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PHOTOREACTIONS OF AROMATIC COMPOUNDS—XXXV[1]

NUCLEOPHILIC PHOTOSUBSTITUTION OF METHOXY SUBSTITUTED AROMATIC COMPOUNDS. MONOPHOTONIC IONIZATION OF THE TRIPLET

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Abstract—Methoxy groups exert an activating and ortho/para directing influence in light induced nucleophilic substitution reactions (cyanation, hydroxylation, etc) of aromatic compounds in aqueous media. The first chemical step in these processes is monophotonic ionization of the aromatic compound in its lowest triplet state, followed by reaction of the radical cation with the nucleophile. Quantum yields of photocyanation of 4-fluoro- and 4-chloroanisole indicate that in 99% (mole fraction) water virtually all triplets formed undergo electron ejection.

This hypothesis is in agreement with the results of charge density calculations for the radical cations. It is directly supported by the similarity of the product composition of these photochemical substitutions with that of anodic substitutions, where the intermediacy of an aromatic cation is generally accepted. The presence of an oxidizing agent (oxygen, or persulphate) is required only when a hydrogen is replaced. The nucleophilic photosubstitution at electron rich aromatic systems in solvents as water can therefore be classified as an $S_{R^{+}N}1(^3Ar^*)$ process.

Electron donating substituents such as the methoxy group appear to have an activating and ortho/para directing effect in nucleophilic aromatic photosubstitution.[1-4] Clearly, as with the nitro group, the effect is opposite to that expected for a ground state reaction.

Thermal $S_N2(Ar)$ reactions are usually not observed when a deactivating group as methoxy is present; moreover the deactivation is greater at the ortho and para positions. The smooth nucleophilic photosubstitution of the halogen in 2-chloro- and 2-bromo-4-nitroanisole relative to the low reactivity of meta halo-nitrobenzene was the first example suggesting an activating influence of the methoxy group.[5] Oxidative photocyanation of anisole has been reported by Nilsson[3] to give the cyanoanisoles, the isomer distribution being 53(o), 0.2(m), 47(p). Lok and Havinga[1] found that irradiation of 1,3,5-trimethoxybenzene in the presence of cyanide ion leads to 1-cyano-2,4,6-trimethoxybenzene with a fair quantum efficiency.

RESULTS

Table 1 presents the experimental conditions and results of irradiations of a number of substituted anisoles in the presence of various anions (CN^-, OH^-, OCH_3^- and OAc^-). Except in the case of 3-fluoroanisole in alkaline medium, substitution takes place at a position ortho or para with respect to a methoxy group. In 1,3-dimethoxybenzene substitution of a hydrogen atom by CN^-, ortho/para to methoxy, is preferred over replacement of the better leaving methoxy group at a meta position, which phenomenon has also been observed in 1,3,5-trimethoxybenzene.[1]

Irradiation of benzene ($\lambda = 254$ nm) in the presence of cyanide ion (0.10 M) in tert-butanol/water (1:3) results in two products: phenol (25.4%) and benzonitrile (3.2%). Under these conditions photosubstitution of anisole is much more efficient (see Table 1).

In nucleophilic photosubstitution of other aromatic ethers as methoxy-substituted naphthalenes and biphenyls (Tables 2 and 3) this ortho/para substitution pattern has been observed to be the rule.

In many cases an "α-effect"[2] plays an important role:† under aerobic conditions in the presence of CN^- 1-methoxynaphthalene gives photosubstitution of an α-hydrogen atom at C-4 (para) and not at C-2 (β, ortho), 2-methoxynaphthalene[6] shows photosubstitution of an α-hydrogen atom at C-1 (ortho) and not at C-3 (β, ortho) nor at C-4 (α, meta). In 2,3-dimethoxynaphthalene the hydrogen atom at C-1 (α, ortho/meta) instead of the better leaving group methoxy at a β position is replaced by cyanide ion (see Table 2). In the photoreaction of 2-methoxybiphenyl with cyanide ion the hydrogen atom at C-5 (para) is substituted instead of that at C-4 (α, but meta).

Under N_2, methoxy substitution appears to be the main reaction path for all these compounds and no substitution of hydrogen is observed. The role of oxygen and other oxidizing agents will be discussed below.

Irradiation (280 nm) of 4-fluoro- and 4-chloroanisole (5×10^{-4} M) in the presence of CN^- in tert-butanol/water mixture results in a very clean and efficient substitution of the halogen atom by CN^- (Fig. 1).

The fluorine atom, having a high ionization potential, does not change the nature of the excited states to a great extent.[7] In anisoles the p-fluoro substituent appears to be an excellent leaving group; 4-fluoroanisole has therefore been chosen as a model compound for kinetic studies.

Figure 2(a) gives the quantum yield dependence of photocyanation of 4-fluoroanisole on the cyanide ion concentration in a mixture of tert-butanol and water (1:3). In this solvent the quantum yield reaches an upper limit of 0.50 at $(CN^-) = 5 \times 10^{-2}$ M. Figure 2(b) shows the relationship between $1/\phi$ and $1/(CN^-)$: $\phi^{-1} = 2.07 + 0.0123(CN^-)^{-1}$; the linear dependence demonstrates second order kinetics. Photocyanation of 4-chloroanisole follows the same kinetic scheme: $\phi^{-1} = 1.85 + 0.0125(CN^-)^{-1}$; the upper limit of the quantum yield in tert-butanol/water (1:3) is 0.55.

The quantum yield of formation of 4-cyanoanisole from

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†The term "α-effect" refers to preference for nucleophilic photosubstitution on position 1 in naphthalene and azulene, positions 2 and 4 in biphenyl, and position 9 in phenanthrene.

Table 1. Nucleophilic photosubstitution of anisole and some derivatives:[a] $X\text{–}Ar\text{–}OCH_3 + Y^- \rightarrow Y\text{–}Ar\text{–}OCH_3 + X^-$

X	[substrate] mmole/l	Y^-	(Y^-) mole/l	time of irrdn. (h)	% conversion starting material	product (yield %) [b]
H [c]	3.32	CN$^-$	0.10	1	67.8	2-CN-anisole (24.7) 4-CN-anisole (24.7) 2,4-diCN-anisole (10.5) 2,6-diCN-anisole (3.2)
2-OCH$_3$ [d]	1.56	CN$^-$	0.05	3	30.2	2-CN-anisole (73.2)
2-OCH$_3$ [d]	1.52	OH$^-$	0.10	3	30.5	2-OH-anisole (51.8)
3-OCH$_3$	1.45	CN$^-$	0.05	3	63.1	3-OCH$_3$-4-CN-anisole (40.4) 3-OCH$_3$-4,6-diCN-anisole (7.4)
4-OCH$_3$	1.46	CN$^-$	0.05	4.5	61.6	4-CN-anisole (22.2) 1,4-diCN-benzene (2.9)
4-OCH$_3$	1.45	OH$^-$	0.10	9.5	56.0	4-OH-anisole (13.9) 3-OH-4-OCH$_3$-anisole (traces)
2,3-diOCH$_3$	1.00	CN$^-$	0.05	1	31.7	2-CN-3-OCH$_3$-anisole (47.6) 2,4-diCN-3-OCH$_3$-anisole (5.5)
2,4-diOCH$_3$ [d]	1.00	CN$^-$	0.05	1	22.5	3-OCH$_3$-4-CN-anisole (34.3) 3-OCH$_3$-4,6-diCN-anisole (4.0)
3,5-diOCH$_3$ [c,e]	1.23	CN$^-$	0.05	1	54.4	3,5-diOCH$_3$-4-CN-anisole (20.2) 2,4-diCN-3,5-diOCH$_3$-anisole (27.6)
2-F [d]	5.11	CN$^-$	0.22	1	14.7	2-CN-anisole (57.6) 2-F-4-CN-anisole (2.5) 2-OH-anisole (traces)
3-F [c,d]	5.56	CN$^-$	0.19	1	18.4	3-F-4-CN-anisole (38.9) 2,4-diCN-3-F-anisole (12.7) 3-CN-anisole (traces)
3-F [d]	1.59	OH$^-$	0.17	4	33.3	3-OH-anisole (36.9)
4-F [f]	4.77	CN$^-$	0.13	1	44.7	4-CN-anisole (94.8) 4-OH-anisole (traces)
4-F [d]	5.78	OCH$_3^-$	0.12	4	21.6	4-OCH$_3$-anisole (64.2)
4-F [d]	5.69	OAc$^-$	0.09	6	30.8	4-acetoxyanisole (19.7)
2-Cl [d]	1.23	CN$^-$	0.08	0.5	81.0	2-CN-anisole (94.8)
4-Cl [d]	1.46	CN$^-$	0.05	0.5	90.0	4-CN-anisole (89.4) 1,4-diCN-benzene (2) 2,4-diCN-anisole (traces)
4-Cl	3.21	OH$^-$	0.13	2.25	81.9	4-OH-anisole (87.8) anisole (4.3)
4-Cl [d]	2.24	OCH$_3^-$	0.10	0.5	91.7	4-OCH$_3$-anisole (46.0) anisole (51.8)
4-Br [d]	3.51	CN$^-$	0.18	4	34.8	4-CN-anisole (29.3) anisole (9.6)
4-I [f]	2.56	CN$^-$	0.14	4	49.2	4-CN-anisole (34.1) anisole (35.3)

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[a] Irradiations were carried out in tert-butanol/water (1:3, 350 ml) with a Hanau TQ 81 high pressure Hg lamp. [b] Yields are based on amount of consumed starting material. [c] In combination with ammonium persulfate. [d] Filter: 1 cm of a solution of 2,7-dimethyl-3,6-diazacycloheptadiene-1,7-perchlorate in water (100 mg/l). [e] Conditions as in Ref. 2. [f] Filter: 1 cm of tetrahydrofuran.

Table 2. Nucleophilic photosubstitution of some methoxynaphthalenes[a]

naphthalene derivative	[substrate] mmole/l	nucleophile	(nucleophile) mole/l	time of irrdn. (h)	% conversion starting material	product naphthalene derivative (yield %)
1-OCH_3 [c]	1.27	CN^-	0.08	24 [d]	83	1-CN (23) [b] 1-CN-4-OCH_3 (11)
1-OCH_3 [e]	1.27	OCH_3^-	0.40	15 [d]	72	1,4-diOCH_3 (6)
2-OCH_3	1.27	CN^-	0.08	24 [f]	41.5	1-CN-2-OCH_3 (24) 2-CN (1)
1,3-diOCH_3	0.85	CN^-	0.09	6 [d]	37.5	1-CN-2,4-diOCH_3 (33)
1,4-diOCH_3	0.32	CN^-	0.06	7.5 [g]	80	1-CN-4-OCH_3 (36) 1,4-diOCH_3,CN (tr.) 1,4-diOCH_3,diCN (tr.)
1,7-diOCH_3	0.80	CN^-	0.09	4 [d]	66	1-CN-4,6-diOCH_3 (7) 1-CN-2,8-diOCH_3 (8) 1-CN-7-OCH_3 (5)
2,3-diOCH_3 [c]	1.06	CN^-	0.09	6 [g]	66	2-CN-3-OCH_3 (19) 1-CN-2,3-diOCH_3 (9)
2,3-diOCH_3	1.43	CN^-	0.07	7 [d]	9.5	1-CN-2,3-diOCH_3 (71)
2,7-diOCH_3	1.06	CN^-	0.09	9 [g]	46	1-CN-2,7-diOCH_3 (74)

[a] Irradiations were carried out in tert-butanol/water (1:3; 350 ml). [b] Yields are based on amount of consumed starting material. [c] Solution saturated with nitrogen. [d] Rayonet Photochemical Reactor RPR 208, 3000 A. [e] In methanol. [f] Rayonet Photochemical Reactor RPR 208, 2537 A. [g] Hanau TQ 81 high pressure Hg lamp.

Table 3. Nucleophilic photosubstitution of methoxybiphenyls with cyanide[a]

biphenyl derivative	[substrate] mmole/l	time of irrdn. (h)	% conversion starting material	product (yield %) [b,c]
2-OCH_3	0.98	12	43	2-CN-biphenyl (31) 2-OCH_3-5-CN-biphenyl (8)
4-OCH_3	0.84	6	41	4-CN-biphenyl (41) 4,4'-diCN-biphenyl (17) 4-CN-4'-OCH_3-biphenyl (11) [d]
4,4'-diOCH_3	0.75	17	24	4-CN-4'-OCH_3-biphenyl (28) 4,4'-diCN-biphenyl (15)

[a] Irradiations were carried out in tert-butanol/water (1:3, 350 ml) in the presence of CN (0.1 mole/l) in a Rayonet Photochemical Reactor RPR 208, 2537 A. [b] Yields are based on amount of consumed starting material. [c] Products were identified by means of IR-, NMR- and mass-spectrometry. [d] In the presence of $(NH_4)_2S_2O_8$ 4-cyano-4'-methoxybiphenyl is the major product of the reaction.

4-fluoro- and 4-chloroanisole does not depend on the intensity of the exciting radiation. In aqueous medium photosubstitution reactions of these anisoles thus proceed via a one-photon process.

4-Fluoro- and 4-chloroanisole also react with water (substitution of halogen) upon irradiation. In the absence of cyanide ion the quantum yield of photohydrolysis is 0.5, i.e. the same as the maximum quantum yield of photocyanation under these conditions (tert-butanol/water, 1:3; $\lambda = 280$ nm). The quantum yield of photohydrolysis becomes negligible in aqueous solutions if the cyanide ion concentration exceeds 10^{-1} M.

At $(CN^-) = 10^{-2}$ M the quantum yield of photocyanation of 4-fluoroanisole is 0.3 and no fluorescence quenching by CN^- can be observed. If the first excited singlet were the reactive state, the intensity of fluorescence would reach only 40% of the maximum value under these circumstances. It is very likely then that the triplet state is an intermediate in the photosubstitution.

Photosubstitution of anisole and haloanisoles can be sensitized by acetone ($E_T = 82$ kcal/mole[8]). The triplet energies of the haloanisoles will not differ much from that of anisole ($E_T = 80.8$ kcal/mole[9]). This high value limits the choice of sensitizers and no others than acetone have been found effective.

The photocyanation of 4-fluoro(chloro)anisole can be

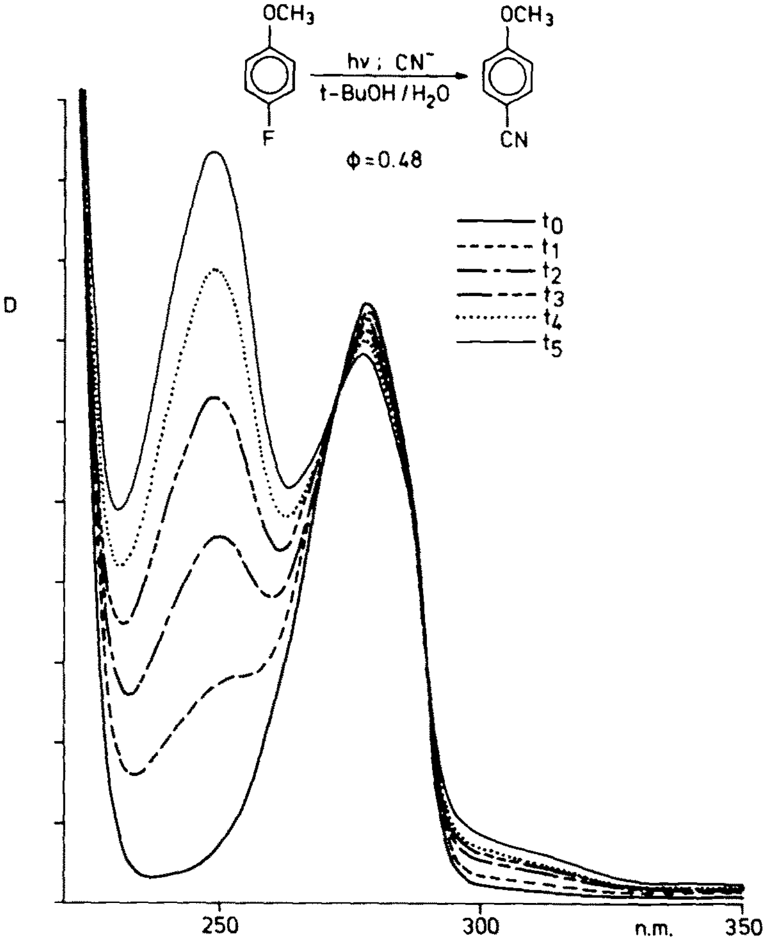

Fig. 1.

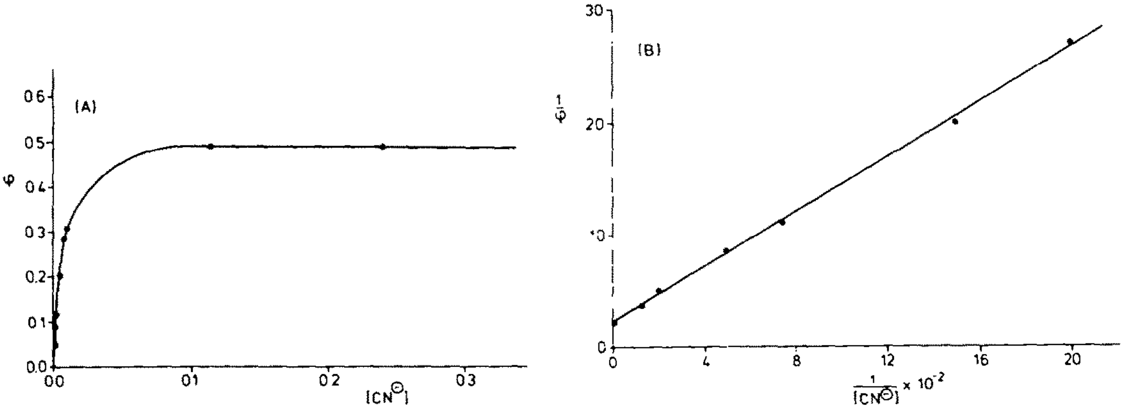

Fig. 2. Quantum yield dependence of photocyanation of 4-fluoroanisole on cyanide ion concentration in tert-butanol/water (1:3).

quenched by trans-1,3-pentadiene ($E_T = 59$ kcal/mole[10]) (see Fig. 3(a)). At $(CN^-) = 10^{-2}$ M a linear dependence exists between the quencher concentration (up to 4×10^{-2} M) and $1/\phi$. At higher piperylene concentrations quenching becomes more efficient. Apparently more than one excited state is quenched in this region.

Figure 3(b) shows the relative intensity of fluorescence vs the concentration of piperylene. At piperylene concentrations up to 4×10^{-2} M the fluorescence is not quenched; at higher concentrations, however, the intensity of fluorescence decreases. It can be concluded that singlet excited states of anisole are not quenched at piperylene concentrations below 4×10^{-2} M. Fluorescence quenching starts at the concentration where the deviation of the linear Stern–Volmer plot begins. The result of the fluorescence, quenching and sensitization experiments show that these photosubstitution reactions proceed via the first excited triplet state. The photosubstitution of

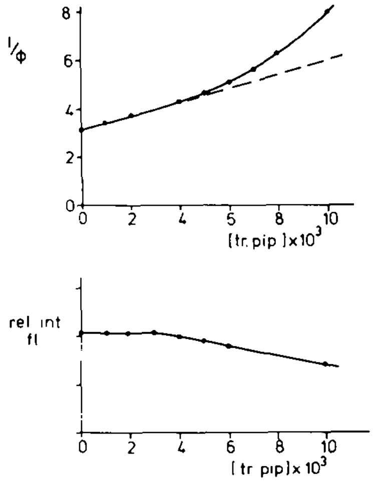

Fig. 3. (a) Stern–Volmer plot: quenching of photocyanation of 4-fluoroanisole by trans-1,3-pentadiene in tert-butanol/water (1:3), $(CN^-) = 10^{-2}$ M. (b) Dependence of the relative intensity of fluorescence of 4-fluoroanisole on the quencher concentration in tert-butanol/water (1:3), $(CN^-) = 10^{-2}$ M.

haloanilines has also been reported to be a triplet reaction.[11] In the naphthalene series the photocyanation of 1,7- and 2,7-dimethoxy derivatives can be sensitized by triphenylene and benzophenone.

In a mixture of tert-butanol and water (1:3) the order of reactivity in photosubstitution of halogen by cyanide ion in 4-haloanisoles is: F = Cl > Br > I (φ: 0.50, 0.55, 0.02, 0.01). This order, which correlates with heterolytic fission of the C–X bond, has also been found in the haloanilines.[11]

In media less polar than water and able to supply hydrogen atoms (e.g. alkanes and alcohols with α-hydrogen) haloanisoles are mostly reduced to anisole via homolytic fission of the C–X bond[12-15] in the triplet state.[16] At high substrate concentrations biphenyl derivatives are formed via radical coupling.[17-19] We have found that photoreduction of haloanisoles can be quenched by trans-piperylene. In CH_3OH with OCH_3^- irradiation of 4-chloroanisole results in both reduction and substitution with equal efficiency (see Table 1); in polar aqueous media photoreduction of haloanisoles is suppressed. Fluoroanisoles cannot be photoreduced since their triplet state energies are not sufficiently high to permit fission of the strong C–F bond.[20]

Under aerobic conditions irradiation of methanolic solutions of anisole in the presence of sodium cyanide results in substitution of hydrogen at C-2 and C-4.[3] In nitrogen atmosphere, however, methoxy instead of hydrogen is substituted, albeit with poor efficiency.[21]

Generally we found the presence of an oxidizing agent to be essential for substitution of hydrogen: 1,3-dimethoxy- and 1,3,5-trimethoxybenzene do not give photosubstitution of a hydrogen atom under nitrogen atmosphere. In photoreactions of methoxynaphthalenes, substitution of a hydrogen atom is suppressed if no oxidizing agent is present (see Table 2).

$(NH_4)_2S_2O_8$ and N_2O were found to be efficient oxidizing agents in photocyanation of anisole and meta substituted derivatives (Table 1) and also of benzene. Since these reactions are carried out in aqueous media, $(NH_4)_2S_2O_8$ is preferable over oxygen because of its higher solubility.[22]

In reactions where substituents like halogen or methoxy are displaced, oxygen, N_2O or $(NH_4)_2S_2O_8$ do not influence the efficiency of the photoreaction.

In the presence of an oxidizing agent the photocyanation of anisole results in four products (see Table 1). Calculations of the quantum yield via UV-spectroscopic analysis of the reaction mixture[23] proved to be impossible since the spectra of the products largely overlap. Estimation of the quantum yield, based on times of irradiation and amounts of products isolated, indicates that in the presence of 10^{-2} M $(NH_4)_2S_2O_8$ photocyanation of anisole (and of 1,3-dimethoxybenzene) proceeds as efficiently as that of 4-fluoroanisole (φ = 0.7).

The quantum efficiency of nucleophilic photosubstitution reactions of anisole derivatives is highly dependent of the tert. butanol/water ratio (see Fig. 4). In 0.17 M cyanide solutions the quantum yield of photocyanation of 4-fluoroanisole increases from 0.01 to 0.69 on going from 64% to 99% (mole fraction) water. At high cyanide ion concentrations in a medium with a given tert-butanol/water ratio the quantum yield reaches a maximum. Since the value of this maximum depends on the alcohol/water ratio, the solvent dependence of the quantum yield is not caused by the viscosity of the medium, but most probably by the polarity.

A possible explanation for the activating influence of the methoxy group and for the quantum yield dependence on solvent polarity could be based on a reaction path in which photoionization gives rise to a radical cation that undergoes reaction with the nucleophile. This assumption can be checked by comparing the results of the photoreactions with those of anodic oxidation. Anodic cyanation of anisole was first described by Koyama *et al.*[24] It has the advantage of producing compounds with higher oxidation potentials than anisole itself. Dimethoxybenzenes were cyanated via anodic oxidation by Andreades.[25] Other nucleophiles (like CH_3O^-,[26] CH_3COOH,[27] CF_3COO^-,[28] CH_3CN[29]) and H_2O, OH^- (see Table 4) can also be used in anodic substitution reactions. Although substitution is accomplished at potentials higher than the oxidation potential of the nucleophile, anodic substitution is generally rationalized as an attack of the nucleophile at the aromatic cation.

Table 4 gives the results of anodic and photochemical cyanation in tert-butanol/water (1:3) of the three isomeric fluoroanisoles.

In all cases, as with anisole[3] and the dimethoxyben-

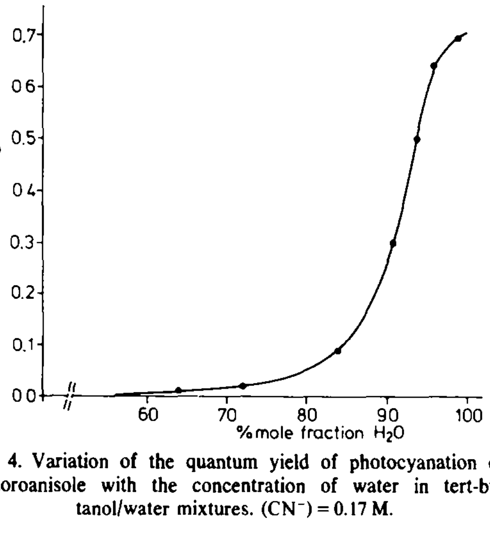

Fig. 4. Variation of the quantum yield of photocyanation of 4-fluoroanisole with the concentration of water in tert-butanol/water mixtures. $(CN^-) = 0.17$ M.

Table 4. Nucleophilic substitution (anodic, 1.6 V or photochemical, 280 nm, 10^{-2} M $(NH_4)_2S_2O_8$) of fluoroanisoles

anisole derivative	nucleophile	product
2-fluoro	CN^-	2-CN-anisole (65.5 %) 2-F-4-CN-anisole (34.5 %)
3-fluoro	CN^-	3-F-4-CN-anisole
4-fluoro	CN^-	4-CN-anisole 2-CN-4-F-anisole (tr.)
4-fluoro	H_2O	4-OH-anisole

zenes (see Table 5), products and product ratios are equal for both techniques. Anodic oxidation of 4-fluoroanisole in the absence of cyanide yields 4-hydroxyanisole, as does the photoreaction under these conditions. Photohydrolysis, with quantum yields up to 0.7 in alkaline media, and anodic substitution are excellent ways of producing phenols with electron-donating substituents.

Electrolysis at the cathode of aqueous solutions of fluoroanisoles did not lead to product formation.

Table 5. Cyanation (anodic[25] or photochemical) of methoxybenzenes

benzene derivative	product
1,2-diOCH_3	1-OCH_3-2-CN-benzene
1,3-diOCH_3	1,3-diOCH_3-4-CN-benzene
1,4-diOCH_3	1-OCH_3-4-CN-benzene
1,2,3-triOCH_3	1,3-diOCH_3-2-CN-benzene

DISCUSSION

The experimental data leave little doubt that the nucleophilic photosubstitutions considered generally proceed via the lowest triplet of the aromatic compound as the chemically reacting species. The at first sight anomalous activation of a nucleophilic substitution by methoxy- and other electron donating groups looses its paradoxical character if one assumes that the initial chemical step consists of the loss of an electron from the triplet, yielding the radical cation of the aromatic compound (Fig. 5).

A flash photolysis survey of Grossweiner and Joschek[30] of a great number of aromatic compounds in aqueous solution showed that generation of solvated electrons is correlated with low gas phase ionization potential, negative Hammett σ_p constants and low reactivity of the parent molecule towards e^-_{aq}. Although photoionization in rigid media is known to proceed via formation of the triplet state in a two-photon process,[31] Grossweiner and coworkers[32] stated that the same mechanism need not apply to aqueous solutions. Since the quantum yield of photosubstitution is not dependent on the intensity of the exciting radiation, ionization of these triplet molecules must be a one-photon process in aqueous media.

The quantum yields of substitution of 4-fluoro- and 4-chloroanisole have a maximum value of 0.70 and 0.80, respectively. The quantum yield of intersystem crossing is about 0.75 (for anisole $\phi_{isc} = 0.74$[9]). This indicates that nearly every triplet molecule that is formed leads to substitution product.

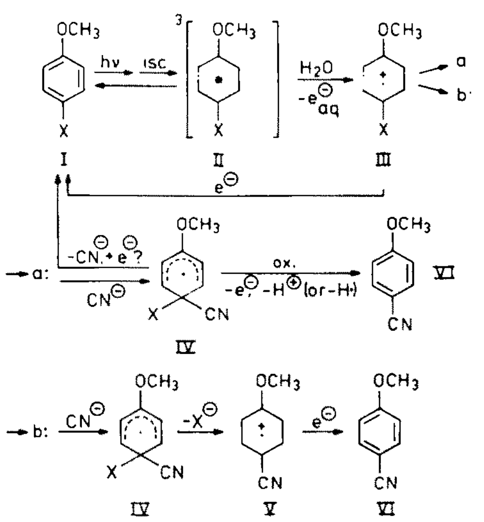

Fig. 5. Mechanism of nucleophilic photosubstitution of anisoles in aqueous media. **a**: X = hydrogen; **b**: X = OCH_3 or halogen.

Figure 4 might be interpreted in terms of insufficient solvation of the radical cation and the electron, causing inefficient ionization in solutions containing less than 99% water.

Strong support for the scheme of Fig. 5 is found in the similarity of the product composition of the photoinduced and the anodic aromatic substitution (Tables 4 and 5). In the cases where calculations have been made (Fig. 7) the reaction is seen to consistently occur at the positions of highest positive charge in the radical cation.

The presentation given in Fig. 5 also accounts for the curious phenomenon that at higher concentrations of para chloroanisole (10^{-3} M) the quantum yield becomes higher than 1 (1.2). The maximum quantum yield (0.80) for the photocyanation of 4-chloroanisole is independent of the aromate concentration as long as this remains below 10^{-4} M. This can be understood on the basis of an electron transfer from 4-chloroanisole to the 4-cyanoanisole cation to form substitution product and new 4-chloroanisole cation (Fig. 6).

An alternative pathway that a priori cannot be ruled out in the case of a good leaving group is that of an $S_N1(Ar^+)$ process, i.e. a primary dissociation of the aromatic compound to form the aromatic σ-cation. However, this mechanism does not appear to be likely for the reactions under consideration since aromatic σ-cations are considered to react rather indiscriminately with various nucleophiles.[33] With the methoxybenzenes we found a strong preference for the reaction with cyanide ion over that with water. In photosubstitution of 4-fluoroanisole cyanide ion is $\sim 5 \times 10^3$ times as reactive as water, indicating a reaction of these nucleophiles with a more stable cation.[34] Moreover the observed order of reactivity of the haloanisoles does not correspond with expectation for an ionic (photo)dissociation. The low reactivity of bromo- and iodoanisole may be due to the short lifetime

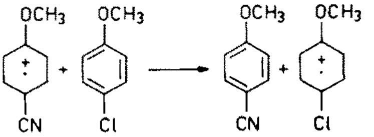

Fig. 6.

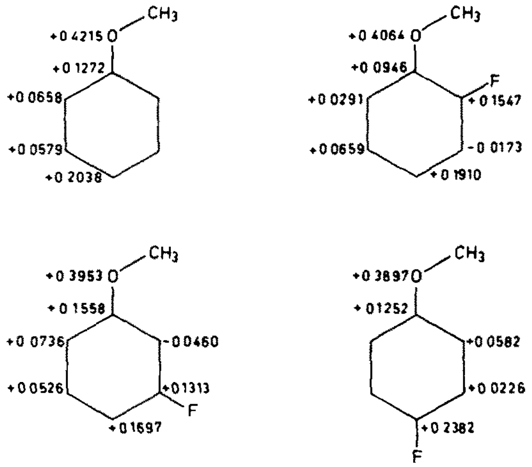

Fig. 7. Charge distribution in the radical cations of anisole and the fluoroanisoles.

of the triplet molecules as a consequence of increased intersystem crossing to the ground state. In addition the smaller inductive effect of these halogen atoms causes inefficient formation of a sigma complex with the nucleophile.

In reactions where hydrogen is substituted, an oxidizing agent is necessary. Departure of hydrogen as hydride ion is very improbable. A more attractive possibility is electron transfer from the neutral complex (IV) to the oxidizing agent ($S_2O_8^{2-}$, O_2 or N_2O) followed by loss of a proton. Recently Mizuno *et al.*[35] showed that 1,4-dicyanobenzene acts as an electron acceptor in the photocyanation of phenanthrene and naphthalene.

In electrochemical cyanation the anode acts as an electron acceptor: polarographic studies[36,37] have demonstrated that anodic substitution of aromatic hydrogen is an ECE process involving the radical cation as an intermediate. An alternative route leading from the complex (IV) to the product (VI) would be abstraction of a hydrogen atom by the oxidizing agent.

Considering all evidence available we may classify the nucleophilic photosubstitution at aromatic carbon atoms activated by electron donating groups, occurring in strongly solvating media, as $S_{R^+N}1(^3Ar^*)$ reactions. The reactions form a counterpart to the light induced nucleophilic aromatic substitutions studied in particular by Bunnett and his coworkers.[38] In these $S_{RN}1(Ar)$ reactions, which we would now specify as $S_{R^-N}1(Ar)$ processes, there is a primary formation of an aromatic radical anion. This species via a series of steps, including a radical chain, reacts to form substitution product. What remains to be accomplished in order to definitely establish the proposed reaction mechanism is the direct proof of the occurrence of the radical cation as the primary intermediate. Investigations to this end using flash techniques are in progress and will be reported separately.

EXPERIMENTAL

All aromatic compounds were distilled or recrystallized before use. UV-spectra were measured with Cary 14 and 15 spectrophotometers. Preparative scale irradiations were carried out in 350 ml tert-butanol/water (1:3) with a TQ 81 Hanau high pressure Hg lamp, in combination with an appropriate filter (Table 1). During the reaction the solution was stirred magnetically and kept at room temperature. After completion of the reaction the solution was saturated with NaCl, the layers were separated and the aqueous layer extracted with diethylether. Yields of volatile products were determined by gas–liquid chromatography on SE-30 and Carbowax (Chromosorb) columns. The combined butanol ether layers were dried over anhydrous $MgSO_4$, filtrated and evaporated. The residue was separated chromatographically on silica gel (eluent: $CHCl_3$–hexane). All products were identified by IR-, NMR- and Mass spectroscopy. Relative quantum yields of fluorescence were measured with a Perkin-Elmer MPF-2A spectrofluorimeter.

Quantum yields of photosubstitution reactions were measured by De Jongh's[23] method (actinometer: $K_3Fe(C_2O_4)_3$) with a Carl Zeiss PMQ II spectrophotometer. The light source was a Philips HP 125 Hg lamp in combination with a Bausch and Lomb High Intensity Monochromator.

Sensitization of 4-fluoroanisole. A solution of 150 mg (1.04 mmole/l) of the aromate, 8.5 g KCN (0.12 mole/l) and 200 ml acetone (2.09 mole/l) in 900 ml tert-butanol/water (1:3) was irradiated with a Hanau TQ 81 high pressure Hg lamp in combination with 3 cm tetrahydrofuran filter (95% of the incident radiation at 280 nm was absorbed by acetone). After 25 min 68% (102 mg) 4-fluoroanisole had been consumed and 57.3% (81 mg) 4-cyanoanisole was isolated.

Quantum yields at 280 nm of photocyanation of 4-fluoroanisole and 4-chloroanisole at various nucleophile concentrations in tert-butanol/water (1:3): *4-fluoroanisole*: (CN^-): 1.15×10^{-1}, 1.00×10^{-2}, 7.50×10^{-3}, 5.00×10^{-3}, 1.33×10^{-3}, 6.67×10^{-4}, 5.00×10^{-4} M; ϕ: 0.50, 0.31, 0.28, 0.12, 0.09, 0.05, 0.04. *4-Chloroanisole*: (CN^-): 5.00×10^{-2}, 1.80×10^{-2}, 9.00×10^{-3}, 4.50×10^{-3}, 1.80×10^{-3} M; ϕ: 0.55, 0.40, 0.29, 0.21, 0.12.

Correlation coefficients of $\phi^{-1} = a + b(CN^-)^{-1}$ were 0.999 and 0.997 for 4-fluoro- and 4-chloroanisole respectively.

Anodic oxidations were carried out in 100 ml stirred tert-butanol/water (1:3) solutions with platinum electrodes (reference: saturated calomel electrode). Electrolysis mixtures were worked up as described for irradiations.

Charge densities in the radical cations were obtained by means of semi empirical PPP–MO calculations.

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REFERENCES

[1] Part XXXIV: C. M. Lok and E. Havinga, *Proceedings Kon. Ned. Akad. Wetensch. B.* **77**, 15 (1974).
[2] J. Cornelisse and E. Havinga, *Chem. Rev.* **75**, 353 (1975).
[3] S. Nilsson, Thesis, Lund (1974); S. Nilsson, *Acta Chem. Scand.* **27**, 329 (1973).
[4] A. V. El'tsov, O. V. Kul'bitskaya and A. N. Frolov, *J. Org. Chem. USSR* **8**, 78 (1972).
[5] D. F. Nijhoff, Thesis, Leiden (1967).
[6] R. L. Letsinger, quoted in *Eléments de Photochimie Avancée* (Edited by P. Courtot), p. 343. Hermann, Paris (1972).
[7] J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules*, p. 221. Wiley, New York (1963); W. West, *Chemical Applications of Spectroscopy*, Chap. VI. Interscience, New York (1956).
[8] M. W. Schmidt, and E. K. C. Lee, *J. Am. Chem. Soc.* **92**, 3579 (1970).
[9] S. L. Murov, *Handbook of Photochemistry*, p. 34. Dekker, New York (1973).
[10] R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.* **87**, 4230 (1965).
[11] A. N. Frolov, O. V. Kul'bitskaya and A. V. El'tsov, *J. Org. Chem. USSR* **9**, 2335 (1973).
[12] J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Letters* 1267 (1969).
[13] N. Kharasch, R. K. Sharma and H. B. Lewis, *Chem. Comm.* 418 (1966).

[14] R. K. Sharma and N. Kharasch, *Angew. Chem.* **80**, 69 (1968).

[15] R. J. Mayer and J. P. Simmons, *Adv. Photochem.* **2**, 137 (1964).

[16] L. O. Ruzo and N. J. Bunce, *Tetrahedron Letters* 511 (1975).

[17] T. Matsuura and K. Omura, *Bull. Chem. Soc. Japan* **39**, 944 (1966).

[18] K. Omura and T. Matsuura, *Chem. Comm.* 1394 (1969).

[19] K. Omura and T. Matsuura, *Tetrahedron* **27**, 3101 (1971).

[20] P. Smith, *J. Chem. Phys.* **29**, 681 (1958).

[21] J. A. Barltrop, N. J. Bunce and A. Thomson, *J. Chem. Soc.* (*C*) 1142 (1967).

[22] L. W. Winkler, *Ber.* **24**, 3609 (1891).

[23] R. O. de Jongh, Thesis, Leiden (1965).

[24] K. Koyama, T. Susuki and S. Tsusumi, *Tetrahedron Letters* 627 (1965).

[25] S. Andreades and E. W. Zahnow, *J. Am. Chem. Soc.* **91**, 4181 (1969).

[26] N. L. Weinberg and B. Belleau, *Tetrahedron* **29**, 279 (1973).

[27] L. Eberson and K. Nyberg, *J. Am. Chem. Soc.* **88**, 1686 (1966).

[28] Z. Blum, L. Cedheim and K. Nyberg, *Acta Chem. Scand. B* **29**, 715 (1975).

[29] L. Eberson and K. Nyberg, *Tetrahedron Letters* 2389 (1966).

[30] L. I. Grossweiner and H. I. Joschek, *Adv. in Chem. Ser. No.* 50, *Am. Chem. Soc.* 279 (1965).

[31] J. Joussot-Dubien and R. Lescleaux, *Compt. Rend.* **258**, 4260 (1964); K. D. Cadogen and A. C. Albrecht, *J. Chem. Phys.* **43**, 2550 (1965).

[32] G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.* **61**, 708 (1965).

[33] E. S. Lewis, *J. Am. Chem. Soc.* **80**, 1371 (1958).

[34] C. D. Ritchie, *Acc. Chem. Res.* **5**, 348 (1972).

[35] K. Mizuno, H. Okamoto, C. Pac and H. Sakurai, *Chem. Comm.* 839 (1975).

[36] H. Lund, *Acta Chem. Scand.* **11**, 1323 (1957).

[37] G. Manning, V. D. Parker and R. N. Adams, *J. Am. Chem. Soc.* **71**, 4584 (1969).

[38] J. K. Kim and J. F. Bunnett, *Ibid.* **92**, 7463 (1970).