Mechanisms for Aromatic Photocyanation: Naphthalene and Biphenyl

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Photocyanation of naphthalene and biphenyl has been studied in the systems ArH–KCN–aqueous CH_3CN and ArH–NaCN–CH_3OH. The reaction is first order in CN^- and in ground state ArH as well as in excited ArH. The proposed mechanism involves the formation of a singlet excimer, which dissociates into radical ions before the attack of cyanide ion. Photocyanations in the presence of oxidants such as *p*-dicyanobenzene and persulphate ion proceed by oxidation of the singlet excited hydrocarbon to form a radical cation directly.

THE direct introduction of cyanide into an unactivated aromatic hydrocarbon has synthetic potential, and is thus of interest. The process has been effected by free radical,[1,2] electrochemical,[2-4] and photochemical methods. Photocyanation of an aromatic system was first observed for *p*-nitroanisole,[5] and extended to unsubstituted arenes by Havinga *et al.*; [6] these workers used aqueous t-butyl alcohol as the solvent and KCN as the cyanide source. Later, Beugelmans and his associates reported improvements to the product yields using aprotic solvent–crown ether combinations to dissolve the alkali cyanide,[7] or by carrying out the reaction under phase transfer conditions.[8]

Various additives also improve the efficiency of photocyanation. Mizuno *et al.*[9] used *p*-dicyanobenzene in the system arene–KCN–dimethylformamide, while Cornelisse and Havinga [10] disclosed that higher yields of cyanides could be achieved if the reaction was assisted by ammonium persulphate. With this last combination, photocyanation could be extended to benzene, a substrate which did not react under the original conditions.

In view of this interest in photocyanation, we have undertaken a study of the reaction mechanism for naphthalene and biphenyl. Our experiments have been carried out using alkali-metal cyanides and either methanol or acetonitrile–water (1 : 1 v/v) as solvents. From the synthetic point of view, we have concluded that photocyanation under these kinds of conditions will be of very limited value on account of poor yields and the instability of the products under the reaction conditions. This conclusion presupposes that our two hydrocarbons are representative. Mechanistically, it has been shown that photocyanation under our conditions involves electron transfer processes in both the absence and presence of the additives persulphate ion and *p*-dicyanobenzene.

RESULTS

The nature of the photolysis products was first confirmed, with irradiations being done at 254 nm in sealed evacuated quartz ampoules, and the products analysed by gas chromatography–mass spectrometry (g.c.–m.s.). When the reaction was followed to various conversions, the rate of hydrocarbon disappearance was non-linear with photon flux, except at extremely low conversion. This effect, which is shown in Figures 1 and 2, was caused by promotion of the reaction by the cyano-compounds formed as products.

Naphthalene afforded a mixture of 1-cyanonaphthalene and a dihydrocyanonaphthalene with the latter predominating. Biphenyl gave a mixture of 2- and 4-cyanobiphenyl as reported previously.[6] Actual yields of these products, based on hydrocarbon consumed, were always rather low; typical values were in the range 12—25%, with 27% being the highest observed.

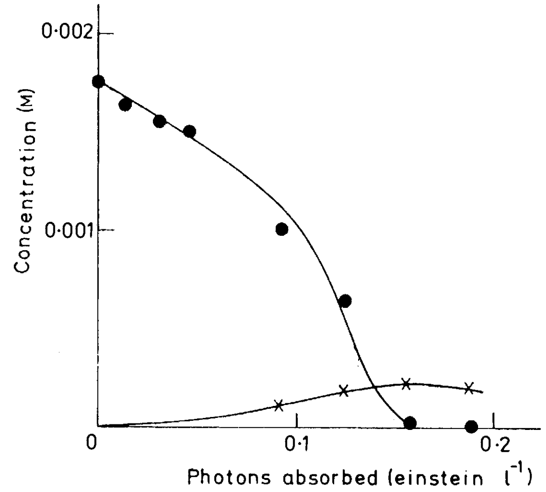

FIGURE 1 Photoreaction of 1.76 × 10^{-3}M-naphthalene with 0.052M-methanolic sodium cyanide: ● disappearance of naphthalene; × formation of cyanonaphthalene; + dihydrocyanonaphthalene

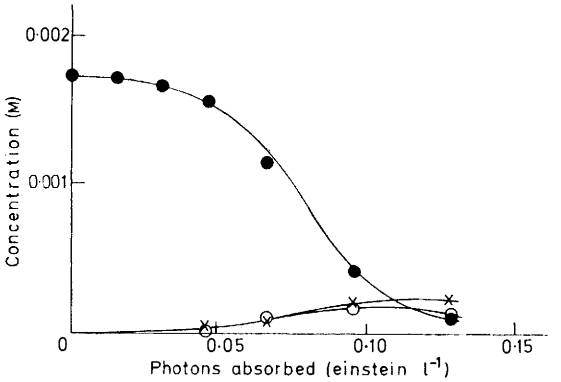

FIGURE 2 Photoreaction of 1.64 × 10^{-3}M-biphenyl with 0.052M-methanolic sodium cyanide: ● disappearance of biphenyl; × formation of 2-cyanobiphenyl; ○ formation of 4-cyanobiphenyl

Although both we and previous authors † find that the

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† Vink *et al.*[6] noted that the yield of dicyanobiphenyl increases with the irradiation time, hence the monocyanobiphenyls react further.

initial products are subject to further cyanation, this is not the whole reason for the low yields. The material balance in the reaction is particularly poor, but the missing product(s) were not detected by g.c. under a variety of conditions. We decided to base the mechanistic studies on quantum yields of disappearance of reactant (ϕ_r) rather than appearance of product because the former were more reproducible; however, we must exercise a certain caution in interpreting our results as representing only the cyanation process.

Multiplicity of the Excited State.—Published [11] values of the triplet yields of naphthalene and biphenyl in dilute solution are 0.7—0.8, compatible with either a singlet or triplet photocyanation mechanism. Vink [12] observed that the photocyanation of biphenyl could be sensitised by benzophenone and inferred a triplet state mechanism. However, we have reached the conclusion that photocyanation is a singlet state process.

Because alkali-metal cyanides are almost transparent at 254 nm, it is the aromatic hydrocarbon which is initially excited. Conventional sensitisation and quenching experiments were carried out to establish the multiplicity of the excited state; these are reported in Table 1. The last column of Table 1 is interpreted such that if 90% of the light is absorbed by sensitiser, then 10% of direct reaction will still occur and no sensitisation will be represented by $\phi_{sens}/\phi_0 = 0.10$.

TABLE 1

Sensitisation and quenching of photocyanation [a]

ArH	Sensitiser (quencher)	Light absorbed (%) by sensitiser (by ArH)	ϕ_{sens}/ϕ_0 (ϕ_{quench}/ϕ_0)
$C_{10}H_8$	Benzophenone	90	0.18
$C_{10}H_8$	Benzophenone	90	0.22 [b]
$C_{10}H_8$	Acetophenone	91	0.14
$C_{10}H_8$	(Biacetyl) [c]	(>99)	(0.87)
$C_{12}H_{10}$	Benzophenone	90	0.44
$C_{12}H_{10}$	Acetophenone	90	0.50
$C_{12}H_{10}$	3-Methoxyacetophenone	95	0.75
$C_{12}H_{10}$	(2,5-Dimethylhexa-2,4-diene)	(88)	0.96 [d]

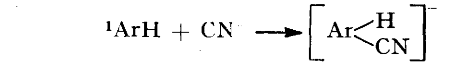
[a] In aqueous CH_3CN, excited at 254 nm, $[CN^-]$ 0.05M. [b] $[CN^-]$ 0.02M. [c] [Biacetyl] 4.8×10^{-3}M. [d] Average of two experiments reported in full in the Experimental section.

Since ketone sensitisers transfer triplet energy efficiency to naphthalene, the sensitisation data can be compatible only with a predominantly singlet state reaction for this hydrocarbon. Moreover, other observations in the naphthalene series suggest that some quenching of singlet naphthalenes by benzophenone may occur, presumably resulting in electron transfer.[13] When the sensitisation by benzophenone was repeated at 300 nm, with essentially all the light absorbed by benzophenone, the quantum yield of disappearance of naphthalene (ϕ_r) was less than in the direct reaction at 254 nm. No cyanation products could be detected in the sensitised reaction at 300 nm.

In the case of biphenyl, whose triplet energy is comparable with that of benzophenone, triplet energy transfer is known to be inefficient.[14] However, even acetophenone derivatives failed to give efficient sensitisation, and experiments with acetone as sensitiser, excited at 300 nm, gave no reaction whatever.

While the sensitisation reactions thus implicate the singlet state as the seat of photocyanation, quenching results were inconclusive. Dienes failed to quench, as expected, but the result cannot be taken to confirm a singlet process because the 'quencher' actually promoted the disappearance of hydrocarbon, while at the same time quenching fluorescence. Low concentrations of biacetyl were without significant effect on the progress of photocyanation, further arguing against a reactive triplet as the predominant cyanation pathway.

Kinetic Experiments.—A singlet state photocyanation proceeding with reasonable quantum yield should allow one to observe quenching of the hydrocarbon fluorescence by cyanide ion. However, CN^- did not quench the fluorescence of either naphthalene or biphenyl at concentrations of CN^- that effect cyanation. Thus, CN^- does not react directly with singlet excited arene, and mechanisms based on equations (1) or (2) can at once be excluded from consideration. This observation gainsays the suggestion [10] that photocyanation involves the attack of CN^- at the position of the photoexcited arene carrying the highest positive charge.

 (1)

$$^{1}ArH + CN^- \longrightarrow \left[Ar{<}^{H}_{CN} \right]^- \qquad (1)$$

$$^{1}ArH + CN^- \longrightarrow ArH + CN \xrightarrow{ArH} \text{free radical cyanation} \qquad (2)$$

A study of the variation of the quantum yield of reaction (ϕ_r) on the reaction variables showed that for both naphthalene and biphenyl, ϕ_r changes with $[CN^-]$ and also with the concentration of the aromatic, even though the reactions were done under conditions where all the light was absorbed by the aromatic hydrocarbon. In aqueous acetonitrile it was found that the percentage conversion was linear with photons absorbed over more of the reaction than in methanol. In the former solvent it was possible to study the effect of aromatic hydrocarbon concentration by analysis of simultaneous photocyanations carried out at different [ArH] and assuming ϕ_r to be proportional to the amount reacted. This was not possible in methanol, where a considerable number of experiments had to be done for every [ArH] with ϕ_r determined as the limiting slope of the line *M* reacted *versus* einstein l^{-1} absorbed (Table 2).

TABLE 2

Limiting values of ϕ_r for photocyanation of ArH in methanol using 0.052M-NaCN

ArH	Initial concentration (M)	ϕ_r (limiting)
$C_{10}H_8$	9.67×10^{-4}	3.8×10^{-3}
	1.76×10^{-3}	5.6×10^{-3}
	3.46×10^{-3}	6.2×10^{-3}
	4.84×10^{-3}	10.8×10^{-3}
	8.65×10^{-3}	20×10^{-3}
$C_{12}H_{10}$	1.64×10^{-3}	0.20×10^{-2}
	4.20×10^{-3}	1.2×10^{-2}
	7.50×10^{-3}	2.3×10^{-2}

The quantum efficiency of photocyanation was much lower in methanol than in aqueous acetonitrile. The effect appears to be one of polarity because the addition of water to methanol greatly promotes the reaction (Figure 3). A similar effect has been noted in the photocyanation of anisole derivatives.[15]

DISCUSSION

The dependence of ϕ_r upon the concentration of ground state ArH implicates the excimer as a reactive intermediate. However, the naphthalene excimer is in equilibrium with its components,[16] so that attack of CN^- should lead to quenching of monomer fluorescence. This was observed neither for naphthalene nor for biphenyl, and the same arguments should apply to biphenyl as to naphthalene because the biphenyl excimer is even less strongly bound.[17] Consequently, we suggest Scheme 1 as a plausible mechanism for the unassisted photocyanation.

$$\begin{aligned}
\mathrm{ArH} &\xrightarrow{h\nu} {}^1\mathrm{ArH} \\
{}^1\mathrm{ArH} &\xrightarrow{k_1} \mathrm{ArH} \\
{}^1\mathrm{ArH} + \mathrm{ArH} &\overset{K}{\rightleftharpoons} \text{excimer} \\
\text{excimer} &\xrightarrow{k_2} 2\mathrm{ArH} \\
\text{excimer} &\xrightarrow{k_3} \text{radical ions} \\
\text{radical ions} &\xrightarrow{k_4} 2\mathrm{ArH} \\
\text{radical ions} + \mathrm{CN}^- &\xrightarrow{k_5} (\mathrm{ArHCN})^\bullet \qquad (1) \\
(1) &\xrightarrow{k_6} \text{unproductive} \\
(1) &\xrightarrow{k_7} \text{product}
\end{aligned}$$

SCHEME 1

Steady state analysis affords the relationships (3).

$$\phi_r = \frac{k_3k_5k_7K[\mathrm{ArH}][\mathrm{CN}^-]}{(k_6 + k_7)(k_4 + k_5[\mathrm{CN}^-])\{k_1 + (k_2 + k_3)K[\mathrm{ArH}]\}} \qquad (3a)$$

$$\frac{1}{\phi_r} = \left(1 + \frac{k_6}{k_7}\right)\left(1 + \frac{k_4}{k_5[\mathrm{CN}^-]}\right)\left(1 + \frac{k_2}{k_3} + \frac{k_1}{k_3K[\mathrm{ArH}]}\right) \qquad (3b)$$

The results obtained are consistent with Scheme 1. At constant [ArH], $\phi_r^{-1} \propto [\mathrm{CN}^-]^{-1}$, while at constant $[\mathrm{CN}^-]$ $\phi_r^{-1} \propto [\mathrm{ArH}]^{-1}$. In methanolic solution, the results were plotted according to equation (3a) because ϕ_r was very small, *i.e.*, $k_1 \gg (k_2 + k_3)K[\mathrm{ArH}]$. In aqueous acetonitrile, it was shown that Scheme 1 was internally self-consistent, as follows. A parameter P was defined as the ratio slope/intercept from the ϕ_r^{-1} *versus* (concentration)$^{-1}$ plots. Then, according to equation (3b), $P_{\mathrm{CN}^-} = k_4/k_5$, while $P_{\mathrm{ArH}} = k_1/(k_2 + k_3)K$. Knowing $P_{\mathrm{CN}^-}/[\mathrm{CN}^-]$, the intercept of the plot of ϕ_r^{-1} *versus* $[\mathrm{ArH}]^{-1}$ can yield $(1 + k_6/k_7)(1 + k_2/k_3)$ which we call α. The latter can also be obtained from $P_{\mathrm{ArH}}/[\mathrm{ArH}]$ and the intercept of the ϕ_r^{-1} *versus* $[\mathrm{CN}^-]^{-1}$ plot. The two values of α are in satisfactory agreement (Table **3**). The variation in α between naphthalene and biphenyl might reflect weaker bonding of the biphenyl excimer making return to the ground state (k_2) more facile.

Deuteriation Studies.—Intermediate (1) in Scheme 1 provides a rationale for the formation of a cyano-product and a dihydrocyano-product. This is shown for naphthalene in equation (4). This mechanism allows

$$2\ C_{10}H_8CN^\bullet \longrightarrow C_{10}H_7CN + C_{10}H_9CN \qquad (4)$$

no exchange of hydrogen with the solvent, as would be predicted if the dihydro-product originated by protonation of the radical anion of naphthalene.

When photocyanation was carried out in CH_3CN-D_2O there was no incorporation of deuterium into either of the reaction products; neither did ϕ_r show any isotope effect. A similar result was obtained for $[^2H_8]$naphthalene in CH_3CN-H_2O. We conclude that equation (4) represents adequately the genesis of these two products.

We compare our proposed mechanism for hydrocarbon photocyanation with that proposed for the functional group replacement reaction of substituted anisoles.[15] Ionization processes are proposed for both, but whereas the latter reaction is thought to involve the monomeric triplet state, we believe that the evidence presented here is most consistent with a reaction in which the singlet excimer participates.

Photocyanation assisted by p-*Dicyanobenzene or Persulphate Ion.*—*p*-Dicyanobenzene is well known as an electron acceptor. We expected that in polar solvents, it would react with the singlet excited arene to produce radical ions [equation (5)]. Indeed, *p*-dicyanobenzene

$${}^1\mathrm{ArH} + \mathrm{Q} \longrightarrow \mathrm{ArH}^{\bullet+} + \mathrm{Q}^{-\bullet} \qquad (5)$$

strongly quenched the fluorescence of both hydrocarbons under study (Table 4). Kinetic experiments with naphthalene showed that in aqueous acetonitrile the reaction is first order in CN^- and in *p*-dicyanobenzene, but not affected by the ArH concentration.

There have been suggestions [10,15] that the beneficial influence of persulphate in photocyanation is that it oxidises an intermediate such as (1). However, we find that persulphate ion behaves in almost all respects parallel to *p*-dicyanobenzene, with strong fluorescence quenching, and kinetic dependence of the reaction on $[\mathrm{CN}^-]$ and $[S_2O_8^{2-}]$ but not on [ArH]. Consequently, we propose Scheme 2 as a reasonable mechanism for

TABLE 3

Kinetic data for direct photocyanation (Scheme 1); $1/\phi_r = a/x + b$

Reagent at constant concentration (M)	x	Slope = a	Intercept = b	Correlation coefficient	P	α
$C_{10}H_8$, 1.0×10^{-3}	CN^-	0.0499 ± 0.0025	13.7 ± 0.3	0.995	3.6×10^{-3}	1.22, 1.25
CN^-, 0.05	$C_{10}H_8$	0.0137 ± 0.0001	1.34 ± 0.08	0.999	1.0×10^{-2}	
$C_{12}H_{10}$, 1.0×10^{-3}	CN^-	0.188 ± 0.017	69 ± 18	0.987	2.7×10^{-3}	38, 24
CN^-, 0.05	$C_{12}H_{10}$	0.0772 ± 0.0091	41.6 ± 5.2	0.987	1.9×10^{-3}	

TABLE 4

Fluorescence quenching constants K_{SV} by the Stern–Volmer method

ArH	Solvent	Q	K_{sv}/l mol^{-1}
$C_{10}H_8$	CH_3CN-H_2O	H_2O_2	7
		$Bu^t{}_2O_2$	13
		$K_2S_2O_8$	82
		DCB [a]	570
	CH_3OH	C_5H_8 [b]	2.1
		C_8H_{14} [c]	105
$C_{12}H_{10}$	CH_3CN-H_2O	$K_2S_2O_8$	58
		DCB	950
	CH_3OH	C_5H_8	29
		C_8H_{14}	130

[a] *p*-Dicyanobenzene. [b] Penta-1,3-diene, mixture of *cis* and *trans*. [c] 2,5-Dimethylhexa-2,4-diene.

these assisted photocyanations. Persulphate differs only in that the dihydrocyanonaphthalene is an insignificant product when persulphate is present suggesting that $S_2O_8^{2-}$ or $SO_4^{-\cdot}$ act as oxidants either for (1) or for the dihydrocyanonaphthalene as proposed before.[10,15]

Scheme 2 leads to equation (6) for the relationship of ϕ_r with the reaction parameters. The data of Table 5

$$
\begin{aligned}
{}^1ArH &\xrightarrow{k_1} ArH \\
{}^1ArH + Q &\xrightarrow{k_2} Q^{-\cdot} + ArH^{\cdot+} \\
ArH^{\cdot+} &\xrightarrow{k_3} \text{unproductive} \\
ArH^{\cdot+} + CN^- &\xrightarrow{k_4} (1) \\
(1) &\xrightarrow{k_5} \text{uuproductive} \\
(1) &\xrightarrow{k_6} \text{products}
\end{aligned}
$$

SCHEME 2

$$\frac{1}{\phi_r} = \left(1 + \frac{k_5}{k_6}\right)\left(1 + \frac{k_3}{k_4[CN^-]}\right)\left(1 + \frac{k_1}{k_2[Q]}\right) \qquad (6)$$

show the expected linear dependence of ϕ_r^{-1} upon $[CN^-]^{-1}$ and $[Q]^{-1}$; there was no dependence of ϕ_r on the naphthalene concentration. The data show scatter because of the large correction of ϕ_r for the control reaction when the variable concentration was zero. This was especially a problem for Q = *p*-dicyanobenzene and the numerical values of k_2 are in poor agreement.

In this system it was possible to extract the rate constant k_2, since k_1 could be obtained from fluorescence measurements.[18] This was done (i) from the K_{SV} measurements (Table 4) using τ_0 determined in aerated solvent and (ii) from the kinetic determination of P_Q, and τ_0 in degassed solution. Values of α ($=1 + k_5/k_6$) were obtained as above.

Conclusions and Synthetic Considerations.—We conclude that both the direct and the assisted photocyanations involve the attack of CN^- on the radical cation of the aromatic hydrocarbon. The photochemical reaction parallels anodic cyanation, a result similar to that obtained recently by Yoshida, who studied the cyanation of nitrogen heterocycles.[19,20] The actual nature of the $ArH^{\cdot+} + CN^-$ interaction is uncertain; while coupling looks reasonable on paper, the possibility of electron transfer cannot be ruled out because CN^- is more easily oxidised than naphthalene in aqueous media. Indeed, Evans and Blount[21] have recently

$$ArH^{\cdot+} + CN^- \longrightarrow ArH + CN\cdot \longrightarrow \begin{matrix}\text{free radical}\\ \text{cyanation}\end{matrix} \qquad (6)$$

advanced evidence for just such a reaction in the CN^-–diphenylanthracene radical cation system.

Although singlet excited naphthalene is oxidised by many reagents, not all these combinations lead to cyanation when CN^- is present. For example, both H_2O_2 and di-t-butyl peroxide quench naphthalene fluorescence; in the presence of CN^-, the former causes rapid destruction of naphthalene but no cyanonaphthalene is formed; the latter peroxide retards the reaction of naphthalene with CN^-. Synthetically, photocyanation will probably be of only limited value, because yields are low and the products are not stable to the reaction conditions. Since the same products can be reached electrochemically, and since the product nitriles are more difficult to oxidise than the substrate hydrocarbons, it seems likely that better selectivity and hence better yields of nitriles will probably be achieved by the electrochemical route.

A final consideration is that these substitution mechanisms should not be unique to cyanide as nucleophile, in that CN^- does not participate in the reaction until after the arene radical cation is formed. Other nucleophiles should thus be able to take the place of cyanide and we are currently investigating this possibility. However, preliminary irradiations of naphthalene with nucleophiles such as OCN^-, SCN^-, acetate, NO_2^-, N_3^-, and Cl^- have so far failed to give clean

TABLE 5

Kinetic data for assisted photocyanation of naphthalene (Scheme 2); $1/\phi_r = a/x + b$

Q	Reagents at constant concentration (M)	x	Slope $= a$	Intercept $= b$	Correlation coefficient	P	k_2 [a]	k_2 [b]	α
$K_2S_2O_8$	Naphthalene, 1.0×10^{-3} $K_2S_2O_8$, 0.020	CN^-	0.087 ± 0.015	1.7 ± 2.0	0.972	0.051	1.8×10^9	2.6×10^9	1.1, 1.7
$K_2S_2O_8$	Naphthalene, 1.0×10^{-3} KCN, 0.050	$S_2O_8^{2-}$	0.035 ± 0.003	3.4 ± 0.8	0.991	0.010			
$C_6H_4(CN)_2$	Naphthalene, 5.0×10^{-3} $C_6H_4(CN)_2$, 5.0×10^{-4}	CN^-	0.0027 ± 0.0002	3.1 ± 0.2	0.992	8.7×10^{-4}	1.5×10^{11}	1.8×10^{10}	2.5, 3.7
$C_6H_4(CN)_2$	Naphthalene, 5.0×10^{-3} KCN, 0.020	$C_6H_4(CN)_2$	0.000 45 ± 0.000 05	3.9 ± 0.5	0.983	1.2×10^{-4}			

[a] $k_2 = (P_Q \times \tau_{degassed})^{-1}$ l mol^{-1} s^{-1}. [b] $k_2 = K_{SV}/\tau_{aerated}$ l mol^{-1} s^{-1}.

photosubstitutions in either the presence or absence of persulphate.*

EXPERIMENTAL

Chemicals were of reagent grade and were free of extraneous impurities (g.c.); solvents were Spectrograde. The fluorometer was a Perkin-Elmer–Hitachi model MPF-2A; fluorescence measurements were made in aerated solutions except as noted. The fluorescence lifetime of naphthalene in degassed and aerated solution in aqueous acetonitrile was determined by a method described previously;[18] the values obtained were 56 and 31 ns respectively. Fluorescence quenching experiments were run at a minimum of five different concentrations of quencher; the Stern–Volmer quenching constants K_{SV} are reported in Table 4. In these experiments [ArH] was 1×10^{-3}M or lower.

Photolyses were run in quartz ampoules of 8 mm o.d. usually containing 2 ml of solution. The ampoules were connected to Pyrex by means of a graded seal for evacuation by the freeze–pump–thaw technique. All reactions were carried out in at least duplicate and analysed at least twice by g.c. For the kinetic experiments, duplicate controls in which the reagent of variable concentration was omitted were always included. The quantum yields of reaction reported in Tables 6 and 7 are corrected for the reaction in the controls. These corrections were small for the direct photolyses, but substantial for the reactions assisted by persulphate ion and, especially, *p*-dicyanobenzene.

TABLE 6

Quantum yields of direct photocyanation

	$[x]$/M	ϕ_r
Naphthalene, 1.0×10^{-3}M, x = CN^-		
	0.005	0.042
	0.008	0.050
	0.010	0.055
	0.020	0.060
	0.030	0.066
	0.050	0.068
Biphenyl, 1.0×10^{-3}M, x = CN^-		
	0.0005	0.0022
	0.0010	0.0045
	0.0020	0.0064
	0.0050	0.0088
	0.0100	0.0091
x = Naphthalene, CN^-, 0.05M		
	0.001	0.066
	0.002	0.121
	0.005	0.248
	0.009	0.355
x = Biphenyl, CN^-, 0.05M		
	0.001	0.0086
	0.002	0.0115
	0.005	0.0193
	0.009	0.0196

TABLE 7

Quantum yields of assisted photocyanation of naphthalene

	x	ϕ_r
Naphthalene 0.001M, $[CN^-]$ 0.05M, x = $S_2O_8^{2-}$		
	0.0025	0.059
	0.005	0.087
	0.010	0.155
	0.025	0.219
Naphthalene 0.001M, $[S_2O_8^{2-}]$ 0.02M, x = CN^-		
	0.0050	0.050
	0.0075	0.083
	0.0100	0.101
	0.0125	0.102
$[CN^-]$ 0.005M, $[S_2O_8^{2-}]$ 0.02M, x = naphthalene		
	0.001	0.19
	0.002	0.20
	0.005	0.22
Naphthalene 0.005M, $[CN^-]$ 0.02M, x = DCB		
	6×10^{-5}	0.085
	8×10^{-5}	0.11
	1×10^{-4}	0.12
	2×10^{-4}	0.15
	4×10^{-4}	0.21
Naphthalene 0.005M, [DCB] 0.0005M, x = CN^-		
	0.0005	0.12
	0.0013	0.20
	0.0025	0.26
	0.0050	0.25
	0.0125	0.28
	0.0250	0.33
$[CN^-]$ 0.0025M, [DCB] 0.0005M, x = naphthalene		
	0.002	0.19
	0.005	0.20
	0.008	0.19

The photolysis apparatus was a Rayonet model RPR photoreactor equipped with 16 model RPR 2537 lamps. A merry-go-round was used to ensure equal light absorption by samples irradiated simultaneously. Ferrioxalate actinometry[22] was used to monitor light absorption; the long wavelength emission from the lamps was measured by actinometry using ferrioxalate solutions with the light filtered through the aromatic hydrocarbon. Then the photon flux absorbed by the hydrocarbon was the difference between the total emission and the filtered measurement.

Reactions were analysed by g.c. (Carle model AGC 211 equipped with flame ionization detector; peak integration was by means of a Spectra-Physics Minigrator). The column was 6 ft × 1/8 in 8% OV 101 on 80—100 Chromosorb W, operated isothermally at 150 °C. Quantitation of peak areas was by the external standard method: a portion of a naphthalene solution was added after reaction to photolyses involving biphenyl, and *vice versa* for photolyses with naphthalene. G.c.–m.s. analyses were run with a 2.5% SE30 on 60—80 Chromosorb W column interfaced with a VG 7070F mass spectrometer operated by Mr. S. McKinnon, to whom we express our thanks.

Effect of Percentage Conversion on Photocyanation.—(i) *Naphthalene.* The stock solutions were as follows: naphthalene, 3.52×10^{-3}M in methanol; sodium cyanide, 0.105M in methanol. The photolysis solutions contained 1.0 ml of each stock solution; they were irradiated at 254 nm for periods in the range 5—60 min (photon flux 1.6×10^{-2}–1.9×10^{-1} einstein l^{-1} absorbed). After photolysis a biphenyl solution (1.0 ml, 3.28×10^{-3}M) was added as a g.c. standard. Naphthalene disappearance and product formation are shown in Figure 1.

(ii) *Biphenyl.* A similar experiment was carried out starting from stock solutions of biphenyl (3.28×10^{-3}M) and sodium cyanide (0.104M). The irradiation times were in the range 5—31 min, after which a naphthalene solution (1.0 ml, 3.46×10^{-3}M) was added as g.c. standard. Figure 2 shows the results of this experiment.

Irradiation of Naphthalene with NaCN *and* 1-*Cyanonaphthalene.*—Commercial 1-cyanonaphthalene was twice recrystallised from ethanol after charcoal treatment. A solution in methanol of concentration 1.04×10^{-3}M was then prepared. Stock solutions of naphthalene and of NaCN in methanol were respectively 1.76×10^{-2}M and

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* These last experiments were carried out by Miss W. de Graaf.

0.105M. Duplicate photolysis mixtures with and without 1-cyanonaphthalene were prepared from NaCN stock (1.0 ml), $C_{10}H_8$ stock (0.5 ml), and either $C_{10}H_7CN$ stock, (0.5 ml) or methanol (0.5 ml). After irradiation at 254 nm for 20 min, the g.c. standard was added. With $C_{10}H_7CN$ present, the consumption of naphthalene was 4.2×10^{-3}M; without $C_{10}H_7CN$, it was 5.1×10^{-4}M.

Sensitisation and Quenching.—The following experiment shows the method for the experiments reported in Table 1. Duplicate solutions (2.0 ml) containing biphenyl (1.0×10^{-3}M; ε_{254} 15 900) in 50% aqueous acetonitrile were prepared from stock solutions, and contained in addition 0, 1.0×10^{-4}M-, and 2.0×10^{-4}M-2,5-dimethylhexa-2,4-diene (ε_{254} 10 600). The six solutions were irradiated simultaneously for 15 min. After photolysis 1.0 ml of a stock solution of naphthalene was added as an external standard to each solution, as well as to an unirradiated pair of samples to serve as a control. By comparison of the peak areas of biphenyl and naphthalene in the irradiated and unirradiated solution, the following values for the extent of reaction were obtained: [Q] = 0, % reaction = 44 ± 1; [Q] = 1.0×10^{-4}M, % reaction = 40 ± 1; [Q] = 2.0×10^{-4}M, % reaction = 44 ± 2. It was concluded that no quenching occurred.

Photocyanation of Naphthalene with Benzophenone at 300 *nm.*—The stock solutions, prepared in methanol, were as follows: NaCN, 0.104M; a mixture of Ph_2CO (0.022M) and $C_{10}H_8$ (3.5×10^{-3}M). The eight samples contained 1.0 ml of each stock solution. The photon flux absorbed and naphthalene consumption are given below. No cyanonaphthalene was detected upon g. c. analysis.

Photon flux (einstein l^{-1})	$[C_{10}H_8]$ used (M)
7.7×10^{-2}	2.0×10^{-4}
1.7×10^{-1}	5.3×10^{-4}
2.6×10^{-1}	5.8×10^{-4}
4.4×10^{-1}	1.13×10^{-3}

Photolysis of Biphenyl in the Presence of NaCN *and Acetone at* 300 nm.—Working solutions contained biphenyl (1.64×10^{-3}M), sodium cyanide (0.052M), and acetone (0.125M) in methanol. Approximately 50% of the incident light was absorbed. After photolyses lasting for up to 2.0 h (0.31 einstein l^{-1}) no change in the concentration of biphenyl could be detected by g. c. analysis.

Photolysis of Hydrocarbons with Methanolic NaCN *in the Presence of Piperylene.*—(i) *Naphthalene at* 300 *nm.* The duplicate solutions contained naphthalene (4.33×10^{-3}M), NaCN (0.055M), and piperylene (0, 0.006, 0.011, and 0.015M). The piperylene was freshly distilled before use. After a total of 5.2×10^{-2} einstein l^{-1} had fallen on the solutions, the concentrations of naphthalene remaining were respectively 4.03×10^{-3}, 3.99×10^{-3}, 3.90×10^{-3}, and 3.78×10^{-3}M.

(ii) *Biphenyl at* 254 *nm.* Duplicate methanolic solutions containing biphenyl (5.5×10^{-4}M), NaCN (0.052M), and piperylene were subjected to the passage of 2.5×10^{-2} einstein l^{-1}. The amount of biphenyl remaining is given below.

$[C_5H_8]$ (M)	$[C_{12}H_{10}]$ remaining (M)
0	4.9×10^{-4}
6.0×10^{-4}	4.0×10^{-4}
1.2×10^{-3}	3.4×10^{-4}
2.0×10^{-3}	2.7×10^{-4}

Effect of Solvent on Naphthalene Photocyanation.—Stock solutions used contained $C_{10}H_8$ in methanol (3.39×10^{-2}M) and NaCN in methanol (0.409M). Six 10 ml volumetric flasks were made up, each containing $C_{10}H_8$ stock solution (1.0 ml), NaCN stock solution (1.0 ml), amounts of water in the range 0.5—5 ml, and filled to the mark with methanol. After the passage of 3.1×10^{-2} einstein l^{-1}, analysis gave the results shown in Figure 3.

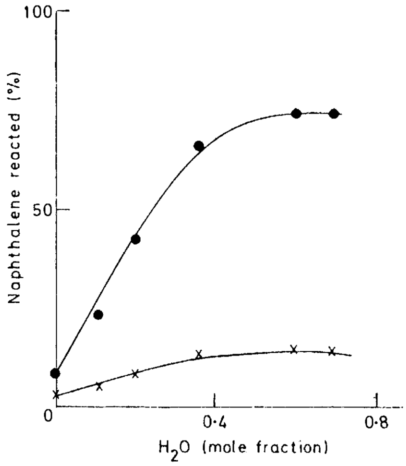

FIGURE 3 Percentage conversion of naphthalene in a 10 min irradiation of 3.39×10^{-3}M-naphthalene with 0.41M-NaCN in aqueous methanol; ● mol % naphthalene reacted; × mol % cyanonaphthalene; + dihydrocyanonaphthalene formed

Deuteriation Studies.—The following experiments are typical. A solution of CH_3CN–H_2O was prepared from CH_3CN (3.928 5 g) and H_2O (5.000 0 g); a CH_3CN–D_2O solution was prepared from CH_3CN (3.916 4 g) and D_2O (5.541 2 g). Weights of naphthalene, KCN, and $K_2S_2O_8$ (where appropriate) were such that in the final solutions, their concentrations were 0.01, 0.05, and 0.05M, respectively. Following irradiation, portions of a stock solution of biphenyl were added as a g.c. standard. Percent reactions were: (a) no persulphate, irradiation time 5 min, CH_3CN–H_2O 71%, CH_3CN–D_2O, 72%; (b) persulphate present, irradiation time 1 min, CH_3CN–H_2O 31%, CH_3CN–D_2O 35%. G.c.–m.s. analyses gave data as follows: (a) no persulphate, CH_3CN–H_2O, cyanonaphthalene, $(M + 1)/M = 0.16$, dihydrocyanonaphthalene $(M + 1)/M = 0.13$; (b) no persulphate, CH_3CN–D_2O, cyanonaphthalene $(M + 1)\ M = 0.17$, dihydrocyanonaphthalene $(M + 1)/M = 0.13$; (c) persulphate, CH_3CN–H_2O, cyanonaphthalene $(M + 1)/M = 0.16$, dihydrocyanonaphthalene $(M + 1)/M = 0.13$; (d) persulphate, CH_3CN–D_2O, cyanonaphthalene $(M + 1)/M = 0.15$, dihydrocyanonaphthalene $(M + 1)/M = 0.13$.

Kinetic Experiments.—(i) *In aqueous acetonitrile.* The solutions were made up to have the concentrations of reagents given in Tables 6 and 7. The duplicates were run by repeating the whole series of data points because the merry-go-round could not accommodate the duplicate simultaneously. Where close agreement between points was not obtained, at least two further replicates were run; a deviant data point was only rejected if at least three of four determinations were concordant. Quantum yields of reaction were corrected for reaction in the controls, and the equations to the plots of $1/\phi_r$ *versus* $1/[X]$ were found using a least squares procedure.

(ii) *In methanol.* In this solvent, the effect of [ArH] upon ϕ_r was difficult to evaluate because of the nonlinearity of the plot of mol ArH consumed *versus* einsteins absorbed. Extrapolation to zero conversion gave the results of Table 2.

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