On the Mechanism of the Photohydroxynitration of Biphenyl by Nitrate Ion

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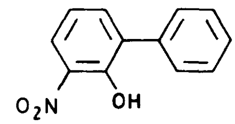
The conversion of biphenyl into isomeric hydroxynitrobiphenyls is a two-step process which involves a photochemical nitration of the first formed *o*- and *p*-hydroxybiphenyls. The initial steps of the reaction involve quenching the biphenyl excited singlet state by NO_3^- to give an exciplex or a caged radical ion pair which then collapses to produce the *o*- and *p*-hydroxybiphenyls.

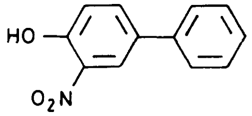
Photochemical substitution of aromatic hydrocarbons with simple anions is a growing field of study. The reaction of arenes with cyanide ion has been investigated both preparatively[1] and mechanistically.[2,3] Cornelisse and his co-workers have reported that pyrene may also be substituted by amide ion.[4]

Suzuki and his collaborators[5,6] have reported that when biphenyl, adsorbed on silica gel, was irradiated with aqueous sodium nitrate solution, a series of mutagenic hydroxynitrobiphenyls (**1**)—(**3**) could be identified by a combination of mass and ^1H n.m.r. spectroscopy.

The notable feature about the structures of these products is that the nitro group is always *ortho* to the hydroxy. On the assumption that the photochemical reaction involves biphenyl (BP) and NO_3^- (as opposed to their transformation products), we considered that a possible intermediate was the nitrate ester of biphenyl, (**4**). Aryl nitrates have never been isolated; attempts to prepare them invariably lead to *o*-nitrophenols.[7,8,†] The purpose of this work was to investigate the mechanism of the photoreaction of biphenyl with nitrate ion.



(1)



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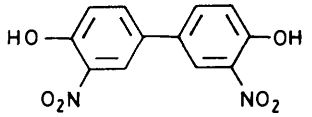
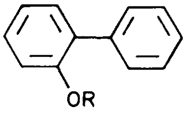
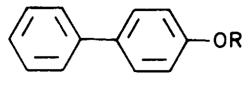


(3)



(4a) R = NO2

(5a) R = H



(4b) R = NO2

(5b) R = H

Results

Most of our reactions were carried out under homogeneous conditions using aqueous methanol as the solvent. It was quickly clear that our original suggestion for a reaction mechanism [equation (1)] could not be correct. Products (**1**) and (**2**) were only formed in significant amounts at high nitrate concentrations; at lower $[NO_3^-]$ the major product was 2-phenylphenol (**5a**), with 4-phenylphenol (**5b**) the only other detectable product. This observation is consistent with a sequential mechanism such as equation (2), where the phenol is the primary product and (**1**) and (**2**) are secondary products.

$$BP + NO_3^- \xrightarrow{h\nu} (\mathbf{4}) \xrightarrow{\text{rearrangement}} (\mathbf{1}) + (\mathbf{2}) \qquad (1)$$

$$BP + NO_3^- \xrightarrow{h\nu} (\mathbf{5}) \longrightarrow (\mathbf{1}) \text{ and } (\mathbf{2}) \qquad (2)$$

Consistent with this interpretation, an irradiation of 4-phenylphenol (**5b**) with NO_3^- yielded 4-hydroxy-3-nitrobiphenyl (**2**) as the only detectable product. The nitrophenol was not formed in a dark control reaction, and furthermore appeared to be stable under the photolysis conditions. The recovery of starting material was > 95% following irradiation of (**2**) in aqueous methanol whether or not nitrate ion was present. Similarly, 2-phenylphenol gave (**1**) as the major product with a very small yield of a hydroxynitrobiphenyl isomer different from either (**1**) or (**2**). In reactions followed as a function of time, there was a lag before any nitrophenols ($\lambda_{max.}$ *ca.* 370 nm) formed, consistent with the sequential mechanism.

We showed that nitrate ion supplied the phenolic oxygen atom of (**5a**) and (**5b**) by irradiating biphenyl in pure methanol (using ammonium nitrate as the nitrate source). If water is the origin of the hydroxy group in (**5**), then this product should be suppressed and the methyl ether should be formed instead. If NO_3^- provides the oxygen atom then (**5**) should still form in reactions where nitrate is originally present. In practice, the reaction of biphenyl and nitrate in pure methanol gave a mixture of (**5a**) and (**5b**) as the only detectable products. At higher nitrate concentration, (**1**) and (**2**) were the major products with small amounts of (**5a**) and (**5b**) and very small amounts of a methoxybiphenyl and a nitrobiphenyl as indicated by g.c.-m.s. These results are consistent with nitrate ion being the source of the hydroxy group in the phenols.[‡]

We next considered the initial interaction between NO_3^- and the biphenyl excited state. Nitrate ion was an efficient quencher of biphenyl fluorescence (Table 1). The Stern–Volmer quenching constant K_{sv} was not very sensitive to the identity of the cation, even when the cation was Ba^{2+} or Pb^{2+}. Fluorescence quenching by NO_3^- was thus dominant over the heavy-atom effect.

[†] This seems to be true in the biphenyl series also. When we attempted to form *p*-biphenylyl nitrate (**4b**) by the reaction of the sodium salt of *p*-phenylphenol with nitryl chloride in dichloromethane solution, the reaction product was (**2**). The corresponding reaction of 2-phenylphenol afforded some (**1**), together with mono- and di-chlorohydroxybiphenyls.

[‡] The possibility that adventitious molecular oxygen is the source of the phenolic oxygen is discounted by the observation that the yield of (**5a**) and (**5b**) is increased in deoxygenated solution.

Table 1. Fluorescence quenching of biphenyl[a] by NO_3^- in aqueous methanol

Quencher	K_{sv}[d]	$10^{-9}k_q$[e]
$NaNO_3$	77	5.9
KNO_3	70	5.4
NH_4NO_3[b]	51	3.9
$Mg(NO_3)_2$	71	5.5
$Ba(NO_3)_2$	76	5.8
$Pb(NO_3)_2$	86	6.6
$Bu^n{}_4NNO_3$[c]	72	5.5

[a] Concentration 1×10^{-4} mol dm^{-3}. [b] In pure methanol. [c] In pure acetonitrile. [d] Units dm^3 mol^{-1} (per mole of NO_3^-). [e] Units dm^3 mol^{-1} s^{-1} using value of $\tau_{BP} = 1.3 \times 10^{-8}$ s (H. Shizuka, M. Kakamura, and T. Morita, *J. Phys. Chem.*, 1980, **84**, 989).

The photoreaction between biphenyl and nitrate ion was inefficient in both the chemical and photochemical senses. Chemically, the yield of phenols (**5a**) and (**5b**) rarely exceeded 10%, while the quantum yield for disappearance of biphenyl was typically in the range 0.002. These facts complicated the elucidation of the reaction mechanism.

The relationship between the reaction quantum yield and the nitrate concentration was investigated. The quantum yield of disappearence of biphenyl (φ_r) was almost independent of the nitrate concentration and had a similar value for the background reaction when no nitrate was present. The quantum yield of formation of 2-phenylphenol (φ_p) varied with the initial nitrate concentration. In the range $0 < [NO_3^-] < 0.1$ mol dm^{-3} a linear relationship between φ_p^{-1} and $[NO_3^-]^{-1}$ was observed, showing that a bimolecular interaction between NO_3^- and a biphenyl excited state occurs.* This excited state was deduced to be the singlet, because the parameter intercept/slope from the plot of φ_p^{-1} *versus* $[NO_3^-]^{-1}$ had the value 52 dm^3 mol^{-1}, of a similar magnitude to the fluorescence quenching constant K_{sv}.

The fate of the nitrate ion in the photoreaction appears to be reduction to nitrite. A plot of $(\varphi_{NO_2^-})^{-1}$ *versus* $[NO_3^-]^{-1}$ was linear to high concentration of NO_3^- and had an intercept/slope parameter of 3.5. However, the interpretation of this observation is complicated by the fact that nitrate was photoreduced to nitrite even in the absence of biphenyl. We attempted to determine whether nitrite was also a companion product to the phenols (**5a**) and (**5b**). Using monochromatic 254 nm radiation, the yield of nitrite was still *ca.* 100 times greater than the yield of 2-phenylphenol even when biphenyl absorbed >95% of the light. In the absence of biphenyl, the nitrite yields were even higher. We thus cannot say whether nitrite and the phenols (**5a**) and (**5b**) were produced from the same reaction.

The effect of the electron acceptors $S_2O_8^{2-}$ and *p*-dicyanobenzene on the reaction rate was investigated since these compounds enhance the photocyanation of aromatic hydrocarbons.[1-3] In the absence of NO_3^-, $S_2O_8^{2-}$ accelerated the photodecomposition of biphenyl, and some hydroxybiphenyls (**5**) were formed. When NO_3^- was present neither $S_2O_8^{2-}$ nor *p*-dicyanobenzene led to the formation of more (**5**) than when these 'promoters' were absent, although the photodecomposition rate was increased.

Discussion

The time studies and the variation of the yields of hydroxynitro compounds with initial nitrate concentration establish firmly that the overall hydroxynitration is a two-step process. The phenols (**5a**) and (**5b**) are the first-formed products, and NO_3^- is the source of the phenolic oxygen.

As already noted, there is good agreement between K_{sv} and the intercept/slope parameter of the plot of φ_p^{-1} *versus* $[NO_3^-]^{-1}$. This may be interpreted to mean that NO_3^- interacts directly with singlet excited biphenyl in the product-forming reaction channel. Consequently we can outline a plausible mechanism for the formation of (**5a**) and (**5b**) as in Scheme 1. We then associate K_{sv} with $k_3/(k_1 + k_2)$ and the relationship between φ_p and $[NO_3^-]$ is given by equation (3). The intercept, from φ_p^{-1} *versus* $[NO_3^-]^{-1}$, of 4 240 can likewise be associated with $(1 + k_4/k_5)$, the high value explaining the energy wastage and the low overall quantum yields. The low chemical yield in the reaction explains why φ_p can be nitrate dependent while no dependence of φ_r on $[NO_3^-]$ is seen.

$$\begin{aligned}
&BP \xrightarrow{h\nu} {}^1BP \\
&{}^1BP \xrightarrow{k_1} \text{(fluorescence and radiationless decay)} \\
&{}^1BP \xrightarrow{k_2} \text{other products (background reaction)} \\
&{}^1BP + NO_3^- \xrightarrow{k_3} X \\
&X \xrightarrow{k_4} \text{other products (including return to } BP + NO_3^-) \\
&X \xrightarrow{k_5} (\mathbf{5a}) + (\mathbf{5b})
\end{aligned}$$

Scheme 1.

$$\varphi_p^{-1} = \left(1 + \frac{k_4}{k_5}\right)\left(1 + \frac{(k_1 + k_2)}{k_3[NO_3^-]}\right) \qquad (3)$$

Further evidence to support a singlet state reaction was obtained in a sensitization reaction using *m*-methoxyacetophenone (E_T *ca.* 310 kJ mol^{-1}). This sensitizes the triplet of biphenyl (E_T *ca.* 275 kJ mol^{-1}), but only inefficiently.[9,10] No phenylphenols (**5**) could be detected when the sensitiser absorbed almost all the light and NO_3^- was present. In addition, the quantum yield for loss of biphenyl was reduced in the presence of the sensitizer. We conclude that bypassing the S_1 state of biphenyl has an adverse effect on the photohydroxylation. In control reactions where NO_3^- was absent, sensitization increased the rate of loss of biphenyl, indicating that the background photodegradation of biphenyl is a triplet reaction.

We have had less success in identifying the intermediate labelled X in Scheme 1. By analogy with photocyanation, which is usually viewed as proceeding by the attack of CN^- on a radical cation intermediate,[2,3] we originally considered $BP^{\cdot+}$ as the identity of X. This seems to be unlikely on the grounds that $S_2O_8^{2-}$ and *p*-dicyanobenzene both promote the formation of $BP^{\cdot+}$, but neither enhances the yield of (**5a**) and (**5b**). This means that if $BP^{\cdot+}$ is to be a plausible intermediate, it must react with the reduced partner (presumably NO_3^{2-}) directly within the solvent cage, rather than reacting as a free radical cation with a second NO_3^- ion.

Another possibility for the interaction between ^1BP and NO_3^- is shown in Scheme 2. We could not establish a 1:1 correspondence between the production of (**5**) and that of NO_2^- due to the large amount of NO_2^- formed independently of hydroxylation. However, it is difficult to picture the zwitterionic intermediate above as X, in that such an intermediate should proceed to give (**5a**) with high efficiency rather than with the very low efficiency observed.

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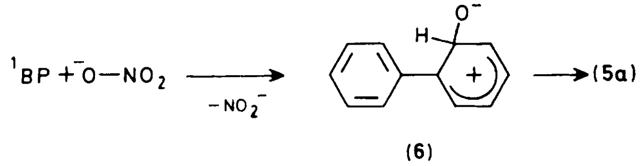
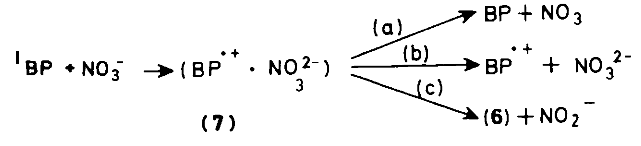
* At higher $[NO_3^-]$ the apparent φ_p levels off and eventually falls again due to competing light absorption by NO_3^-.



Scheme 2.



Scheme 3.

We therefore favour the solvent cage model shown above. The charge-transfer intermediate (7) then principally undergoes the reverse electron transfer (a), some ions escape the cage (b), and some proceed to product (c). This mechanism explains the inefficiency of the overall reaction. It is rather similar to the reaction studied by Frank and Grätzel, involving NO_3^- and photoexcited phenothiazines.[11] The difference is that because $BP^{\bullet +}$ is so much stronger an oxidant than phenothiazine radical cation, pathway (a) is much more favoured in our case.

The ideal experiment to test this mechanism would be to prepare NO_3^{2-} and $BP^{\bullet +}$ independently, and mix them together. Unfortunately, NO_3^{2-} can only be made as a transient intermediate by pulse radiolysis,[12] and so this aspect of our mechanism cannot be tested at the present time.

Evidence in favour of $BP^{\bullet +}$ leaving the cage was sought by an experiment in which biphenyl was irradiated in the presence of NO_3^- and CN^- simultaneously. Cyanide ion does not quench the fluorescence of biphenyl,[2] and photocyanation relies on indirect methods of generating $BP^{\bullet +}$. Under conditions where 98% of all the biphenyl excited states were trapped by NO_3^- no cyanobiphenyls were detected. This result rules out a free biphenyl radical cation as the initial product of the reaction between NO_3^- and the biphenyl excited state. We therefore conclude that our results may most easily be accommodated by the mechanism outlined in Scheme 1, where intermediate X is (7), an exciplex or a caged radical ion pair.

Experimental

Fluoresence spectra were recorded at room temperature in 1 cm × 1 cm square quartz cuvettes using a Perkin-Elmer LS-5 instrument. Quenching constants were determined by the Stern–Volmer method. The complete experimental method has been described previously.[9] The results were complicated by the fact that NO_3^- is not completely transparent in the u.v. region. Its first absorption band [$\lambda_{max.}$ 303 nm ($\varepsilon_{max.}$ 6.8) in aqueous CH_3OH] overlaps both the emission of biphenyl ($\lambda_{max.}$ 335 nm) and typical excitation wavelengths. By using 265 nm as the excitation wavelength (where NO_3^- has an absorption minimum) and restricting $[NO_3^-]$ to $\leqslant$ 0.03 mol dm^{-3}, linear Stern–Volmer plots were obtained. These plots showed pronounced curvature at greater nitrate concentrations.

Photolyses were carried out in duplicate using quartz ampoules of 8 mm o.d. Sample size was 2.0 cm^3. The photolysis equipment was a Rayonet RPR photoreactor equipped with 16 low-pressure mercury lamps with emission mainly at 254 nm. A 'merry-go-round' was used to ensure equal illumination of the samples. Photolysed samples were analysed for substrate disappearance by g.l.c. using Carle 211 or 9500 gas chromatographs, equipped with flame-ionization detectors and 6 ft × 1/8 in stainless steel columns of 3% OV-101, 3% SE-30, or 10% SE-30 on Chromosorb W. All samples were analysed at least in duplicate using pentadecane or fluorene as external standards.

Preparative photolyses were conducted in a 350 cm^3 quartz immersion well equipped with a Hanovia 450 W medium-pressure mercury lamp. Solutions were stirred with a magnetic stirrer.

G.c.–m.s. results were obtained using a VG 7070F mass spectrometer interfaced to a temperature-programmable Perkin-Elmer Sigma III gas chromatograph with a 6 ft column of 3% OV-1 on Chromosorb W. U.v.–visible spectra were recorded on a Perkin-Elmer Lambda 3 u.v.–visible spectrophotometer.

Analysis of nitrite was adapted from the method of Flamerz and Bashir[13] using 4-nitroaniline and 2-naphthol as the coupling reagents.

Authentic 2- and 4-hydroxy-3-nitrobiphenyl were prepared by nitration of the corresponding phenols with dilute nitric acid in nitromethane. The crude products were recrystallized from methanol. 2-Hydroxy-3-nitrobiphenyl was obtained as bright yellow needles, m.p. 59.5—60 °C; *m/e* 216 (9.7%), 215 (72.8), 199 (7.1), 198 (50.0), 169 (13.5), 168 (100), 141 (8.0), 140 (10.0), 139 (43.9), and 115 (29.1), similar to a reported spectrum.[6] 4-Hydroxy-3-nitrobiphenyl was obtained as yellow needles, m.p. 67.5—68 °C; *m/e* 216 (19.2%), 215 (100), 169 (11.9), 168 (16.6), 141 (18.9), 140 (15.0), 139 (41.8), and 115 (20.4), similar to a reported spectrum.[6]

4-Phenylphenol + Nitryl Chloride.—Nitryl chloride was prepared by addition of chlorosulphonic acid to a mixture of fuming nitric and sulphuric acids.[14] A flow of nitrogen was used to blow the nitryl chloride produced into a mixture of 4-phenylphenol and sodium hydride in dichloromethane. This gave an immediate colour change. Acidification, extraction, chromatography on alumina, and recrystallization from methanol afforded impure 4-hydroxy-3-nitrobiphenyl as a pale green solid, m.p. 64—65 °C. It had the same t.l.c., g.l.c., and mass spectrum as an authentic sample.

A similar reaction of 2-phenylphenol gave yellow crystals of impure 2-hydroxy-3-nitrobiphenyl, m.p. 45—47 °C. G.c.–m.s. also showed the presence of a monochlorohydroxybiphenyl, *m/e* 206 (32.9%), 205 (19.1), 204 (100), 203 (20.7), 168 (18.9), 141 (17.7), and 139 (22.0) and a dichlorohydroxybiphenyl, *m/e* 242 (11.3%), 240 (64.5), 239 (21.0), 238 (100), 202 (19.3), and 168 (28.7).

Preparative-scale Irradiations.—Biphenyl–$NaNO_3$*–aqueous* CH_3OH. Irradiation of biphenyl (4.0 × 10^{-3} mol dm^{-3}) and nitrate (1.6 × 10^{-2} mol dm^{-3}) in 60% aqueous methanol for 6 h gave only 2-phenylphenol, *m/e* 171 (12.3%), 170 (M^+, 100), 169 (48.8), 141 (22.1), 122 (19.2), 115 (16.1), and 105 (33.2), and 4-phenylphenol, *m/e* 171 (12.5%), 170 (100), 141 (13.7), 115 (11.0), and 105 (14.2), as the only detectable products along with large amounts of unchanged biphenyl. Irradiation of biphenyl (1.67 × 10^{-2} mol dm^{-3}) and nitrate (6.67 × 10^{-2} mol dm^{-3}) in 2:1 $CH_3OH–H_2O$ for 6 h under a stream of O_2 gave a 45% loss of biphenyl and a 1.3% yield of 2-phenylphenol (by g.l.c.). A similar reaction under a stream of O_2-free N_2 gave a 12% loss of biphenyl and a 4.0% yield of 2-phenylphenol.

Following the irradiation of biphenyl for 6 h with no nitrate present, g.l.c. analysis indicated *ca.* 50% loss of biphenyl but no products were detected by g.l.c.

Irradiation of 4.1 × 10^{-3} mol dm^{-3} biphenyl with 1.0 × 10^{-1} mol dm^{-3} of nitrate gave 2- and 4-phenylphenol as minor products with the major products being 2- and 4-hydroxy-3-nitrobiphenyl as shown by g.c.–m.s.

Table 2. Percent loss of biphenyl[a] as a function of nitrate concentration after 94 min irradiation in methanol

10^1[NH_4NO_3]/mol dm^{-3}	Loss (%)
0	13.5
0.58	16.1
1.15	12.7
1.73	15.4
3.46	13.5
4.61	8.4

[a] Initial concentration of biphenyl was 5.1 × 10^{-3} mol dm^{-3}.

Table 3. Percent loss of biphenyl[a] in aqueous methanol (1:1 v/v) as a function of nitrate concentration after 120 min irradiation

10^2[$NaNO_3$]/mol dm^{-3}	Loss (%)
0	10.3
1.95	17.8
3.89	15.1
5.84	11.7
7.78	12.1
9.73	12.2

[a] Initial concentration of biphenyl was 5.1 × 10^{-3} mol dm^{-3}.

Table 4. Quantum yield of 2-phenylphenol formation as a function of nitrate concentration after 2 h irradiation of biphenyl[a]

[$NaNO_3$]/mol dm^{-3}	10^4 φ_r
0	0
0.01	0.80
0.02	1.17
0.03	1.50
0.05	1.70
0.10	1.63
0.15	1.57
0.20	1.46
0.50	0.31

[a] Initial concentration of biphenyl was 5.02 × 10^{-3} mol dm^{-3} in 3:2 methanol–water.

Table 5. Visible absorbance (at 418 nm) of crude reaction mixture[a] as a function of nitrate concentration

10^2[$NaNO_3$]/mol dm^{-3}	Absorbance
0	0
1.26	0.196
9.82	0.630

[a] Irradiation of 4.99 × 10^{-3} mol dm^{-3} biphenyl for 120 min in aqueous methanol (1:1 v/v).

Table 6. Visible absorbance of crude reaction mixture[a] as a function of irradiation time

Time (h)	Absorbance (418 nm)
0.5	0.115
1.0	0.444
3.0	1.31
5.0	2.34

[a] Irradiation of 5.0 × 10^{-3} mol dm^{-3} biphenyl in aqueous methanol (1:1 v/v).

Table 7. Quantum yield of nitrite formation as a function of nitrate concentration after 2 h irradiation of biphenyl[a]

[NO_3^-]/mol dm^{-3}	10^3 φ_r
0.010	0.57
0.012	1.45
0.013	1.66
0.017	2.08
0.025	3.00
0.033	4.04
0.050	5.68
0.067	7.12
0.100	9.46

[a] Initial concentration of biphenyl was 5.07 × 10^{-3} mol dm^{-3} in 3:2 methanol–water.

Irradiation of a mixture of biphenyl (4.2 × 10^{-3} mol dm^{-3}), $NaNO_3$ (1.6 × 10^{-2} mol dm^{-3}), and ammonium persulphate (5.0 × 10^{-2} mol dm^{-3}) in 60% aqueous methanol for 45 min resulted in *ca.* 80% loss of biphenyl (by g.l.c.). G.c.–m.s. indicated that 2- and 4-phenylphenol were the major products along with a small amount of a dihydroxybiphenyl, *m/e* 187 (12.4%), 186 (M^+, 100), 185 (20.0), and 157 (15.5).

The irradiation of biphenyl (4.3 × 10^{-3} mol dm^{-3}) with ammonium persulphate (5 × 10^{-2} mol dm^{-3}) in 60% aqueous methanol for 35 min gave *ca.* 70% loss of biphenyl (by g.l.c.). The same product mixture was obtained as in the case of the reaction with added nitrate as shown by g.l.c. and g.c.–m.s.

Biphenyl–NO_3^-–CH_3OH. Biphenyl (3.3 × 10^{-2} mol dm^{-3}) and ammonium nitrate (1.7 mol dm^{-3}) in methanol were irradiated for 20 h after which *ca.* 60% biphenyl had reacted (by g.l.c.). Unchanged biphenyl (0.76 g, 57%) was recovered. The major products (by g.c.–m.s.) were the two hydroxynitrobiphenyls (*ca.* 0.2 g) with small amounts of 2- and 4-phenylphenol and very small amounts of a methoxybiphenyl, *m/e* 185 (15.1%), 184 (M^+, 100), 169 (33.5), 141 (30.5), and 115 (24.9), and a nitrobiphenyl, *m/e* 200 (13.7%), 199 (M^+, 100), 153 (70.4), 152 (84.2), and 151 (19.1).

The reaction using the same concentration of biphenyl and 1.3 × 10^{-1} mol dm^{-3} of nitrate gave only 2- and 4-phenylphenol as detectable products (by g.l.c.).

Irradiation of biphenyl (10 mmol), ammonium nitrate (500 mmol), and 1,4-dicyanobenzene (1 mmol) in methanol (300 cm^3) for 20 h gave *ca.* 0.3 g of the two hydroxynitrobiphenyls along with small amounts of 2- and 4-phenylphenol as indicated by g.c.–m.s.

Biphenyl–NO_3^-–CH_3CN. Biphenyl (4.2 × 10^{-3} mol dm^{-3}) and tetrabutylammonium nitrate (1.6 × 10^{-2} mol dm^{-3}) in acetonitrile were irradiated for 1 h, after which 50% of biphenyl had reacted (by g.l.c.). G.l.c. gave only an acidic product of short retention time that decomposed on the column.

4-Hydroxy-3-nitrobiphenyl–aqueous CH_3OH. A solution of 4-hydroxy-3-nitrobiphenyl (0.73 g) in 2:1 methanol–water (*ca.* 315 cm^3) was irradiated for 6 h. Methanol was evaporated to leave crude starting material (0.73 g, 100%), m.p. 60—63 °C, as the only detectable compound (by t.l.c.). Irradiation of 4-hydroxy-3-nitrobiphenyl (8.5 × 10^{-3} mol dm^{-3}) in the presence of nitrate (3.4 × 10^{-1} mol dm^{-3}) gave a 95% recovery of crude starting material. G.l.c. and t.l.c. did not show the presence of any identifiable products.

2-Phenylphenol–NO_3^-*–aqueous* CH_3OH. Irradiation of 2-phenylphenol (1.7 × 10^{-2} mol dm^{-3}) and sodium nitrate (8.3 × 10^{-1} mol dm^{-3}) in 50% aqueous CH_3OH for 8 h gave 2-hydroxy-3-nitrobiphenyl as the principal product with a very small amount of another hydroxynitrobiphenyl isomer, *m/e* 216 (14.0%), 215 (100), 185 (8.8), 168 (9.5), 141 (26.7), 139 (15.9), and 115 (22.3), which had a different mass spectrum from either (**1**) or (**2**).

Similar reaction of 4-phenylphenol gave 4-hydroxy-3-nitro-

Table 8. Percent biphenyl loss[a] in the presence and absence of sodium nitrate and *m*-methoxyacetophenone ($C_9H_{10}O_2$)[b]

Experiment	Ampoule	$10^2[NO_3^-]$/mol dm^{-3}	$10^2[C_9H_{10}O_2]$/mol dm^{-3}	Loss (%)
1	Pyrex	0	0	0
2	Pyrex	0	3.4	3.4
3	Pyrex	1.45	0	0
4	Pyrex	1.45	3.4	0
5	quartz	0	0	16.7
6	quartz	0	3.4	4.0
7	quartz	1.45	0	24.0
8	quartz	1.45	3.4	5.3

[a] Irradiation of 4.71×10^{-3} biphenyl in 50% aqueous methanol for 2 h. [b] The concentrations were such that the sensitizer when present absorbed 81% of the light at 254 nm.

biphenyl as the only detectable product. The mixture was stable in room light, even after refluxing for 3 h.

Determination of φ_r *in Aqueous* CH_3OH (1:1 v/v).—The actinometry method of Bunce *et al.*[15] was used to determine φ_r for biphenyl loss. The concentration of biphenyl was 4.81×10^{-3} mol dm^{-3} and that of azoxybenzene was 1.42×10^{-3} mol dm^{-3}. Solutions, in duplicate, were irradiated for 2 h; g.l.c. analysis gave 11.5% loss of biphenyl and visible spectrophotometry gave 31% loss of azoxybenzene. This corresponded to a quantum yield of 2.1×10^{-3}, using the value of φ (azoxybenzene) as 0.017 at 254 nm.

Kinetic Analyses.— Stock solutions of biphenyl (*ca.* 5×10^{-2} mol dm^{-3}) and nitrate were prepared. Into 10 cm^3 volumetric flasks were pipetted 1.0 cm^3 of stock biphenyl and an appropriate amount of nitrate (0—8 ml). Each solution (2 cm^3) was pipetted into quartz ampoules, in duplicate. Typical irradiation times for each run were 90 min—2 h. Analysis for biphenyl loss was by g.l.c. using fluorene or pentadecane as external standards. Analysis of phenylphenol formation was complicated due to the low yields of these products in the kinetic analysis (*ca.* 1% based on initial amount of biphenyl present). To overcome this problem, 25 cm^3 of initial solution was irradiated in 18 × 160 mm quartz test tubes. The acidic products were extracted with 5% NaOH, then neutralized, and extracted into dichloromethane. The solution was concentrated and an external standard solution was added to the residue. In control experiments the recovery of the 2-phenylphenol was > 90% from this work-up procedure. Tables 2—8 give the kinetic results under a variety of conditions.

Biphenyl–NO_3^-–CN^-.—Solutions of biphenyl (5×10^{-3} mol dm^{-3}) and sodium cyanide (0.034 mol dm^{-3}) with and without nitrate or ammonium persulphate in 3:2 methanol–water were irradiated for 40 min. The results of the product analysis are as follows:

$[NO_3^-]$/ mol dm^{-3}	$[S_2O_8^{2-}]$/ mol dm^{-3}	Products
0	0	Cyanobiphenyls
0	0.02	2-Phenylphenol + cyanobiphenyls
0.65	0	2-Phenylphenol

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