

AROMATIC PHOTOSUBSTITUTIONS

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Abstract - Aromatic photosubstitution reactions are reviewed and discussed from the mechanistic and theoretical point of view. Examples of free-radical, electrophilic, and nucleophilic photosubstitutions are given.

INTRODUCTION

In organic photochemistry, photosubstitution reactions of aromatic compounds have been a somewhat less popular topic than various other types of photochemical reactions, many of which have been studied in sufficient depth and detail both experimentally and theoretically. One of the reasons is undoubtedly the fact that, in many cases, it is more difficult to establish the mechanism of a photosubstitution reaction than that of other photochemical reactions.

The overall course of a photosubstitution reaction can be described by eq. 1 where R is an aromatic or heteroaromatic system, X is a leaving group (a substituent or a hydrogen atom), and Y is a new substituent.



Aromatic photosubstitutions have been reviewed in numerous articles and book chapters (1-19) as well as in a series of reviews published by the Royal Society of Chemistry (20-22) and in other annual surveys (23). A new monograph which will be devoted to aromatic photosubstitutions is in preparation (24).

In mechanistic and theoretical studies of aromatic photosubstitutions, quenching and sensitization experiments, the use of trapping techniques, ESR and CIDNP spectroscopy, the determination of quantum yields, investigation of solvent effects, kinetic and equilibrium data, and conventional flash photolysis and laser photolysis play an important role. Electronic absorption and emission (fluorescence, phosphorescence) spectroscopy remains one of the main tools as well. Finally, at least in some cases, additional valuable information can be obtained from the results of quantum-chemical calculations carried out at different levels of sophistication (for classical examples of papers in this area, see refs. (25,26)).

Havinga, Cornelisse, and Lodder (15,18) have developed a classification of aromatic photosubstitutions which is based on the kinetics of the respective reactions (unimolecular, bimolecular) and their type (free-radical, polar - electrophilic or nucleophilic) and which takes into account the effect of substituents in the aromatic system. Additional aspects of the classification of these reactions include the nature of the substrate (an aromatic hydrocarbon, a substituted aromatic hydrocarbon, a heterocyclic system), the nature of its excited state undergoing the reaction (a singlet state, a triplet state, $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ excitation) and the nature of the attacking species (a charged electrophile or nucleophile, an electron-deficient or electron-rich electro-neutral species).

According to the reaction type, photosubstitutions can be divided into several major groups:

- a) free-radical photosubstitutions,
- b) electrophilic photosubstitutions,
- c) nucleophilic photosubstitutions,
- d) photosubstitution reactions of aromatic cations and anions, and
- e) electron-transfer assisted photoreductions and photodehalogenations.

Whereas some of these reactions are true photosubstitutions, other reactions are just light-induced processes. A photosubstitution reaction can be thought of as an excited-state counterpart of ground-state substitution reactions.

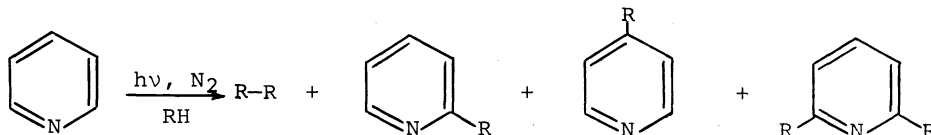
In this contribution, an attempt will be made to present a general overview of the information available on aromatic photosubstitutions at the present time, with a special attention being paid to the theoretical aspects concerning these reactions. Selected examples of the above reaction types will be given and, in at least some cases, supporting experimental and theoretical evidence for their mechanism will be discussed.

It is well known that, in general, the substitution patterns in excited-state aromatics are different from those in the ground-state species. However, because Havinga, Cornelisse, de Gunst, and Lodder have formulated the rules which govern orientation in aromatic photosubstitutions, especially the nucleophilic ones, they will not be discussed here and the reader is referred to several excellent reviews covering this topic (10-12,18).

FREE-RADICAL PHOTOSUBSTITUTIONS

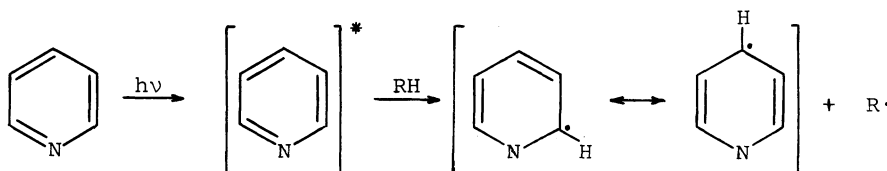
Free-radical photosubstitutions will be reviewed in detail in a book chapter devoted to this type of reactions (27). Some of these reactions can be classified as addition-elimination reactions involving free-radical intermediates (e.g., the formation of hydrocarbon, alcohol, or ether adducts). In other cases, free-radical adducts are obtained *via* photogenerated aromatic radical anions (reactions of aromatic with amines, acids, and arenes) or aromatic radical cations (cyanation). Another possibility is the introduction of a substituent through a direct attack of photogenerated radicals upon various aromatic substrates (hydroxylation, nitrosation, nitration, halogenation, cyanation, trimethylsilylation, etc.). Finally, photochemical homolytic cleavage of aryl-hydrogen bonds and other carbon-heteroatom bonds also represents a route to photosubstitution.

Photoalkylation of pyridine, quinoline, and isoquinoline is an example of a free-radical photosubstitution in the heteroaromatic series (6,28-30). Thus, the irradiation of a solution of pyridine in cyclohexane gives bicyclohexyl, 2- and 4-cyclohexylpyridine, and 2,6-dicyclohexylpyridine.



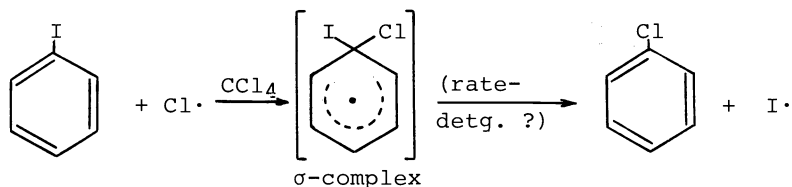
R = cyclohexyl

The postulated mechanism of the reaction involves the formation of a pyridinyl radical *via* abstraction of a hydrogen atom from the solvent by the photoexcited pyridine, followed by the recombination of the resulting radicals in the solvent cage. The substituted dihydro derivatives formed then undergo rearomatization and yield the corresponding substituted pyridines (6,28).

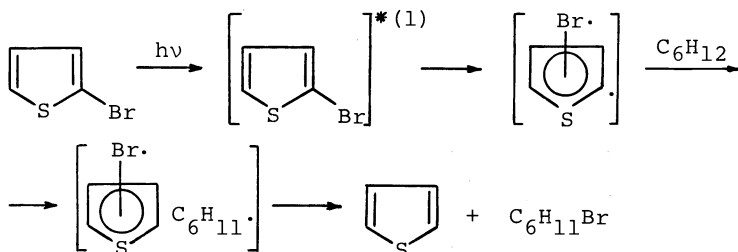


Halogen exchange reactions are an often cited example of photoinduced free-radical substitutions in which a heavier halogen atom is replaced by a lighter halogen (or another isotope of the same halogen). Although some authors have postulated a rather complex mechanism for these reactions, it seems that, at least in many cases, they are free-radical substitutions as exemplified here by the replacement of iodine in iodobenzene with chlorine (31). The primary step is the photochemical homolytic cleavage of iodine monochloride.





An interesting mechanism has been proposed for the photodebromination of 2- and 3-bromothiophenes (19,32). When irradiated in a hydrogen-donating solvent, the substrate undergoes photodebromination with the formation of thiophene as the major reaction product. On the basis of the available experimental data, the plausible mechanism of the reaction involves homolytic cleavage of the carbon-bromine bond in the photoexcited bromothiophene followed by the formation of a π -complex between the thieryl radical and the bromine radical in the solvent cage.



The following experimental evidence supports the above mechanism.

- a) The reaction takes place in various hydrogen-donating solvents (cyclohexane, diethyl ether, methanol, ethanol, 2-propanol) and does not require the presence of a nucleophile.
- b) Cyclohexyl bromide is formed as the second major organic product when cyclohexane is used as the solvent (no bicyclohexyl and no cyclohexene were identified in the reaction mixture).
- c) Quantum yields are lower than one (0.04-0.10) (no chain mechanism).
- d) Oxygen does not exhibit any effect upon the quantum yields (no oxygen quenching).
- e) Bromothiophenes do not phosphoresce.
- f) Flash photolysis experiments carried out with 2-bromothiophene in cyclohexane reveal the existence of a transient species with main absorption at 380 nm.

Our search for CIDNP was unsuccessful. The formation of tars in the photolysis of 3-bromothiophene can be ascribed to the high instability of the intermediate 3-thienyl radical which undergoes ring opening followed by polymerization.

PPP calculations carried out for both bromothiophenes indicate that the first singlet state of these substrates is the species undergoing photodebromination. The typical bond dissociation energy of an aromatic carbon-bromine bond is about 73 kcal/mole. The energy gained by the bromothiophenes in their first excited triplet state is not sufficient for the cleavage of their carbon-bromine bond, however, it is more than adequate in the first excited singlet state (~ 108 kcal/mole).

Finally, it should be pointed out that, although less likely, a more conventional free-radical mechanism of the reaction can be envisioned as well (19).

ELECTROPHILIC PHOTOSUBSTITUTIONS

In the rapidly expanding field of polar aromatic photosubstitutions, the large number of known nucleophilic photosubstitution reactions by far exceeds the few reported cases where the mechanism is electrophilic (17,33). This, of course, is in sharp contrast to the ground-state aromatic chemistry where the most typical reaction of benzene and benzenoid hydrocarbons is electrophilic aromatic substitution - probably the best studied single field of organic chemistry. On the other hand, ground-state nucleophilic aromatic substitutions are restricted mainly to heteroaromatic systems (e.g., pyridine-

like heterocycles) and to substituted aromatics with strongly electron-withdrawing groups (such as the nitro group) which make the parent system more susceptible to an attack by a nucleophile.

The small number of known electrophilic photosubstitutions is quite surprising as it has been shown that the acid-base properties of aromatics usually change considerably upon excitation and that, in most cases, the change is more pronounced in the first excited singlet state than in the first excited triplet state (5,9). Any increase of the basicity of the system upon excitation would be expected to increase the reactivity of the excited-state substrate as compared to the ground-state species (5). It should be noted, however, that this increase in basicity is not a sufficient condition for a successful excited-state electrophilic substitution (5). The low rate of success in the field of electrophilic aromatic photosubstitutions is not necessarily caused by low reactivity of the photoexcited aromatics toward electrophiles. Some of the possible reasons which can be used to explain, why the number of known electrophilic photosubstitutions is still so small, are as follows (5,10-12,15,19).

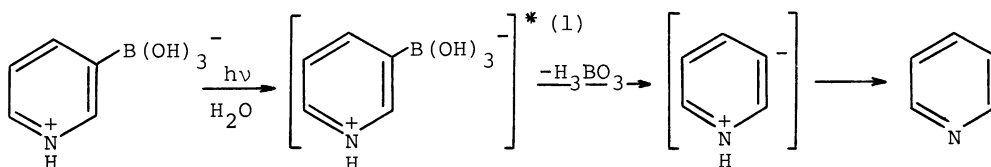
- a) Many electrophilic reagents react with the ground-state substrates and thus it is impossible to separate the excited-state reaction from the analogous ground-state reaction.
- b) Various electrophiles are efficient quenchers of excited states of aromatics (fluorescence studies).
- c) It is difficult to find suitable media with sufficiently high concentration of an electrophile which would react with the short-lived excited-state species.
- d) π, π^* excited molecules have a tendency to transfer an electron to the electrophilic medium and the resulting radical cation is not reactive toward electrophiles.
- e) Under the conditions used, other processes may occur with the photoexcited aromatic substrates giving rise to various photolysis products.
- f) In the case of azaheterocycles, their protonation in acid media makes electrophilic substitution difficult.
- g) The competing radiationless decay of the photoexcited species has to be sufficiently slow.

The examples of electrophilic photosubstitutions reported so far in the literature include hydrogen-deuterium and hydrogen-tritium exchange, deboronation, destannylation, nitration, acylation and ethoxycarbonylmethylation, and the rearrangement of aromatic azoxy compounds (33).

According to the classification devised by Havinga, Cornelisse, and Lodder (15,18), electrophilic photosubstitutions can be divided into three principal groups: $S_{E1}(Ar^*)$, $S_{E2}(Ar^*)$, and $S_{EA}(Ar^*)$. The first two designations refer to the excited-state analogs of the S_{E1} and S_{E2} ground-state substitutions. The notation $S_{EA}(Ar^*)$ designates a photostimulated S_{EA} process by analogy with Bunnett's photoinduced nucleophilic substitution (34,35).

$S_{E1}(Ar^*)$ photosubstitutions

The light-induced protodeboronation of pyridineboronic acids and benzeneboronic acids is a typical example (36,37).

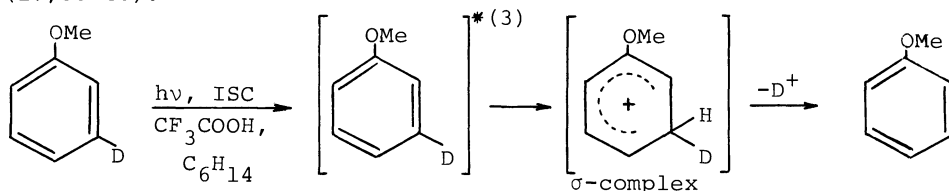


In addition to 3-pyridineboronic acid, also 4-pyridineboronic acid and substituted benzeneboronic acids give this reaction (2-pyridineboronic acid is unstable). The experimental evidence and the PPP calculations corroborate the above mechanism. In the theoretical interpretation of the reaction, it was assumed that the differences in activation energy for the various boronates can be approximated by the differences in the change of the electrostatic energy when going from the initial state to the transition state. During this process, the negative charge is transferred to the aromatic nucleus.

$S_E2(\text{Ar}^*)$ photosubstitutions

Acid-catalyzed protium-deuterium and protium-tritium exchange in aromatics is undoubtedly the best studied electrophilic photosubstitution and was investigated by several research groups on various aromatic substrates (17).

As an example, the photochemical protodeuteriation of anisole-3-*d*, which does not undergo almost any hydrogen exchange in the ground state, can be mentioned (17,38-40).



The order of reactivities of anisole-2-*d*, -3-*d*, and -4-*d*, as well as of naphthalene-1-*d* and -2-*d* in photochemical protodeuteriation is different from that in the thermal reaction. However, no clear-cut correlation could be found between the experimental data and the quantum-chemical reactivity indices (electron densities, localization energies) obtained by the PPP calculations. On the other hand, a comparison of the reactivities of the three positions of toluene in hydrogen isotope exchange reactions with the calculated electron density changes between the ground state and the singlet and triplet excited states of toluene seems to indicate the involvement of either an S_2 or a T_1 state in the photochemical exchange. Because the participation of higher excited states in substitution reactions is unlikely, the first excited triplet state appears to be the state undergoing the exchange (cf. Table 1). This is supported by an indication of possible oxygen quenching.

TABLE 1. Photochemical protodeuteriation of toluene (40)

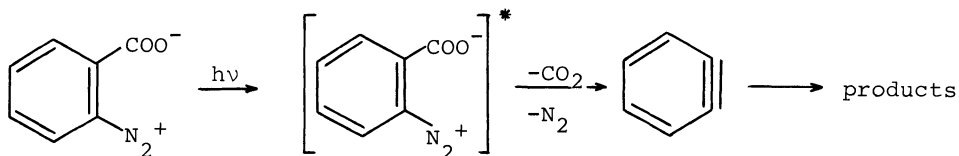
Compound/position	Dedeuteriation, % ^a		$\Delta q(S_1)^b$	$\Delta q(T_1)^c$
	Run A	Run B		
Toluene-2- <i>d</i>	44	51	0.0098	-0.0176
Toluene-3- <i>d</i>	20	27	0.0426	0.0139
Toluene-4- <i>d</i>	28	35	-0.0537	0.0044

^a Difference in the deuterium content prior to and after irradiation (acetic acid, 8 h). For detailed conditions, see ref. (40). ^b Electron density difference between the first excited singlet state and the ground state (41). ^c Electron density difference between the first excited triplet state and the ground state (41).

In the theoretical interpretation of the electrophilic hydrogen exchange reactions of aromatics, both the Dewar's perturbation method and the conventional HMO method were used to calculate the stabilization energy of the carbon-deuterium bond in the delocalized π -electron system (42).

 $S_{EA}(\text{Ar}^*)$ photosubstitutions

These processes are the electrophilic counterparts of photoinduced nucleophilic substitutions studied by Bunnett (34,35). An example is the photodecomposition of benzenediazonium-2-carboxylate leading to benzyne (dehydrobenzene) (43).



NUCLEOPHILIC PHOTOSUBSTITUTIONS[†]

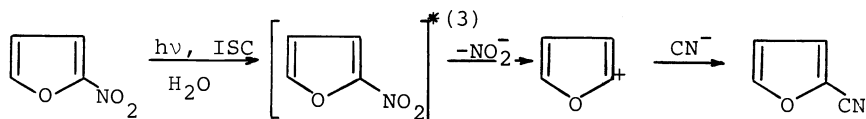
From the mechanistic and theoretical point of view, nucleophilic photosubstitutions are clearly the most studied group of aromatic photosubstitutions (44). In contrast to aromatic electrophilic substitutions and real free-radical photosubstitutions involving a photoexcited aromatic substrate, nucleophilic aromatic photosubstitutions are fairly general and take place with a large variety of aromatic and heteroaromatic systems and their derivatives. They occur in various solvents (protic and aprotic, usually in combination with water) and a large number of leaving groups and attacking nucleophiles have been studied. The leaving groups studied include H_2PO_4^- , SO_4^{2-} , OR^- , NO_2^- , F^- , Cl^- , Br^- , I^- , CN^- , SO_3^{2-} , N_2 , H^- . The examples of nucleophiles used as the attacking species are: H_2O , ROH , NH_3 , RNH_2 , R_2NH , R_3N , pyridine, OH^- , OR^- , CN^- , CNO^- , CNS^- , H^- , Me^- , MeCOO^- , NO_2^- , Cl^- , SO_3^{2-} .

Havinga, Cornelisse, de Gunst, and Lodder (10-12,18) have studied in detail the activating and deactivating effects of various electron-donating and electron-withdrawing substituents and orientation patterns in nucleophilic aromatic photosubstitution which are different from those in the ground-state substitutions. Thus, for example, electron-withdrawing groups (e.g., the nitro group) exhibit *m*-activating effect whereas the presence of electron-donating groups (e.g., the methoxy group) leads to *o,p*-activation. These electron-withdrawing and electron-donating effects play a significant role in the product formation steps and the nucleophile attacks the position in the aromatic substrate which results in the formation of the most resonance-stabilized product (merging resonance stabilization).

From the mechanistic point of view, five different mechanisms have been proposed for aromatic nucleophilic photosubstitution (18,45).

 $S_N1(\text{Ar}^*)$ photosubstitutions

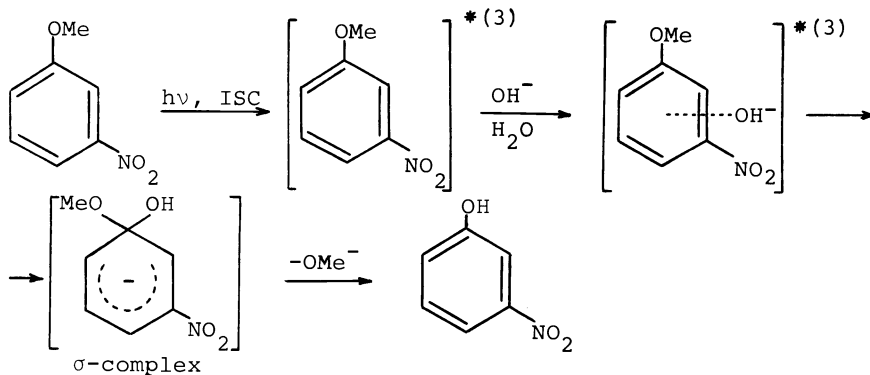
These reactions involve a primary photodissociation of the aromatic substrate into the corresponding aromatic cation and the leaving group anion, followed by the interaction of the cation with the nucleophile. The photocyanation of 2-nitrofuran can serve as an example (46).



The reactive species in this reaction is the cation formed by dissociation of the photoexcited triplet-state substrate.

 $S_N2(\text{Ar}^*)$ photosubstitutions

In this mechanism, the first step is the formation of a charge-transfer complex between the photoexcited triplet-state substrate and the nucleophile (47,48) leading to a σ -complex(es) which can decay back into the starting materials or lead to the formation of a substitution product. Photohydrolysis of 3-nitroanisole takes place via this route (47,48).

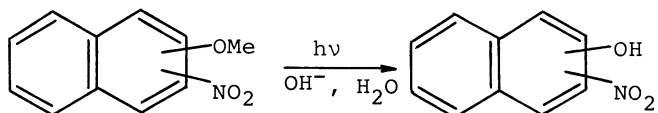


[†] In expanded form, the material on nucleophilic photosubstitutions will form a chapter co-authored by J. Cornelisse and E. Havinga which will be included in a forthcoming monograph on aromatic photosubstitutions (44).

The formation of an exciplex of the above type between a photoexcited aromatic molecule and a nucleophile has originally been formulated in a spectroscopic situation (49).

It is likely that many of the nucleophilic photosubstitution reactions studied so far follow this reaction mechanism.

One of the examples which seems to fit the above reaction scheme is the photohydrolysis of methoxynitronaphthalenes which will be discussed in some detail (50-58). Out of the fourteen possible isomeric methoxynitronaphthalenes, ten have been studied experimentally. Methoxynitronaphthalenes undergo photohydrolysis in various aqueous solvents (methanol, ethanol, 2-propanol, dimethyl sulfoxide, acetonitrile) containing sodium or potassium hydroxide.



The reaction does not take place in the dark, with the exception of 1-methoxy-4-nitronaphthalene which undergoes very slow hydrolysis in the ground state. However, its rate is negligibly low. As a rule, the corresponding nitronaphthols are the reaction products. However, in at least two cases (1-methoxy-4-nitronaphthalene, 2-methoxy-1-nitronaphthalene), also a limited substitution of the nitro group takes place as evidenced by the presence of nitrite ions in the solution and the formation of colored substances derived from the unstable methoxynaphthols formed as by-products. No photohydrolysis was observed with 1-methoxy-5-nitronaphthalene and 2-methoxy-6-nitronaphthalene. The reaction is easily followed spectrophotometrically because the resulting nitronaphtholate ions absorb in the visible region. Isosbestic points obtained when monitoring the reaction course indicate the presence of only one major reaction product in each case. The linear dependence of $1/\phi$ against $1/[\text{OH}^-]$ suggests that the rate-determining step is bimolecular and involves the photoexcited methoxynitronaphthalene and the hydroxide ion.

The typical quantum yields of photohydrolysis are in the range between 0.03 and 0.16. Methoxynitronaphthalenes give phosphorescence, with the 0-0 bands between 495-545 nm and the lifetimes in the 15-277 ms range indicating that the lowest-lying triplet state of methoxynitronaphthalenes is a π, π^* state. The splitting in the phosphorescence spectra is about 1400-1430 cm^{-1} and can be attributed to the Raman frequency characteristic of the nitro group (59, 60). The information on the emission spectra and photohydrolysis of methoxynitronaphthalenes is summarized in Table 2.

TABLE 2. Phosphorescence data and quantum yields for the photohydrolysis of methoxynitronaphthalenes (56,58)

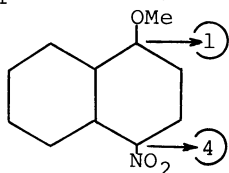
Isomer	τ^a (ms)	0-0 band (nm)	ϕ (313 nm)
1-Methoxy-2-nitro	158	498	-
1-Methoxy-3-nitro	15	545	0.109
1-Methoxy-4-nitro	126 (50)	521	0.1
1-Methoxy-5-nitro	34 (50)	510	0
1-Methoxy-6-nitro	35	530	0.158
1-Methoxy-7-nitro	180	530	-
2-Methoxy-1-nitro	127	503	-
2-Methoxy-5-nitro	20 (20)	542	0.054
2-Methoxy-6-nitro	277 (200)	495	0
2-Methoxy-7-nitro	200	495	0.026

^a Phosphorescence lifetime at 77°K in ethanol (the value without parentheses is from ref. (58), the value in parentheses from ref. (56)).

Similarly as other nitroaromatics, methoxynitronaphthalenes phosphoresce - this means that triplet states in these molecules are easily generated and suggests that, at least in most cases, the first π, π^* triplet state of

methoxynitronaphthalenes is the species involved in photohydrolysis. Additional supporting evidence for this assumption is that the reaction is quenched by oxygen and sensitized by benzophenone and sodium 2-naphthalenesulfonate.

PPP calculations have been successfully used to interpret the electronic absorption and phosphorescence spectra of these compounds (54). Although calculations of this type and molecular diagrams have often been used to predict or to interpret the course of aromatic photosubstitutions, the case of methoxynitronaphthalenes is an example of a situation in which the calculations cannot be used as supporting evidence. It is obvious from a comparison of the π -electron densities in the positions 1 and 4 of 1-methoxy-4-nitronaphthalene (61) that the carbon atom bearing the methoxy group will be more susceptible to the attack by a nucleophile in both the first excited singlet and triplet states. Thus, the order of reactivities of both positions bearing



1 S_0 0.928 S_1 0.905 T_1 0.934

4 S_0 1.128 S_1 1.035 T_1 1.130

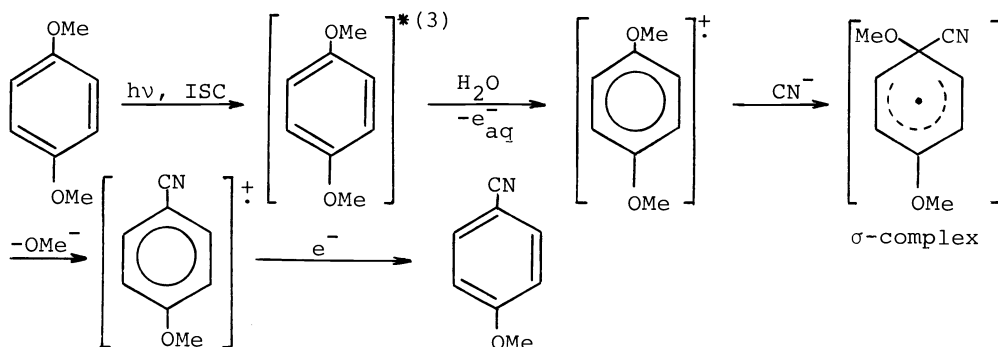
the substituents remains the same and the information cannot be used to decide about the nature of the excited state undergoing the reaction.

A number of theoretical studies on $S_N2(Ar^*)$ photosubstitutions are available in the literature, with the PPP and CNDO/2 methods most commonly used (18). In addition to the static reactivity indices (charge densities, electron densities), also the potential energy surfaces and differences in the energy contents of the σ -complexes and products have been calculated in some cases. Whereas with some substrates and reactions the results of the calculations have been successfully used to explain or to support a postulated mechanism, in many other situations the use of theoretical data is hampered by numerous complications.

$S_{R+N}+1(Ar^*)$ photosubstitutions

When aromatic molecules undergoing nucleophilic photosubstitution contain one or several electron-donating substituents, the reaction often involves the intermediate formation of radical cations, with photoionization as the primary reaction step (45,62,63).

Photocyanation of *p*-dimethoxybenzene (*p*-methoxyanisole) can be used as an example to illustrate this mechanism.



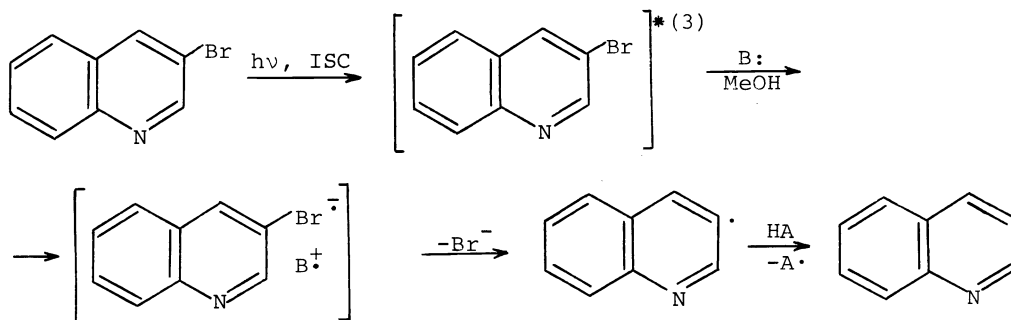
Charge distributions for various aromatic radical cations postulated in reactions of this type have been calculated by the PPP method with the Roothaan open-shell restricted Hartree-Fock formalism and the results have been compared with the experimental data. The comparison strongly supports the existence of the radical cations as intermediates in the above mechanism. The ionization of the photoexcited molecule is the primary step after excitation.

$S_{R-N}-1(Ar^*)$ photosubstitutions

These reactions are similar to the $S_{R+N}+1(Ar^*)$ photosubstitutions except that they involve the intermediate formation of radical anions. They are closely related to the $S_{RN}1$ mechanism described by Bunnett (34,35).

As an example of this mechanism, the photodebromination of bromoquinolines and 4-bromoisoquinoline will be discussed (64).

The compounds studied in this reaction were 3-bromoquinoline, 4-bromo-2-methylquinoline, 6-bromoquinoline, 8-bromoquinoline, and 4-bromoisoquinoline. Solvents used in the reaction were methanol, ethanol, 2-propanol, and acetonit-



B: = base, HA = solvent

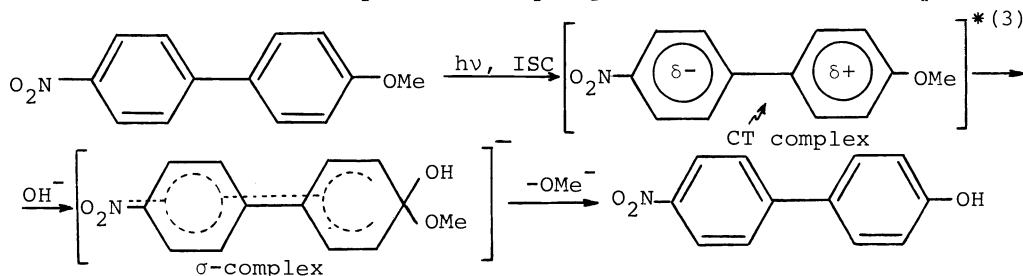
riole, sodium or potassium hydroxide or aliphatic amines (methylamine, triethylamine) served as the nucleophiles (bases). However, the reaction does not take place in the combination hydroxide ion/acetonitrile (acetonitrile is a relatively poor hydrogen donor). The reaction requires the presence of an electron donor and of a hydrogen donor (the solvent).

Quantum yields obtained for this reaction at 254 nm and 300 nm are in the 0.015-0.065 range in the presence of oxygen. They are much higher in degassed solutions. For example, the quantum yields for 3-bromoquinoline ($c = 1.5 \times 10^{-3} M$) in 0.1M aqueous NaOH-methanol (4 : 1) at 300 nm are 0.062 and 0.33 for non-degassed and degassed solutions, respectively. This indicates that the reaction is quenched by oxygen. On the other hand, it is sensitized by Michler's ketone. A linear dependence of $1/\phi$ versus $1/[OH^-]$ or $1/[amine]$ indicates a bimolecular process between the photoexcited substrate and the attacking species. When methanol is used as the solvent, the hydrogen atom comes from the methyl group and not the hydroxy group (experiments with MeOD in NaOD/D₂O). The mass spectrum of the reaction mixture indicates the presence of hydroxymethyl derivatives (with methanol as the solvent) and a signal was observed in the ESR spectrum of the frozen matrix obtained from the irradiated reaction mixture. Radical anions of the bromoheterocycles under study can be generated electrochemically (cyclic voltammetry) under conditions analogous to those used in the photolysis. Finally, bromoquinolines phosphoresce (π, π^* states) (65). PPP calculations have been carried out for the compounds under study (61).

All the above evidence supports the above-proposed mechanism taking place with the lowest π, π^* triplet state of the heteroaromatic substrates.

Nucleophilic photosubstitutions via intramolecular charge transfer [$S_N ICT(Ar^*)$]

This mechanism has been proposed by Shadid (45) for the photolysis of some methoxynitroaromatics. 4-Methoxy-4'-nitrobiphenyl can serve as an example.



INDO calculations of charge densities for the radical ions and the neutral molecules of the systems under study support this mechanism.

PHOTOSUBSTITUTION REACTIONS OF AROMATIC CATIONS AND ANIONS

Some of the reactions discussed in the previous sections involve the intermediate formation of aromatic cations, anions, or radical ions. Because of the limited scope of this contribution, additional examples will not be discussed here. However, these reactions will be treated in detail in a separate chapter in a monograph on aromatic photosubstitutions (66).

ELECTRON-TRANSFER ASSISTED PHOTOREDUCTIONS AND PHOTODEHALOGENATIONS

An example of such a reaction is the photodebromination of bromoquinolines and

4-bromoisoquinoline discussed above (64). Because of their special features, these reactions can be treated as a separate group. They have been extensively reviewed (67,68).

CONCLUSION

The present contribution is a review of the knowledge in the field of aromatic photosubstitutions at this time, from the mechanistic and theoretical point of view. It can be seen that, although the results of quantum-chemical calculations have been successfully used in some cases to interpret or to support a reaction mechanism, there are many other cases where such attempts have been unsuccessful or unconvincing. Much more theoretical work is needed in this area to provide a solid theoretical base for mechanistic studies.

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