



INVESTIGATION ON THE PHOTOREACTIONS OF NITRATE AND NITRITE IONS WITH SELECTED AZAARENES IN WATER

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ABSTRACT

The photoreactions of selected azaarenes with nitrate and nitrite ions were investigated under irradiation at $\lambda = 313$ nm. The excitation of both anions leads to several photochemical reactions forming mainly hydroxyl radicals and nitrogen oxides. The purification capability of natural waters i.e. the oxidation of inorganic and organic substances results from the formation of hydroxyl radicals. Nitrated isomers of azaarenes were found among the main products of the investigated photoreactions. The nitrogen oxides were responsible for the production of nitrated derivatives which possess a high toxic potential. Their formation was explained by the parallel occurrence of two mechanisms, a molecular and a radical one. The molecular mechanism became more important with increasing ionisation potentials of the azaarenes. The spectrum of oxidized products corresponded to the one got in the photoreactions of azaarenes with hydrogen peroxide. The formation of several oxidation and nitration products of the pyridine ring with its low electron density was explained by the reaction of excited states of azaarenes. The photoreactions with nitrite ions only led to the formation of oxidized and nitrated products. Nitroso products were not formed. The reactivity of nitrogen monoxide is too low for its reaction with the azaarenes. ©1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Nitrite and particularly nitrate ions occur in natural waters ubiquitously. The interaction of both ions with sun light ($\lambda > 290$ nm) and with artificial UV-light ($\lambda = 254$ nm) leads to many decomposition and rearrangement reactions as part of a very complex reaction mechanism. Hydroxyl radicals and nitrogen oxides (NO and NO₂) are important products in the photolysis of nitrate and nitrite ions.

Kotzias [1,2] and Zepp [3] explained the process of natural purification of water by the oxidative degradation of organics in reactions with the photochemically formed hydroxyl radicals. Zepp et al. [3] showed that for lake Greifensee the photoproduction of hydroxyl radicals results from the photolysis of nitrate. Suzuki showed that nitrogen oxides were responsible for the formation of mutagenic and carcinogenic substances like nitroaromatics [4-6].

Von Sonntag et al. [7] studied the disinfection of drinking water by irradiation with UV-light ($\lambda = 254$ nm). The authors point to the possible formation of nitrite as a main product of the photolysis of nitrate, but the values found were not above the EU-limits of 0.1 mg/l. However, this might also lead to the formation of mutagenic and carcinogenic nitroaromatics. To study the possible formation of nitroazaarenes was one aim of this work.

The UV-absorption spectrum of the nitrate ion shows two bands at 200 nm ($\epsilon = 9900$ l/(mol · cm)⁻¹) and at 302 nm ($\epsilon = 7.2$ l/(mol · cm)⁻¹). The mechanism of the photolysis is very complex. The quantum efficiency of the single reaction steps is influenced by many factors like nitrate concentration, concentrations and kind of additives dissolved in the water (e. g. oxygen, organics), intensity and wave length of the radiation or pH-value of the water. The following reaction scheme (Fig.1) represents only an incomplete part of the mechanism.

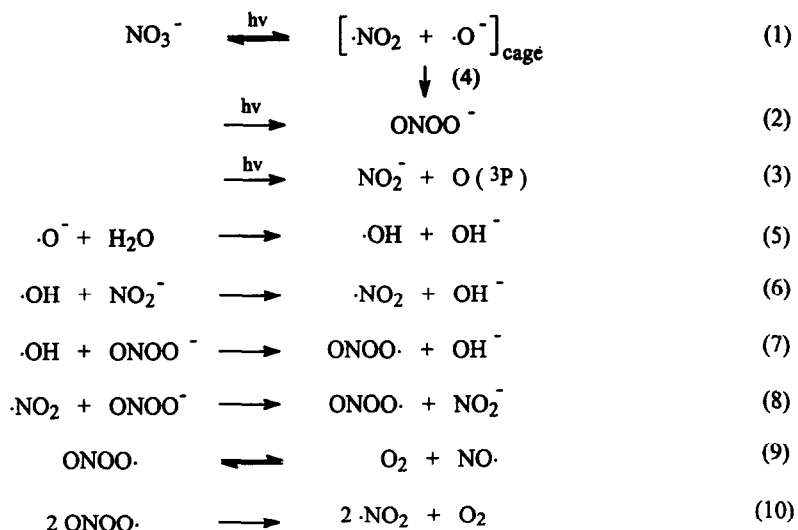


Figure 1: Reaction steps within the mechanism of the nitrate photolysis

The nitrate photolysis at $\lambda > 290$ nm was studied by Zepp [3] and Warneck [8]. The reaction steps 1 and 3 are found to be the primary reactions in those experiments with quantum efficiencies of $(0.9 - 1.7) \cdot 10^{-2}$ and $1.1 \cdot 10^{-3}$, respectively. Irradiation at $\lambda = 254$ nm [7] additionally leads to the formation of peroxonitrite in the primary reaction (2). Peroxonitrite also results from the cage effect including reaction (1) and (4). It is only formed in basic solutions because the protonated analogue under acidic conditions is not stable. If no other oxydations occur, the hydroxyl radicals oxidize the peroxonitrite according to reaction (7) forming the corresponding radical which decomposes into O₂ and NO (9) [7]. Addition of methanol in milimolar quantities changes the quantum efficiency of reaction (3) (nitrite formation) from 0.01 to 0.06. Under acidic conditions formaldehyde and peroxy radicals are formed with quantum yields comparable to nitrite [7]. Under basic conditions peroxonitrite and formaldehyde react to formic acid. Under anaerobic conditions the photoreaction of cyclopentane and nitrate ($\lambda = 254$ nm) formed nitrated compounds. Boule [9,10] and

Suzuki [4-6] showed that photoreactions of aromatics and nitrate at $\lambda > 290$ nm generate nitroaromatics beside other reaction products.

Nitrite concentrations in natural water are much lower than nitrate concentrations. The higher toxicity and the higher absorption values of nitrite ions are the reason to study their photoreactions too. The absorption coefficient of nitrite at $\lambda = 352$ nm ($\epsilon = 22 \text{ l}/(\text{mol} \cdot \text{cm})^{-1}$) equals three times that of nitrate at $\lambda = 302$ nm. There is no decrease in nitrite concentration during photolysis in distilled water (efficient regeneration of nitrite ions). In natural waters a net decrease was observed [11]. The nitrite photolysis is not as complex as the nitrate photolysis. Two reactive products, hydroxyl radicals and nitrogen monoxide, are formed in equal proportions [11] (Fig.2).

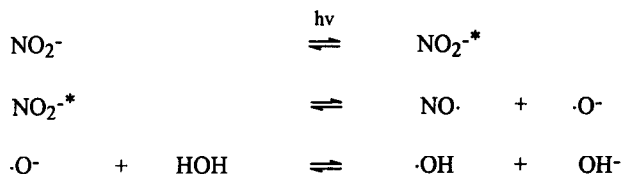


Figure 2: Photolysis mechanism of nitrite ions

Boule [10] studied photoreactions of nitrate and nitrite ions with substituted benzene derivatives. He found oxidized compounds but also nitro- and nitrosoaromatics as reaction products. The latter are known to be potentially mutagenic and carcinogenic agents.

Our aim is it to study the influence of the molecular structure of azaarenes on the yield of oxidation, nitration and nitrosation products and to estimate the environmental relevance of the reactions. For benzene derivatives [9,10] the reaction products are known. This facilitates the interpretation of the reaction paths of the radical reactions which have only little selectivity and produce many different products in very small concentrations. For mechanistic investigations benzene derivatives are unsuitable because of the very small differences in the electron density distribution within the aromatic ring. We use binuclear and trinuclear azaarenes possessing benzene rings with higher electron density and pyridine/diazine rings with lower electron density in the molecules. The nitrogen atoms further lead to a clear differentiation of the electron density within the heterocyclic rings. This favours the attack of the radicals on special points of the molecules. The excitation of molecules also influences the distribution of electron density. Therefore, the importance of excited states in the reaction paths was studied. So far photonitration was investigated for aromatics which possess a electron density comparable to or larger than benzene. The azaarenes are electron deficient aromatics and should hinder the nitration reaction.

Azaarenes were investigated for environmental reasons too. Like polynuclear aromatic hydrocarbons they occur ubiquitously. Compared with PAH their solubility in water is 3 - 4 orders of magnitude higher [12] what influences the reaction behaviour and bioavailability in the environment.

EXPERIMENTAL SECTION

Materials: Naphthalene (reference compound), quinoline, isoquinoline, phthalazine, quinoxaline, quinazoline, acridine, phenazine, phenanthridine, benzo[h]quinoline (BhQ), benzo[c]cinoline (BcC), 1,7

phenanthroline and 4,7-phenanthroline were purchased from Aldrich in maximum purity grade. Ethyl acetate and dichloromethane used for solvent extraction (resi analysed) and hexane (GC 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) from Hereaus was used as immersion lamp in a 400-ml-photo reactor thermostated at 25 °C. The monochromatic radiation at $\lambda=313$ nm was isolated from the complex line spectrum of the high pressure mercury lamp by a filter solution (aqueous sodium dichromate solution). The azaarene concentrations varied between 0.01 and 1 mM. To dissolve the trinuclear azaarenes methanol or acetonitrile (HPLC gradient grade, Baker) was added ($V<0.1\%$). Analogous treatment of the binuclear compounds showed no differences to their reactions in pure water. To the azaarene concentrations nitrate and nitrite concentrations in 10 and 100 molar excesses were applied. Aqueous samples were extracted with ethyl acetate (+ NaCl). An aliquot of the ethyl acetate extract was evaporated to dryness and dissolved in 500 μ l hexane for GC injection. The products were identified by GC/MS (GC HP 5890 series II and MSD HP 5971, Hewlett Packard). As column a HP-5 (30 m x 0.25 mm x 0.25 μ m film thickness) was used. The temperature programs (GC) are given in tables 1 and 2.

Table 1: Temperature program for binuclear azaarenes

Level	Heating Rate [K / min]	End Temperature [°C]	End Time [min]
starting level		70	2.5
1	7.0	130	0
2	8.0	230	0
3	20.0	260	0

Table 2: Temperature program for trinuclear azaarenes

Level	Heating Rate [K / min]	End Temperature [°C]	End Time [min]
starting level		120	0.5
1	10.0	160	0
2	6.0	280	3.5

The identification of most of the reaction products was confirmed by reference compounds (Aldrich, Merck). The products were determined in SCAN and SIM mode.

RESULTS

Photoreactions of naphthalene, quinoline and isoquinoline with nitrate ions

The photoreactions of naphthalene, quinoline and isoquinoline with nitrate ions formed 31, 28 and 32 products, respectively. This underlined the high complexity of the nitrate photolysis generating a large number of oxygen and nitrogen containing radicals which are able to react with aromatics. The low yield of the products and the low selectivity of the reactions, both typical features of radical reactions, complicated

the identification of the products. The photoreactions with nitrate ions showed two reaction paths, oxidative degradation and formation of nitro or nitrohydroxy products.

The spectrum of the oxidation products of the two azaarenes resembled that found in photoreactions of the aromatics with hydroxyl radicals at $\lambda = 313$ nm (photolysis of hydrogen peroxide) [13]. Progressive oxidation of the benzene and pyridine ring occurred. The concentration of the oxidation products of the pyridine ring was higher for isoquinoline than for quinoline. According to the assessment of the frontier orbitals this result was expected.

In the second reaction path nitrated compounds of the three aromatics were generated. Naphthalene formed the two possible nitro isomers and quinoline and isoquinoline formed five nitro isomers each. Furthermore, the formation of two nitrohydroxy compounds was observed. Altogether the nitro isomers were the reaction main products. The low selectivity of the position at which the aromatics were nitrated is remarkable. The two nitro isomers of naphthalene were formed in comparable concentrations and the differences in the concentrations of the five nitro isomers of the azaarenes were also very small. Among them for both azaarenes one product was nitrated at the pyridine ring. The distribution of the electrostatic charges suggested nitration at position 3 of quinoline and 4 of isoquinoline.

The ratio of nitration and oxidation products increased from naphthalene via quinoline to isoquinoline. Contrary to our expectations the electron deficient compounds quinoline and isoquinoline were nitrated to a higher extend. Another interesting trend was that the ratio of nitrohydroxy and nitro compounds decreased from naphthalene to isoquinoline.

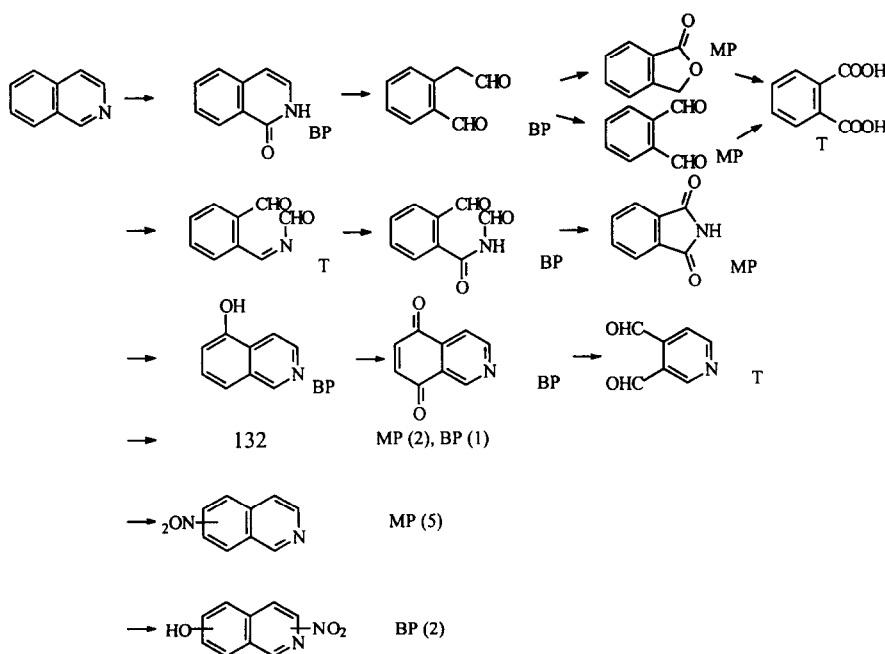


Figure 3: Photoreaction of isoquinoline with nitrate ions at $\lambda = 313$ nm (MP...main product, BP...byproduct, T...trace; (number)...number of products; 132...pyridinedialdehyde derivatives, structure unknown)

Photoreactions of quinoxaline, quinazoline und phthalazine with nitrate ions

The photoreaction of quinazoline led to a high yield of the four nitro isomers with the nitro group at the benzene ring. Oxidation mainly occurred at the pyridine ring.

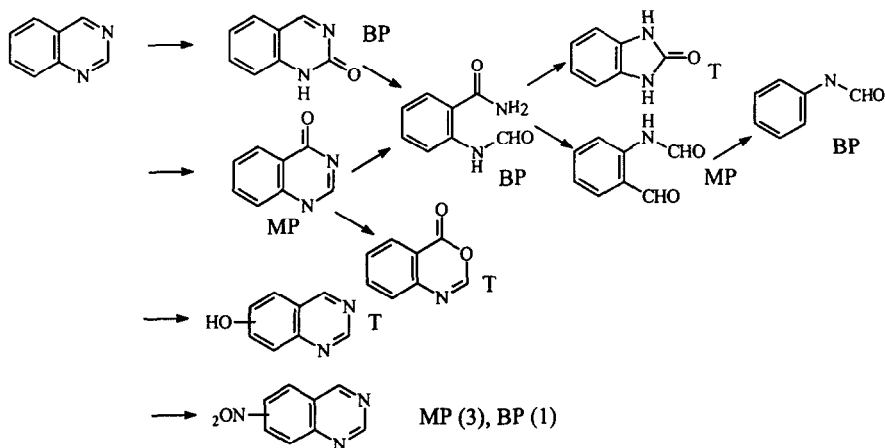


Figure 4: Photoreaction of quinazoline with nitrate ions

In the photoreaction of quinoxaline and nitrate ions 11 oxidation products, 2 nitro products and traces of one nitrohydroxy compound were found. Nitration was the main reaction path. The distribution of the electrostatic charges within the molecule suggested nitration at positions 5 and 6. Oxidation also occurred nearly only at the benzene ring as it is known from the photoreaction with hydroxyl radicals [13].

In the photoreaction of phthalazine 11 products were detected. Nitration was the main reaction path and led to 5-nitrophthalazine as the only product.

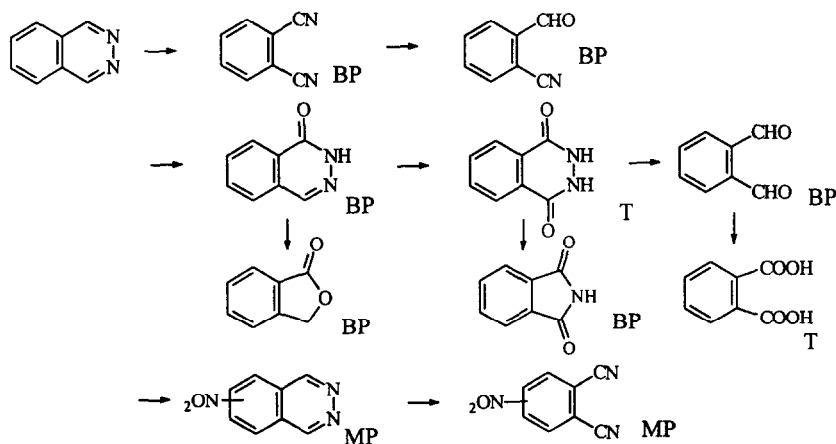


Figure 5: Photoreaction of phthalazine with nitrate ions

The oxidation to 1,2-dicyanobenzene and 2-cyanobenzaldehyde was another important reaction. The concentration of the nitrated 1,2 dicyanobenzene was comparable to that of 5-nitrothalazine and it distinctly exceeded that of 1,2-dicyanobenzene. The oxidation mainly occurred at the pyridazine ring. Oxidation products of the benzene ring were of less importance. As proven for the photoreaction with hydroxyl radicals, phthalazine and quinoxaline clearly differed in their oxidation mechanisms [13].

Photoreactions of trinuclear azaarenes with nitrate ions

The ratio of nitration and oxidation products strongly changed for the trinuclear angularly annellated azaarenes. For benzo[c]cinnoline (BcC), which is more stable against oxidation, two nitrated isomers were formed in high concentrations. Benzo[h]quinoline (BhQ), and 1,7-phenanthroline were oxidized but not nitrated. For 4,7-phenanthroline only traces of a nitration product were found. The number and amount of nitration products increased as follows: BhQ, 1,7-phenanthroline < 4,7-phenanthroline < phenanthridine < BcC. For phenanthridine the ratio of oxidation and nitration was 60 : 40 (nine oxidation and seven nitration products). Oxidation of the less stable azaarenes mainly occurred at the central nucleus and only to a small amount at the terminal benzene ring. For the two trinuclear linearly annellated azaarenes the yield of nitrated derivatives exceeded that of the oxidation products. Nitration proceeded more selectively. So, the nitrated isomers of acridine differed in their concentrations in a factor of about 20. For phenazine the two possible nitro isomers were the main products. Hydroxyl radicals attacked the molecule at the terminal benzene rings and formed 1-hydroxyphenazine, 1,4-dihydroxyphenazine, quinoxaline-2,3-dialdehyde and quinoxaline-2-aldehyde. The photoreaction of acridine led to three derivatives nitrated at the positions 1, 2 and 4. Traces of a nitrohydroxy product were also identified. There were two oxidation paths, the oxidative degradation of the terminal benzene ring analogous to phenazine and the oxidation of the carbon atom 9 producing acridone and oxidized biphenyles, respectively.

Photoreaction of quinoline and isoquinoline with nitrite ions

In the photoreactions with nitrite ions two groups of main products were found, nitro compounds and hydroxy compounds. Compared with the photoreaction with nitrate ions the portion of nitro compounds among the products was clearly larger. Isoquinoline for example formed six of the seven possible nitro isomers (four with quinoline). It was surprising that two isomers with the nitro group at the electron deficient pyridine ring were formed. Oxidation reactions of the both azaarenes proceeded only at the pyridine ring. 2-aminobenzaldehyde (quinoline) and 1(3H)-isobenzofuranone (isoquinoline) were formed. The photolysis of nitrite ions produces nitrogen monoxide. Therefore in the photoreactions of phenol derivatives with nitrite ions Boule [9] identified nitroso compounds among the reaction products. In our case nitroso compounds of the aromatics were not formed.

DISCUSSION

The comparison of the oxidation products in the photoreactions of the azaarenes with nitrate/nitrite or with hydroxyl radicals shows large conformity. Beside oxidation products of the benzene ring, which dominate

in dark reactions, oxidation products of the pyridine ring were formed. In the photoreactions with hydrogen peroxide the shift of the oxidation centre to the pyridine ring takes place along with the shift of the electron density observed in excited states of the azaarene molecules [13]. The shift of electron density can be derived from theoretical calculations on the basis of the frontier orbital concept and is proved experimentally by an increase of pK_a -values if azaarenes are transferred from ground to the excited S_1 and T_1 states.

The hydroxyl radicals could react with azaarenes in ground and excited states (T_1 state has significantly higher half-times than the S_1 state, that allows bimolecular reactions with radicals). The reaction of the ground state dominated because the excited molecules occurred only in a small steady state concentration. The hydroxyl radicals interacted with azaarenes at places of higher electron density in the molecule. Rate constants of the reactions of the azaarenes with carbonate or bromine radicals give also evidence for the parallel reactions of excited and nonexcited molecules [13]. The rate constants for hydroxyl radicals follow the same graduation but because of the high reactivity of the radicals they only differ in a coefficient of about 4 (Table 3).

Table 3: Second order rate constants of the photoreaction of azaarenes with nitrate ($\lambda = 313 \text{ nm}$)

Substance	Rate Constant [$10^{10} \text{ l} \cdot (\text{mol} \cdot \text{s})^{-1}$]	Absolute (Relative) Error [$10^{10} \text{ l} \cdot (\text{mol} \cdot \text{s})^{-1}$]
binuclear azaarenes		
phthalazine	3.71	± 0.15 (4.05 %)
cinnoline	3.78	± 0.19 (5.06 %)
quinazoline	5.01	± 0.47 (9.50 %)
quinoxaline	6.62	± 0.21 (3.32 %)
quinoline	7.09	± 0.44 (6.22 %)
isoquinoline	10.20	± 0.62 (6.08 %)
trinuclear azaarenes		
benzo[c]cinnoline	5.79	± 0.16 (3.26 %)
phenazine	5.98	± 0.15 (2.69 %)
phenanthridine	7.13	± 0.21 (3.04 %)
4.7-phenanthroline	7.92	± 0.44 (5.27 %)
acridine	9.70	± 0.68 (6.68 %)
benzo[h]chinoline	9.80	± 0.67 (7.26 %)
1.7-phenanthroline	10.04	± 0.86 (8.03 %)

The reactions nearly proceed controlled by diffusion [14]. The concentration of oxidation products of the pyridine ring was higher for isoquinoline than for quinoline according to considerations of the frontier orbital concept. The photooxidation of benzodiazines can be treated analogous to quinoline and isoquinoline. The structure of quinoxaline can be understood as superposition of the structure of quinoline and in a same manner phthalazine as superposition of isoquinoline. While quinoxaline analogous to quinoline was oxidized mainly at the benzene ring, the oxidation of phthalazine analogous to isoquinoline was observed at the pyridazine ring. For quinazoline with its structure between quinoline and isoquinoline a

stronger oxidation of the benzene ring compared with phthalazine was found.

The proof of nitrated and nitrosated benzene derivatives as main products in photoreactions confirmed papers of Suzuki [4-6] and Boule [9,10] who investigated their formation under toxicological and mechanistic aspects. Now with the azaarenes the number of compounds nitrated by nitrate photolysis is extended to substances with significantly lower electron density (the nitrating species is electrophilic) what remarkably increases the environmental potential of the nitrate photolysis.

To observe the nitration the nitrating agent must be formed in a high concentration (in competition to the hydroxyl radicals) and in a highly reactive form. In the literature two nitrating species are known the nitronium ion NO_2^+ in polar solvents and the $\cdot\text{NO}_2$ -radical in nonpolar solvents. The latter can react with PAH in an electron transfer step forming the PAH radical cation and nitrite (occurring as ion pair).

In the literature several mechanisms for the nitration of aromatics by nitrate photolysis were discussed [10]. Boule [10] favours two mechanisms, a radicalic one and a molecular one (Figure 6).

The reactive species of the molecular mechanism is the dimer N_2O_4 , which is polarized in the aqueous phase. A possible hypothesis is the formation of the intermediate $[\text{NO}_2^+ \dots \text{NO}_2^-]$. The NO_2^+ can electrophilically attack the aromatics leading to the respective nitrated derivatives. The dependence on the pH-values supports this assumption. A stronger protonation of N_2O_4 assists the formation of the intermediate.

The reactive species of the radicalic mechanism is the $\cdot\text{NO}_2$ -radical that adds on the aromatics. As intermediate a σ -complex is formed which further reacts with another $\cdot\text{NO}_2$ -radical or an oxygen species to form a nitrated derivative or a nitrohydroxy product.

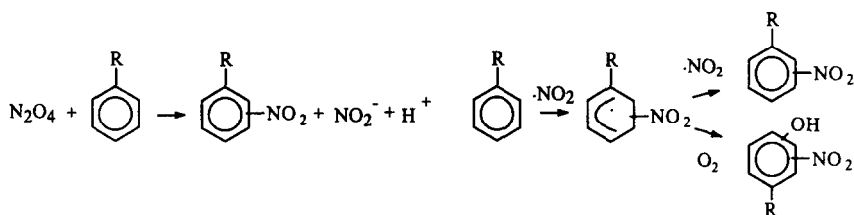


Figure 6: Molecular and radical nitration mechanisms of benzene derivatives [10]

As conclusions three important trends can be deduced from the results. At first the ratio of nitration/oxidation products increased from naphthalene via quinoline, isoquinoline to the benzodiazines quinazoline and quinoxaline. This trend has its reason in the competition of the parallel reactions, the oxidation and the nitration. The benzodiazines show a higher oxidation stability compared to naphthalene or quinoline.

As a second trend the ratio of nitration / nitration-oxidation products increased in the same manner from naphthalene to quinoxaline. This ratio demonstrates the participation of molecular and radicalic mechanisms. The parallel occurrence of both mechanisms was already supposed by Boule [9]. The portion of the molecular mechanism increases from naphthalene to quinoxaline. This hypothesis correlates well with the parallel increase of the ionization potentials. A possible objection, that nitration-oxidation products perhaps could be the result of oxidation of the nitrated derivatives, is unlikely as the concentrations of both products were similar.

A third remarkable result was the nitration of the pyridine ring, not expected for electrophilic reactions. The

low electron density of this ring and the whole molecule at benzodiazines should cause a low reaction probability for electrophilic species. Thus the formation of the nitrated isomers can only be explained by the reaction of excited states of the azaarenes. The shift of the electron density from benzene to the pyridine ring within excitation increases the nucleophilicity of the pyridine ring and makes an electrophilic attack easier. The two benzodiazines, quinoxaline and quinazoline have a high quantum yield of spin inter state crossings (ISC; $S_1 \Rightarrow T_1$, of 0.9 and 0.7). The quantum yield for isoquinoline is only 0.21. This ISC-values and the higher absorbance coefficients at $\lambda=313$ nm were responsible for a significantly higher steady-state concentration of reactive T_1 states of both benzodiazines and led to the surprisingly high yield of nitrated derivatives.

The investigation of trinuclear azaarenes confirmed the results discussed above and showed some new specific qualities. Again the nitration degree depended on the ratio of both parallel reactions, the oxidation and the nitration and also on the nucleophilicity of the terminal rings. The concentration of nitrated derivatives of angular anellated azaarenes decreased as follows: BcC > phenanthridine > BhQ, 1,7- and 4,7-phenanthroline. BcC has a central nucleus which is deactivated by two nitrogen atoms and therefore stable against an oxidative degradation. This resulted in a high yield of nitrated compounds. For the less stable phenanthridine a ratio of oxidation to nitration of 60 : 40 was observed. The three compounds BhQ, 1,7- and 4,7-phenanthroline were not nitrated. This can be explained by the strong oxidizability of their central benzene rings which follows the π -sextett concept of Clar. According to this concept the maximum number of sextetts is formed (at both terminal nuclei) and therefore the central nucleus should be oxidized. The terminal pyridine rings are too low in their electron density for an electrophilic attack. The transition from the binuclear to the trinuclear azaarenes was accompanied by an increase in charge differentiation. This led to a higher differentiation of the concentrations of nitrated isomers. The increasing position selectivity for example can be observed for the substance pair phenazine / acridine. Nitrohydroxy products were formed only as traces. Obviously the molecular mechanism became more important in the transition from the binuclear to the trinuclear azaarenes. With increasing number of anellated rings the nucleophilicity of the aromatic system increases. For the electrophilic species (NO_2^+) an attack becomes easier. On the other hand the resonance energy per electron (REPE) decreases, i. e. the lower resonance stabilization of the aromatic system led to an easier formation of the intermediate σ -complex.

The higher yield of nitrated isomers in the photoreaction of azaarenes with nitrite is based on the reaction of hydroxyl radicals (Fig. 3, reaction 1) with nitrite ions. In that reaction additional $\cdot\text{NO}_2$ -radicals are formed. A large surplus of nitrite ions traps the hydroxyl radicals quantitatively. For the selective formation of oxidation products of the pyridine ring again reactions of excited states of the azaarenes with $\cdot\text{NO}_2$ -radicals were responsible. The absence of nitrosated azaarenes was remarkable. Boule [10] found nitroso products in the photoreactions of benzene derivatives. He supposed the formation of nitrosated isomers by a molecular (by N_2O_3) and a radicalic mechanism ($\cdot\text{NO}$) analogous to the nitrate photolysis. In the case of the azaarenes the $\cdot\text{NO}$ or NO^+ species are not reactive enough for the electron deficient compounds. Compounds with a lower electron density than benzene derivatives are nitrated but not nitrosated in photoreactions with nitrite at $\lambda = 313$ nm.

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