaction). This can be the formation of the σ complex. The kinetic experiments support the thesis of the formation of this intermediate, which can be formed from the ground and the excited states resulting in the same gradation of rate constants.

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