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Further Evidence for the Triplet Mechanism in the Photosubstitution of Nitroaryl Ethers in Alkaline Medium.

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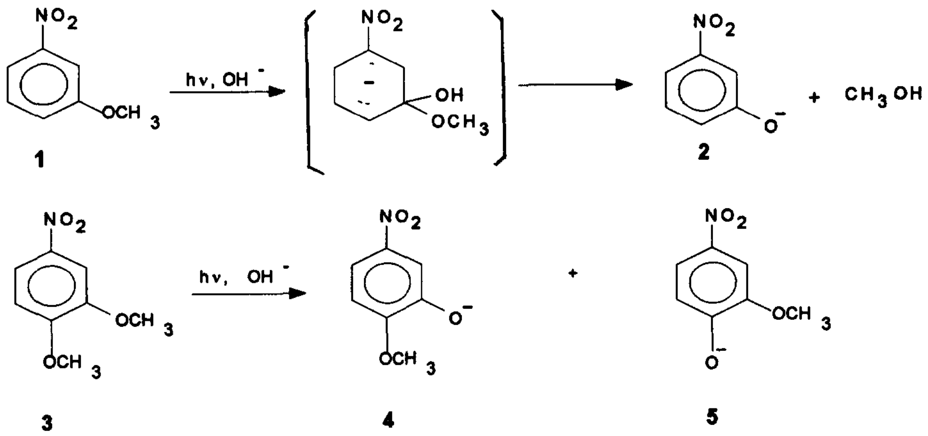
Abstract Mechanistic studies show that nitroaryl ethers (3-nitroanisole, 3-nitrophenetole, n-butyl 3-nitrophenyl ether, 2-chloro-5-nitroanisole, 2-bromo-5-nitroanisole and 3,5-dinitro anisole) undergo nucleophilic aromatic photosubstitution with hydroxide ions through an $S_N2^3Ar^*$ mechanism An investigation of the quenching of excited states of nitroaryl ethers by bromide and thiosulfate ions in aqueous solutions is reported and lends support to the proposed $S_N2^3Ar^*$ mechanism

INTRODUCTION

Nucleophilic aromatic photosubstitution has been extensively studied since its discovery in 1956[1,2] and it has been suggested that there are three possible pathways leading to nucleophilic aromatic photosubstitutions 1) direct displacement (S_N2Ar^*), 2) electron transfer from the nucleophile to the excited aromatic substrate ($S_{R^-N}1Ar^*$), and 3) electron transfer from the excited aromatic to an appropriate electron acceptor, followed by attack of the nucleophile on the resultant aromatic radical-cation ($S_{R^+N}1Ar^*$)

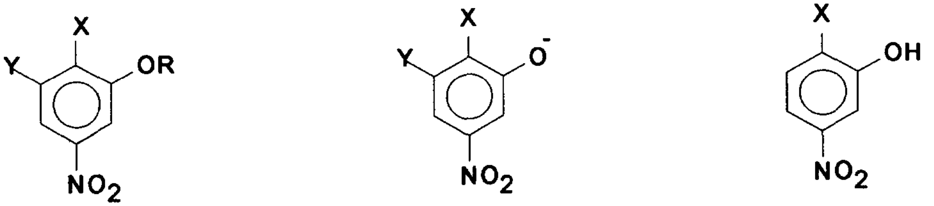
As more examples of photoinduced nucleophilic aromatic substitution accumulate, the effect of substituents on the regioselectivity has attracted great interest [3] Among the substituents, the nitro group is probably the most extensively studied because of its meta-directing effect For instance (Scheme 1), the irradiation of 3-nitroanisole,**1**, in alkaline media leads clearly to the 3-nitrophenoxide ion,**2**, [4,5] while irradiation of 3,4-dimethoxynitrobenzene,**3**, under similar conditions gives predominantly the 2-methoxy-5-nitrophenoxide ion,**4**, with only traces (ratio of 370 1)[2] of the 1-methoxy-5-nitrophenoxide ion,**5**. At room temperature, compound **1** is inert towards OH^-, while thermal hydrolysis of **3** in alkaline medium affords **5** as the sole product From the kinetics of alkaline photohydrolysis of 3-nitroanisole, **1**, it was concluded that

Scheme 1



this hydrolysis may be described as a quenching of the triplet excited state by hydroxide ion,[6] in which some of the encounters result in chemical reaction Addition of piperylene in concentrations ≥ 4×10^{-2}M completely quenches the photoreaction of **1** (2×10^{-4}M) with NaOH (10^{-2}M) [7] A study of the alkaline photohydrolysis of **1** in the presence of ^{18}O-labelled OH^- showed that the attack and substitution indeed occur at the aromatic ring carbon of **1*** [5] Many other examples of nucleophilic aromatic photosubstitution reactions have been reported in recent years [8-20]

Scheme 2 Molecular structures of compounds used in this study



NArE

1 X =Y = H, R = CH_3
6 X = H, Y = NO_2 , R = CH_3
7 X = Y = H , R = Et
8 X = Y = H, R = n-Bu
9 X = Cl, Y = H, R = CH_3
10 X = Br, Y = H, R = CH_3
13 X = I, Y = H, R = CH_3

NArP

2 X = Y = H
11 X = Cl, Y = H
12 X = Br Y = H

NArPH

14 X = Cl
15 X = Br

Varma *et al*[11] have used laser flash photolysis to study the photohydrolysis of **1** and 3,5-dinitroanisole, **6**, proposing a general mechanistic scheme involving fast reaction between the nucleophile (hydroxide ion) and the nitroaryl ether triplet excited state which gives rise to a series of σ-complexes in the ground state We report here the photosubstitution of several derivatives of 3-nitroanisole (Scheme 2) with sodium hydroxide in aqueous solutions upon irradiation with some related studies of these systems in the presence of added salts to test the proposed S_N2Ar^* mechanism The results presented here point to a $S_N2^3Ar^*$ mechanism which rationalizes most of the available data for nucleophilic photosubstitution of nitroaromatic compounds [2,3,7-10]

RESULTS AND DISCUSSION

Laser flash study

Van Zeijl *et al* [11] determined a bimolecular rate constant of k_{OH} = 3 5x10^8 M^{-1}s^{-1} for quenching of **1** in the presence of OH$^-$ from the change in the decay constant of the initial laser-induced absorption in aqueous solutions In the case of aqueous solutions of **6** the results of continuous and flash irradiation experiments gave k_{OH} = 2 7x10^{9}M^{-1}s^{-1}

In order to obtain evidence for the nucleophilic photosubstitution of nitroaryl ethers, the transient spectrum of a solution of **1** (3x10^{-4} M) in H_2O (pH = 7 0) irradiated with a Nd-YAG laser (355 nm) was observed The spectrum for λ> 370 nm (Figure 1) is similar to the spectrum reported by Van Zeijl *et al*[11] and the transient species absorbing at 405 nm had a lifetime of ca 1650 ± 100 ns Under similar laser flash photolysis conditions, **6** in H_2O gave a transient with an absorption maximum at 435 nm and a lifetime of 1250 ns

When NaBr or $Na_2S_2O_3$ are added to the aqueous solutions of **1**, the triplet lifetimes are reduced (Table I), but the same transient spectra are observed As in the case of **1**, there is no detectable fluorescence or phosphorescence from **6** under any circumstances [8] The triplet state lifetimes of **6** in aqueous solutions in the presence of a quencher are given in Table I

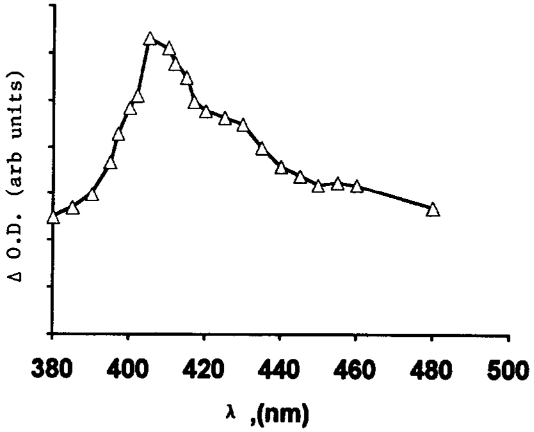


Figure 1 Transient absorption band of 3-NA in H_2O measured at Δt = 2 5μs after laser excitation at 355 nm

Table I Triplet lifetime of 3-nitroanisole (**1**) and 3,5-dinitroanisole (**6**) in aqueous solutions of NaBr ($[Q_1]$) and $Na_2S_2O_3$ ($[Q_2]$) as triplet quenchers

1 [3 0 x 10^{-4} M]

$[Q_1]$,mM	0 0	0 054	0 086	0 108	0 129	0 350	0 470
τ,ns	1580	1200	1090	1060	990	580	470

$[Q_2]$,mM	0 0	0 026	0 051	0 077	0 103	0 128	0 154	0 350	0 470	0 700
τ,ns	1700	1440	1270	1230	1040	890	860	490	425	270

6 [3 0 x 10^{-4} M]

$[Q_1]$,mM	0 0	0 026	0 040	0 075	0 100	0 110	0 145	0 310	0 420
τ,ns	1250	1070	970	820	730	700	620	350	280

$[Q_2]$,mM	0 0	0 010	0 028	0 058	0 082	0 105	0 132	0 232	0 322	0 385
τ,ns	1250	1170	1020	850	750	675	600	430	350	300

Similar triplet lifetimes are observed for transients at 435 nm (See Table IV) for 3-nitrophenetole (**7**), n-butyl 3-nitrophenylether (**8**), 2-chloro-5-nitroanisole (**9**) and 2-bromo-5-nitroanisole (**10**) in H_2O

If the reduction in the triplet lifetime is attributed to a bimolecular quenching reaction of the triplet state by Br^- or $S_2O_3^=$ ions, the following Stern-Volmer equation should apply

$$\tau^\circ / \tau = 1 + k_q \tau^\circ [Q] \qquad (1)$$

where τ and τ° are the triplet lifetimes for solutions in the presence and absence of quencher, respectively, k_q is the second-order rate constant for quenching and [Q] is the concentration of the quencher

Figure 2 shows the Stern-Volmer plots, which are linear and provide the constants $K'_{SV} = k_q\tau^\circ$ for quenching of 1^{3*} by Br^- and $S_2O_3^=$ ions of $K'_{SV}(Br) = 5000\ M^{-1}$ and $K'_{SV}(S_2O_3) = 7200\ M^{-1}$, respectively For the quenching of $(6)^{3*}$ by Br^- and $S_2O_3^=$ (Figure 3), the corresponding values are K'_{SV} (Br) = 7100 M^{-1} and K'_{SV} (S_2O_3) = 8100 M^{-1}

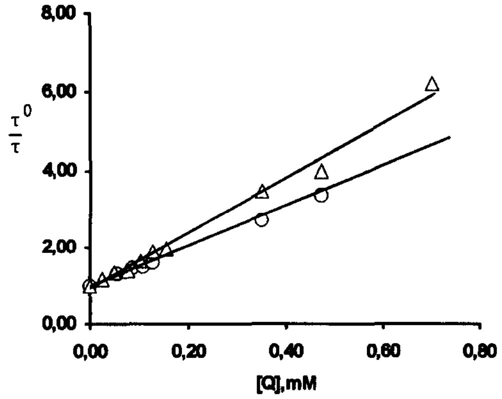


Figure 2 Plot of the triplet lifetime ratio of **1** vs quencher concentrations [Q] = bromide ion (O), thiosulfate ion (Δ) Data from Table I

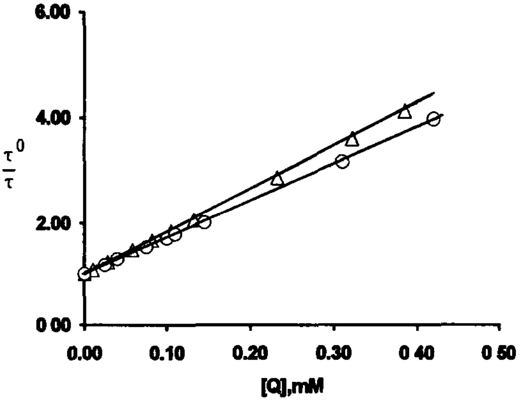


Figure 3 Plot of the triplet lifetime ratio of **6** vs quencher concentrations [Q] = bromide ion (O), thiosulfate ion (Δ) Data from Table I

Photochemical Studies

In agreement with literature reports,[1-7] we found no thermal reaction of nitroaryl ethers (NArE = **1**, **7**,**8**, **9** and **10**) with aqueous NaOH However, when irradiated, **2**, **11** and **12** ions (NArP) were formed as the only photoproducts Without added OH^-, the quantum yield Φ of photoreaction is less than 10^{-3} Overall quantum yields for the production of NArP were measured at 313 nm at different $[OH^-]$ concentrations The variation of the quantum yield of methoxy group substitution of **1** with $[OH^-]$ (Table II) is in agreement with results reported by De Jongh and Havinga[5]

Table II Overall quantum yields of production of arylphenolate ion in the photohydrolysis of nitroaryl ethers with hydroxide ion in water at different nucleophile concentrations

$[OH^-]$,mM	Φ_2	Φ_2	Φ_2	Φ_{11}	Φ_{12}
1 43	0 126	0 105	0 080	0 168	0 105
1 78	0 138	0 118	0 092	0 191	0 121
1 99	0 147	0 126	0 094	0 200	0 123
2 51	0 171	0 143	0 106	0 226	0 130
3 16	0 189	0 155	0 122	0 250	0 165
3 55	0 197	0 162	0 129	0 260	0 174
3 98	0 201	0 172	0 135	0 271	0 182
5 00	0 224	0 182	0 150	0 290	0 199
5 95	0 226	0 194	0 155	0 305	0 211
7 08	0 235	0 203	0 162	0 318	0 223
7 94	0 240	0 208	0 170	0 320	0 229
10 00	0 246	0 218	0 176	0 340	0 240

Table III - Overall quantum yields of production of arylphenolate ions in the photohydrolysis of nitroaryl ethers with hydroxide ion (0 01M) in water in the presence of different concentrations of sodium bromide or thiosulfate [Q]

[Q]mM	Φ_2	Φ_2	Φ_2	Φ_2	Φ_{11}	Φ_{12}
0	0 250	0 246	0 240	0 176	0 340	0 240
0 1	0 230		0 200			
0 2	0 215		0 186			
0 3	0 210		0 174			
0 4	0 188		0 163			
0 5	0 177		0 153	0 122		0 173
0 6	0 168		0 144			
0 7	0 160		0 137			
0 8	0 150		0 130			
1 0	0 138	0 112	0 118	0 091	0 180	0 134
1 5	0 112	0 088	0 096	0 073	0 148	0 110
2 0	0 100	0 072	0 078	0 061	0 125	0 092
2 5	0 079		0 075		0 105	0 080
3 0	0 075		0 058	0 048	0 095	0 071
3 5	0 063		0 057		0 084	0 083
4 0	0 058	0 042	0 048	0 038	0 076	0 057
5 0		0 035	0 044	0 032		
7 0			0 032	0 023		

a) Presence of [NaBr] b) Presence of [$Na_2S_2O_3$]

For **1**, **7** and **8**, the quantum yields for photohydrolysis increase markedly with increasing hydroxide ion concentration and reach values from 0 246 to 0 176 (10^{-2} M NaOH) The quantum yields at 313 nm for the formation of **11** and **12** ions in 0 01 M NaOH are 0 34 and 0 24, respectively The results for **10** are very similar to those for **1**

A remarkable feature shows up in the case of the photoreaction of **9**, the dependence of Φ on [OH^-] concentration being different from that with the other NArE investigated The quantum yield is 38% higher than that for photohydrolysis of **1** under the same conditions The photoproduct quantum yields for **9**, **10** and 2-iodo-5-nitroanisole (**13**) decrease in the order 0 34, 0 24 and <0 001, respectively, as the atomic number of the halogen substituent increases

The multiplicity of the reactive excited state was investigated using sodium bromide or thiosulfate as selective triplet quenchers (Table III) There is a significant quenching effect due to these ions which indicates the involvement of a triplet excited state These facts furnish evidence for a photochemical step involving a triplet state In Scheme 3 the route from NArE to NArP is divided into the formation of a σ-complex between NArE and OH^- and subsequent formation of the final product from the σ-complex In this Scheme , S_0 , S_1 and T are, respectively, the ground state, the first excited singlet state and the triplet state of NArE The intersystem crossing yield is denoted by Φ_{ISC}, a triplet-state quencher by Q As usual rate coefficients are denoted by k with an appropriate subscript The overall conversion efficiency from the σ-complex to NArP is indicated by β

$$S_0 \xrightarrow{h\nu} S_1 \xrightarrow{\Phi_{isc}} T$$

$$T \xrightarrow{1/\tau^\circ} S_0$$

$$T + OH^- \xrightarrow{k_{OH}[OH]} S_0$$

$$T + Q \xrightarrow{k_q'[Q]} S_0$$

$$T + OH \xrightarrow{k_r[OH\text{-}]} \sigma\text{-Complex}$$

$$\sigma\text{-Complex} \xrightarrow{k_d} S_0$$

$$\sigma\text{-Complex} \xrightarrow{k_p} NArP$$

Scheme 3 - Route from NArE to NArP

In the absence of quencher Q, this scheme predicts the following double reciprocal dependence of the photoproduct quantum yield (Φ) on the hydroxide ion concentration

$$1/\Phi = 1/\Phi\infty \{ 1 + 1/\ K_{SV} [OH^-] \} \quad (2)$$

where $\Phi\infty = \Phi isc\beta$, $\beta = kp/(kp + kd)$ and $K_{SV} = k_{OH}\ \tau^\circ$ Regression analysis of the dependence of Φ^{-1} upon $[OH^-]^{-1}$ for the photohydrolysis of **1** case, using the values of the Table II, gave the linear equation (r = 0 999),Φ^{-1} = (3 33 ± 0 005) + (0 0065 ± 0 0001) $[OH^-]^{-1}$, corresponding to a limiting quantum yield at high OH^-($\Phi\infty$) of 0 30 and a Stern-Volmer constant K_{SV} for quenching of aqueous excited **1** by $[OH^-]$ of 510 M^{-1} Since $K_{SV} = k_{OH}\,\tau^\circ$, calculation of k_{OH}, the second order rate constant for quenching of excited **1** by $[OH^-]$, using the triplet lifetime of **1** in nondeoxygenated aqueous solution (τ°=1600ns at 30°C) provides a value of 3 2 ± 0 2 x 10^8 M^{-1} s^{-1} Comparison of this value with that for quenching of the **1** triplet state by OH^- (k_{OH} = 3 5x10^8 $M^{-1}s^{-1}$)[11] clearly implies that the reactive state is the triplet state of **1**

Addition of 2% methanol decreases (≈10 %) the quantum yield of photohydrolysis of **1** in the presence of 10^{-2} M NaOH, an effect previously observed by other authors [2,11]Taking into consideration this influence of methanol on the photohydrolysis of **1**,[5] our results (Φ° = 0 25 and K_{SV} = 510 M^{-1}, 10^{-2} M NaOH) are in reasonable agreement with the values of Φ° = 0 22 and K_{SV} = 720 M^{-1} determined for the same reaction in aqueous 0 01 M NaOH containing 2% methanol

For the photoreactions of **7**, **8**, **9** and **10** , the values of Table II also gave good straight lines in accord with eqn 2 The corresponding Stern-Volmer constants (K_{SV}) and limiting quantum yields at high $[OH^-]$ ($\Phi\infty$) are given in Table IV

In the presence of bromide or thiosulfate ions as triplet quenchers for **1**, the quantum yields for production of the ion **2** are much lower, as shown in Table III From Scheme 3 one derives

$$\Phi = \{\Phi_\infty \; K_{SV}[OH^-]\} / \{1 + K_{SV}[OH^-] + K_{SV'}[Q]\} \qquad (3)$$

$$1/\Phi = 1/\Phi_\infty \{1 + 1/ K_{SV}[OH^-] + K_{SV'}[Q] / K_{SV}[OH^-]\} \qquad (4)$$

where $\Phi_\infty = \Phi_{isc}\,\beta$, $\beta = k_p/(k_p + k_d)$, $K_{SV} = K_{OH}\,\tau^\circ$ and $K_{SV}' = k_q'\,\tau^\circ$

If β is independent of $[OH^-]$ and [Q], eqn (4) predicts a linear dependence of $1/\Phi$ on $[Q]/[OH^-]$ at constant $[OH^-]$ Figures 4-6 show plots of the quantum yield data of Table III according to equation 4

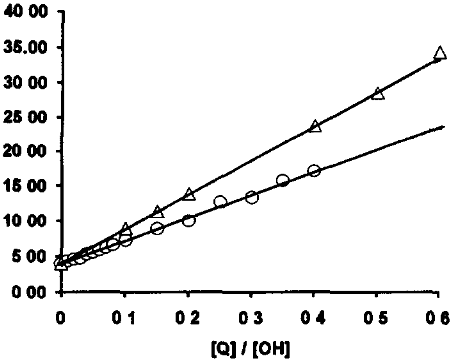


Figure 4 Plot of inverse quantum yield of photosubstitution of **1** vs relative (quencher/nucleophile) concentrations ([Q]/[OH]) [Q] = bromide ion (O), thiosulfate ion (Δ) Data from Table III

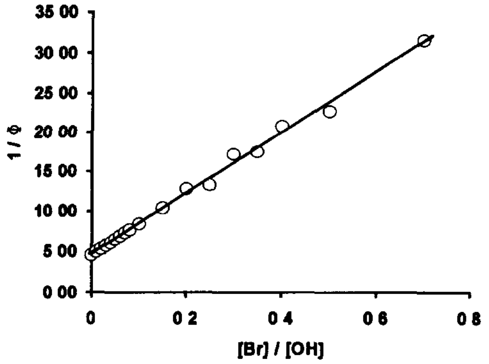


Figure 5 Plot of inverse quantum yield of photosubstitution of **7** vs relative quencher / nucleophile concentrations ([Br]/[OH]) Data from Table III

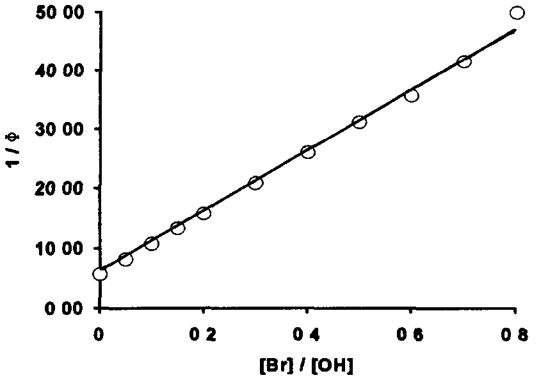


Figure 6 - Plot of inverse quantum yield of photosubstitution of **8** vs relative quencher / nucleophile concentrations ([Br]/[OH]) Data from Table III

Alkaline photohydrolysis of **1** , **7** and **8** in aqueous solutions produces the ion **2** and the corresponding alcohols The quantum yield (Φ^o) of **2** is not constant but depends on the length of the n-alkyl chain, varying from 0 25 (**1**) to 0 18 (**8**) Sodium thiosulfate is a more effective quencher of the triplet state of **1** than sodium bromide (Figure 4)

The photohydrolysis quantum yields of **9** and **10** in the presence of NaOH (10 mM) and NaBr (0 0 - 4 0 mM) also agree with eqn 4 (linear plots of 1/Q vs [Q]/[OH] This analysis of the quenching of these NArE leads to the Stern-Volmer constants (K_{SV}') and limiting quantum yields ($\Phi\infty$) summarized in Table IV

Table IV Quantum yields for photoreaction of NArE with hydroxide ion (10^{-2}M) in water in the presence of various concentrations of [Br $^-$] and [$S_2O_3^=$]

3-NArE	Φ^o [a]	Φ_∞ [b]	K_{SV}(OH) M^{-1} [a]	K_{SV}'(Br) M^{-1}	Ksv'(S_2O_3) M^{-1}	τ^o, ns [e]
6	0 500	0 500	4900	7060[c],7080[d]	8100[c],8000[d]	1250
1	0 246	0 30	510	5000[c],5000[d]	7200[c],7500[d]	1400[e],1650[f]
9	0 340	0 410	490	5100[c]		1880
10	0 241	0 290	360	3800[c]		625
7	0 230	0 260	470	4750[c]		1300
8	0 176	0 220	400	4700[c]		1250

a) Φ^o is the observed quantum yield for NArE photohydrolysis in 10^{-2}M NaOH solution Excitation λ = 313nm

b) Φ_∞ is the corresponding limiting quantum yield at high [OH$^-$]

c) From direct lifetime measurements by laser flash photolysis (eqn 1)

d) From competitive quenching of the alkaline photohydrolysis (eqn 4)

e) In pure water non-deoxygenated The estimated error in the lifetime is about 10%

f) In completely deoxygenated aqueous solution

The agreement between the K_{SV} values determined directly (laser flash photolysis) and indirectly (quenching of photohydrolysis) shows that OH$^-$, Br$^-$ and $S_2O_3^=$ are competitive quenchers of NArE^{3*} This in accord with the recent study of Berci *et al*[21] who proposed that electron transfer quenching of the 2-nitrothiophene triplet state by Br$^-$ and $S_2O_3^=$ is competive with nucleophilic aromatic photosubstitution by CN$^-$ and OH$^-$

EXPERIMENTAL

All melting points are uncorrected, ^1H NMR spectra were recorded at 80 MHz on a Brucker AC 80 spectrometer in CCl_4 or $CDCl_3$ solutions with TMS as internal standard UV spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer Mass spectra were recorded on a Hewlett-Packard 5895B mass spectrometer Quantum yield determinations were performed at 30 ± 1 °C in a conventional merry-go-round apparatus[22,23] The 313-nm line of a 450-W Hanovia medium-pressure mercury immersion lamp (quartz well) was isolated with aqueous K_2CrO_4 and colored glass (UG 11) filters[23] Incident light intensities at 313 nm, monitored by potassium ferrioxalate actinometry,[23] were of the order of $6\ 0\text{-}6\ 2 \times 10^{-8}$ einstein/min for this configuration

*3-Nitroanisole(**1**)* This compound was prepared by methylation of m-nitrophenol with dimethyl sulfate and crystallized several times from methanol, mp 38-39°C, ^1H NMR ($CDCl_3$) 3,85(s, 3H), 7 0-7 9 (m, 4H), MS m/e(%) 153 (M^+, 73), 139(12,5), 111(18), 93(16), UV(H_2O) λ max 270 (ε 6100) and 327nm (ε 2290)

*3-Nitrophenetole(**7**)* This compound was prepared in 90% yield by the same procedure as its methyl homologue using diethyl sulfate, m p 34-35°C, ^1H NMR($CDCl_3$) 1,45(t, J = 6 7 Hz, 3H), 4,10(q, J= 6 7 Hz, 2H), 7 1- 7 9(m, 4H), MS m/e(%) 167(M^+,55), 139(100), 111(26), 93(52), UV(H_2O) λ max 271(ε 6090) and 328nm (ε 2060)

*n-Butyl 3-nitrophenylether (**8**)* A mixture of 6 00g (34 mmol) of potassium 3-nitrophenolate and 8,77g(64 mmol) 1-bromobutane was heated for 19 0 h in 100mL of methanol After cooling the solvent was removed and the remaining mass was poured onto ice ,filtered, then extracted with ethyl ether following by drying over anhydrous $MgSO_4$ The 1-bromobutane was removed by distillation and the residue was distilled in vacuum to give 3 6g (54%) of **8** (bp 117-119°C (1mm)) ^1H NMR($CDCl_3$ 1,00 (t, J = 6 7 Hz, 3H), 2 05-1 25(m,4H), 4 05(t, J = 6 7 Hz,2H), 7 10-7 85(m,4H), MS m/e(%) 195(M^+,4,8), 139(87), 111(0,6), 109(5,7), 93(76), 81(54), 65(100), UV(CH_3CN-H_2O 10%) λmax 270 (ε 5827) and 330nm (ε 1918)

*2-Chloro-5-nitroanisole(**9**)* This compound was synthesised from 2-methoxy-4-nitroanilline by a Sandmeyer reaction as described by Blanksma[24] From 10 0g (0 06 mols) of 2-methoxy-4-nitroaniline, 1 12g (10 0 % yield) of 2-Cl-5-NA was obtained, m p 82-83°C ^1H NMR ($CDCl_3$) 4 0 (S,3H) and 7 45-7 90 (m,3H), MS m/e(%) 187 05 (M^+,100), 165 20 (29 83), 141 15 (35 67), 129 15 (52 84), 111 15 (61 05), 98 15 (42 56), 83 05 (52 06), 77 05(59 26), 71 05 (57 59), 69 05 (62 54), 62 95(64 55), 57 05(68 52), 55 05(51 60) UV (H_2O) λ max 231 (ε 8100), 285 (ε 6800) and 328 nm (ε 4000)

*2-Bromo-5-nitroanisole(**10**)* This compound was synthesised as described by Blanksma[24] by a Sandmeyer reaction, 10 0g (0 060 mols) of 2-methoxy-4-nitroaniline yielded 6 28g (45% yield) (**10**) after crystallization from alcohol, m p 103-104°C ^{1}HNMR ($CDCl_3$) 4 0(s,3H) and 7 5-7 9(m,3H), MS m/e(%) 233 15(M^++1, 96 59), 231 15(M^+-1, 100),187 05 (23 8), 185 05 (24 44), 175 05(27 91),173 05(32 09), 172 05(50 67), 170 05(52 26),157 05 (39 3),155 05 (38 46), 91 05 (10 5), 83 05(21 19), 81(13 13), 78 05(53 60), 77 05(22 20), 62 95(86 54), 61 95(26 05) UV(H_2O) λmax 230(ε 7800), 286(ε 7400) and 330nm(ε 4300)

2-Iodo-5-nitroanisole (**13**) Prepared from 2-methoxy-4-nitroaniline via diazotation and reaction with KI Yield 47%, m p 128 - 129°C, ^{1}NMR ($CDCl_3$) 3 99 (S, 3H) and 7 55 - 7 91 (m, 3H), MS m/e (%) 2/97 20 (M+, 100), 233 15 (9 79), 221 15 (14 50), 218 15 (17 15), 190 05 (5 52), 127 00 (10 77), 77 95 (29 05) 75 95 (33 44) , 74 95 (20 93) UV (H2O) λmax 231 (ε 5650), 284 (ε 3050) and (ε 3210)

2-Chloro-5-nitrophenol (**14**) Prepared by refluxing 0 50g of **9** with 35% HCl (Merck, 20mL) for 18hs After cooling to room temperature, the reaction mixture was poured onto ice, made strongly alkaline and filtered The product was precipitated from the filtrate by acidification After crystallisation from dilute hydrochloric acid 0 23g of 2-chloro-5-nitrophenol was obtained, m p 118-119°C

2-Bromo-5-nitrophenol (**15**) This compound was prepared from 0 50g of **10** by heating with 48% HBr for 16hs The reaction mixture was worked up as described for 2-Chloro-5-nitrophenol After crystallization from dilute hydrochloric acid, 0 2g of 2-bromo-5-nitrophenol was obtained, m p 119-120°`C

Experiments for the determination of quantum yields (Tables II to III) were performed at 30°C, generally without removal of oxygen For the photohydrolysis studies at pH values below 12, the appropriate quantity of standard 0 100 M NaOH containing NArE (2 5 - 3 0 X 10^{-4}M) was added to the filtered aqueous NArE stock (2 5 - 3 0 X 10^{-4} M),in the dark, followed by filtration through a Millipore 220 nm membrane filter For studies of quenching by sodium bromide or sodium thiosulfate, a concentrated pH 12 stock solution of sodium bromide or thiosulfate and the filtered basic NArE stock were used to prepare solutions containing NArE (2 5 - 3 0 X 10^{-4} M), NaBr (0 0 - 7,0 mM) or $Na_2S_2O_3$ (0 0 - 6 0 mM),and NaOH (0 01 M)

Aliquots (3 00 mL) of each final NArE solution contained in 1 cm pathlength Teflon-stoppered quartz absorbance cells, were subjected to sequential irradiations at 313 nm The absorbance changes were followed at 313 nm and 410 nm Irradiation was carried out at 311 nm using a Hanovia 450 W medium pressure mercury immersion lamp (Pyrex well) as a light source and a conventional "merry-go-round" as described previously[22,23] Incident light intensities were monitored by potassium ferrioxalate actinometry[23] Photoreaction quantum yields were calculated from the variation of the optical densities at 313 nm and 410 nm

The laser flash photolysis experiments were carried out using an Applied Photophysics laser flash photolysis system with a Spectron SL 402 laser as excitation source Nanosecond flash photolysis experiments were carried out using 2 5 - $3\text{x}10^{-4}$M solutions of the NArE contained in a 1cm path length quartz fluorescence cells

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