ON THE DETERMINATION OF QUANTUM YIELDS OF REACTION IN SOLUTION

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Summary

Expressions were developed to calculate the quantum yields of reaction in solution in systems where the reaction products compete with the starting material for absorption of the incident light. These expressions are applied to problems currently being studied in our laboratory, both for determining quantum yields of reaction and for testing whether excimers participate in selected photoreactions.

1. Introduction

The quantum yield ϕ_r of reaction for a photochemical process may be defined as the ratio of the number of molecules (or moles) of the substance undergoing the reaction in question to the number of photons (or einsteins) absorbed by the substrate. In solution a common strategy is to use concentrations of reactants such that all the incident light is absorbed during the whole period throughout which the reaction is monitored. Provided that the reactant is the only light-absorbing species, the absorbed light intensity I_{abs} is equal to the incident light intensity I_0. Then, for the hypothetical reaction $A \xrightarrow{h\nu} B$, ϕ_r is given simply by eqn. (1).

$$- \frac{d[A]}{dt} = \phi_r I_{abs} = \phi_r I_0 \tag{1a}$$

$$[A]_0 - [A]_t = \Delta[A] = \phi_r I_0 t \tag{1b}$$

Under these conditions, ϕ_r is obtained by measuring only two quantities, *i.e.* the total dose of light absorbed (usually by conventional actinometry) and the amount of substrate reacted (using some analytical method such as spectrophotometry or gas chromatography). Whether these conditions are satisfied will be shown by the direct dependence of $\Delta[A]$ on the photon dose and the independence of $\Delta[A]$ on the initial substrate

concentration. A familiar example of this situation is the photoreduction of benzophenone in solvents such as isopropyl alcohol, using radiation $\lambda > 300$ nm.

$$Ph_2CO \xrightarrow[\text{[H]}]{h\nu} \tfrac{1}{2}Ph_2\overset{\displaystyle OH}{\overset{|}{C}}\!\!\!-\!\!\!\overset{\displaystyle OH}{\overset{|}{C}}Ph_2 \tag{2}$$

The product of this reaction has essentially no absorption at wavelengths above 300 nm and eqn. (1b) will hold provided that the concentrations are not so high that the product precipitates from solution.

A common problem is that the products of a photochemical reaction are not transparent to the exciting radiation. Substitution reactions of aromatic compounds would constitute a typical case. If product B is formed quantitatively and acts simply as a filter, then eqn. (1a) must be modified as follows:

$$-\frac{d[A]}{dt} = \phi_r I_{abs} = \phi_r I_0 \, \frac{\epsilon_A[A]}{\epsilon_A[A] + \epsilon_B[B]} \tag{3}$$

Here ϵ_A and ϵ_B are the spectroscopic extinction coefficients of A and B at the wavelength of interest. The integrated form of an equation analogous to eqn. (3) has been obtained previously by Zimmerman $et\ al.$ [1]. More generally, there will be a series of products B, C, D, . . . formed in mole fractional yields $\beta, \gamma, \delta, \ldots$ and eqn. (3) becomes

$$-\frac{d[A]}{dt} = \phi_r I_0 \, \frac{\epsilon_A[A]}{\epsilon_A[A] + \beta\epsilon_B([A]_0 - [A]) + \gamma\epsilon_C([A]_0 - [A]) + \ldots} \tag{4}$$

Rearranging eqn. (4) we obtain

$$-d[A] + \left(1 - \frac{[A]_0}{[A]}\right)\frac{\Sigma\beta\epsilon_B}{\epsilon_A}\,d[A] = \phi_r I_0\,dt \tag{5}$$

The integration of eqn. (5) gives

$$\Delta[A]\left(1 - \frac{\Sigma\beta\epsilon_B}{\epsilon_A}\right) + [A]_0\,\frac{\Sigma\beta\epsilon_B}{\epsilon_A}\,\ln\left(\frac{[A]_0}{[A]}\right) = \phi_r I_0 t \tag{6}$$

In principle, ϕ_r can be extracted from eqn. (6). However, this is not often practical because of the need for a complete material balance in the reaction, together with extinction coefficients for all products. We therefore devised two useful approximations to eqn. (6).

1.1. Approximation 1

We assume that the products B, C, D, . . . can be represented by one hypothetical composite product P which is formed from A in 100% yield

and which has an extinction coefficient ϵ_p. Equation (7) then follows from manipulations corresponding to those given earlier.

$$\Delta[A]\left(1 - \frac{\epsilon_p}{\epsilon_A}\right) + [A]_0 \frac{\epsilon_p}{\epsilon_A} \ln\left(\frac{[A]_0}{[A]}\right) = \phi_r I_0 t \qquad (7)$$

The form of eqn. (7) can be checked as follows: when $\epsilon_p = 0$ (transparent product), eqn. (7) reduces to eqn. (1b); when $\Delta[A]$ is very small (conversion is kept very low)

$$\frac{[A]_0 \epsilon_p}{\epsilon_A} \ln\left(\frac{[A]_0}{[A]}\right) = -[A]_0 \frac{\epsilon_p}{\epsilon_A} \ln\left(1 - \frac{\Delta[A]}{[A]_0}\right)$$

$$\approx \Delta[A] \frac{\epsilon_p}{\epsilon_A}$$

and again eqn. (7) reduces to eqn. (1b).

Evaluation of ϕ_r now requires the following measurements: (i) actinometry to measure $I_0 t$; (ii) analysis for the disappearance of starting material A; (iii) absorption spectroscopy to apportion the total absorbance between unreacted A and the amount of product P, equal to $[A]_0 - [A]$, which has been formed.

1.2. Approximation 2

Approximation 2 is useful for high yield substitution reactions. The reactant and product are assumed to have equal extinction coefficients. Then eqn. (3) becomes eqn. (8) which integrates into eqn. (9). Equation (9) is also obtained by substituting $\epsilon_p = \epsilon_A$ into eqn. (7).

$$-\frac{d[A]}{dt} = \phi_r I_0 \frac{[A]}{[A]_0} \qquad (8)$$

$$[A]_0 \ln\left(\frac{[A]_0}{[A]}\right) = \phi_r I_0 t \qquad (9)$$

2. Quantum yields of reaction

The quantum yields of reaction in solution are usually evaluated according to eqn. (1b) even when the reaction product(s) are not transparent to the incident radiation. Equation (7) shows that this approach will work provided that the conversion of starting material is kept sufficiently low. Normally this is easy to accomplish if the quantum yields of product formation are desired, since the appearance of a product can be measured at very low conversions. However, when the quantum yields ϕ_r for the disappearance of reactant are to be measured, the use of eqn. (1b) is tedious at best; this is because the graph of moles reacted against einsteins absorbed ought to be extrapolated to zero conversion and ϕ_r estimated from the slope of the lim-

iting linear portion of the graph. This may be difficult to achieve because in order to measure $\Delta[A]$, the amount of substrate reacted, at all accurately the values of $[A]_0$ and $[A]_t$ must be significantly different. For example, for analysis by gas chromatography we would usually like $\Delta[A]$ to represent *at least* 10% conversion.

Now, if the product is strongly absorbing, serious underestimates of ϕ_r will be made by applying eqn. (1b) compared with ϕ_r obtained by evaluating the left-hand side of eqn. (7), which we shall term f(A). Thus, if $\epsilon_p = 3\epsilon_A$, then f(A) = $1.16\Delta[A]$ at 10% conversion and $1.35\Delta[A]$ at 20% conversion.

We now apply these equations to some problems under study in our laboratory. The photodechlorination of chlorobiphenyls [2] is such a case. The o-substituted biphenyls are much less strongly absorbing than the biphenyls with only m and p substituents. Photolysis of o-chlorobiphenyls leads to a preferential loss of o -substituents and hence to a more strongly absorbing product.

The photodechlorination of 2-chlorobiphenyl as a function of photon dose is shown in Fig. 1 where cyclohexane is the solvent. Biphenyl (67%) is the chief product early in the reaction. It is very difficult to obtain ϕ_r from the limiting slope of Fig. 1 at zero conversion. However, a plot of f(A) against photon dose, shown in Fig. 2, allows ϕ_r to be deduced easily as 0.35 in this solvent. The data were calculated in two ways: (i) by taking the yield of biphenyl (67%) and multiplying the ratio of the measured extinction coefficients of 2-chlorobiphenyl and biphenyl at 254 nm by 0.67 (Fig. 2, open
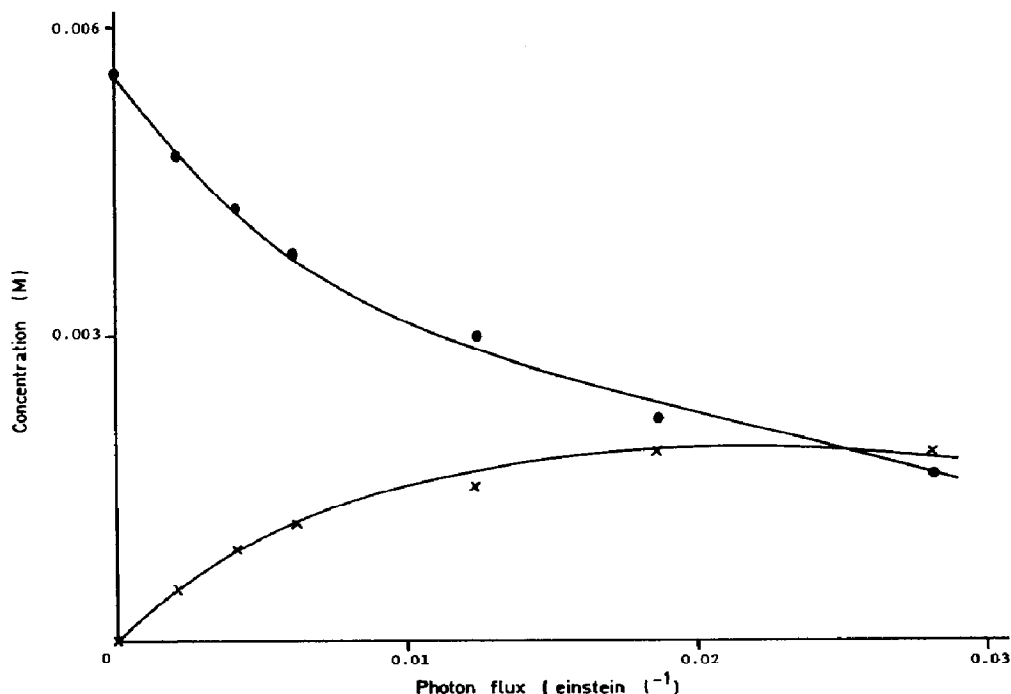

Fig. 1. Photodechlorination of 2-chlorobiphenyl as a function of photon flux: ●, disappearance of 2-chlorobiphenyl; ×, formation of biphenyl.
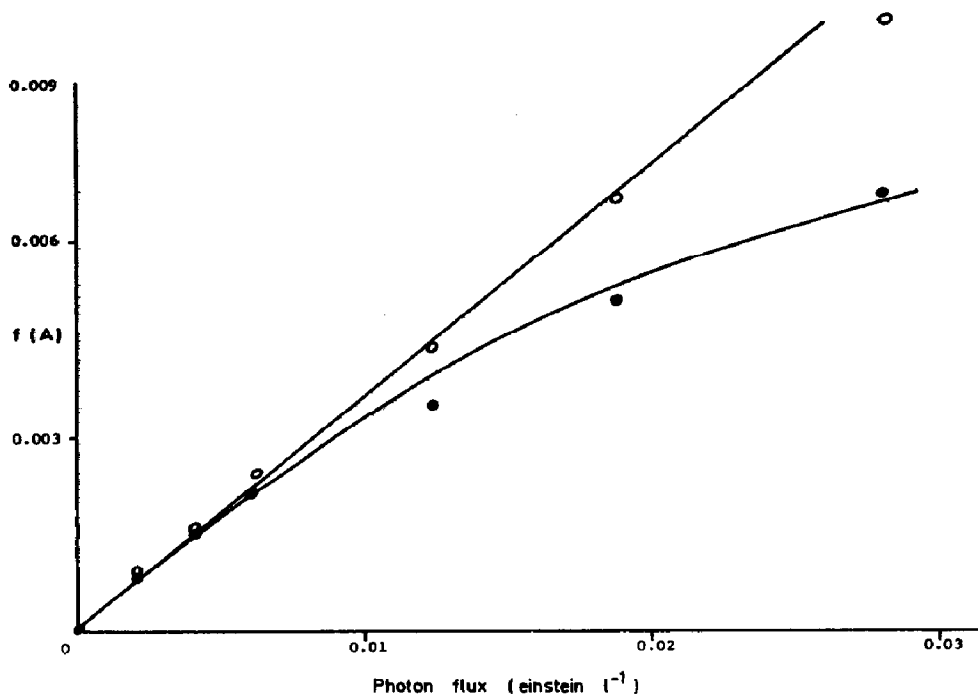
Fig. 2. Photodechlorination of 2-chlorobiphenyl with the data plotted according to eqn. (7): ○, calculated by method (i); ●, calculated by method (ii).

circles); (ii) by the apportionment of the total absorbance as described above (Fig. 2, full circles). The apportionment method suffers more from error accumulation and there is more divergence from a straight line. Significantly, however, both methods yield the same value of ϕ_r.

A similar but rather more complicated situation is found for the photolysis of 2,4,6-trichlorobiphenyl in cyclohexane. Figure 3 shows the progress of the reaction; it is seen that once again ϕ_r cannot confidently be determined directly. In addition, it is clear that secondary photolysis is occurring, for the initial product 2,4-dichlorobiphenyl never accumulates in solution and 4-chlorobiphenyl seems to be formed essentially from time zero. Presumably excitation migration accounts for the rapid photolysis of 2,4-dichlorobiphenyl, for which ϕ_r has previously [2] been determined as about 0.6. When absorption measurements were made on the photolysed solutions, only small changes in absorption were found with increased conversion of starting material; and since the product composition varies with conversion because of secondary photolysis, the data were analysed by eqn. (9). This is shown in Fig. 4, from the initial slope of which we deduce $\phi_r = 0.21$ for 2,4,6-trichlorobiphenyl photodechlorination in cyclohexane.

3. Role of excimers in photoreactions

The participation of excimers in a photochemical reaction can be expected to lead to changes in ϕ_r as the initial concentration of ground state
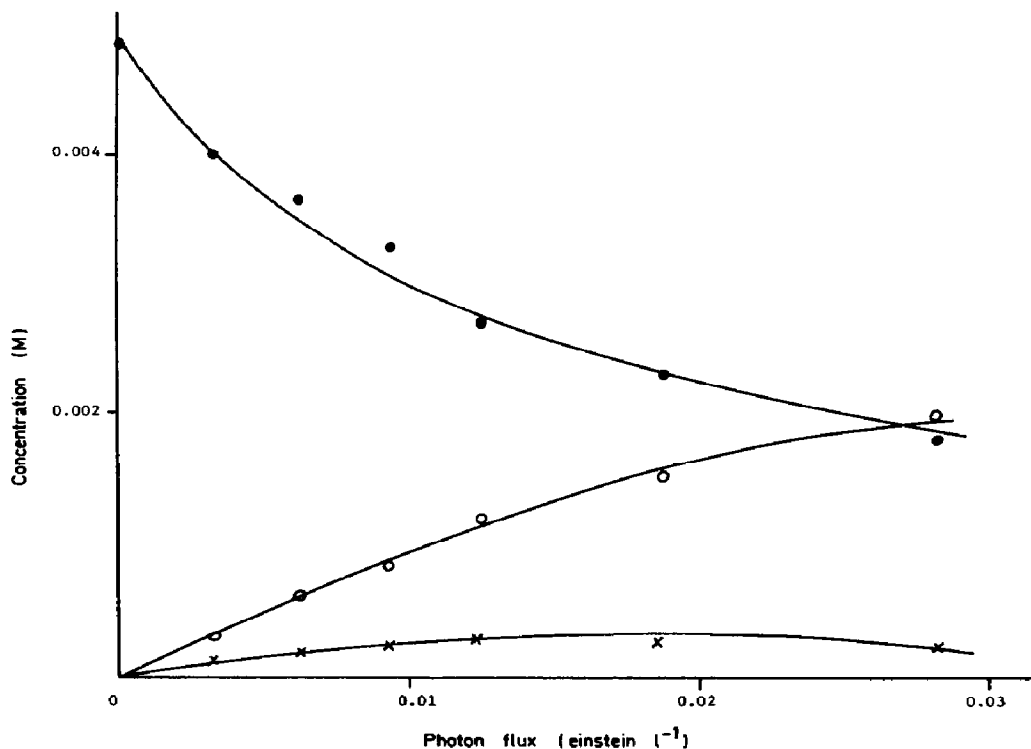
Fig. 3. Photodechlorination of 2,4,6-trichlorobiphenyl as a function of photon flux: ●, disappearance of 2,4,6-trichlorobiphenyl; ×, formation of 2,4-dichlorobiphenyl; ○, formation of 4-chlorobiphenyl.

substrate is varied. In order to test photochemical reaction schemes kinetically, it will be necessary to obtain ϕ_r at a range of initial substrate concentrations; as we have seen already, the determination of ϕ_r is not always straightforward. In the examples which follow, we have applied our expressions for quantum yield determination to reactions where excimer participation may be implicated. The kinetic effect, or its absence, is seen much more easily than by the conventional method of extrapolating the graph of $\Delta[A]$ against photon dose back to zero conversion.

As a first example, let us consider the photoreduction of 4-chlorobiphenyl assisted by triethylamine. This reaction is believed [3] to involve the quenching of the excited monomeric chloro compound by triethylamine [3]. No involvement of an excimer would be expected in this reaction and ϕ_r should be independent of $[ArCl]_0$.

$$ArCl^* + Et_3N \rightarrow Et_3N^{\cdot+} + ArCl^{\cdot-} \rightarrow \rightarrow ArH + HCl$$
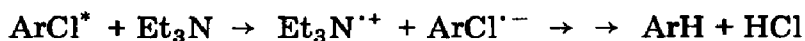
The data of Table 1 were obtained by exposing methanolic solutions of equal triethylamine concentration and varying 4-chlorobiphenyl concentration to equal photon fluxes. From the amount $\Delta[A]$ of 4-chlorobiphenyl reacted, photolability appears to rise with initial substrate concentration. If ϕ_r is calculated from eqn. (1b), a good straight-line relationship between ϕ_r^{-1}
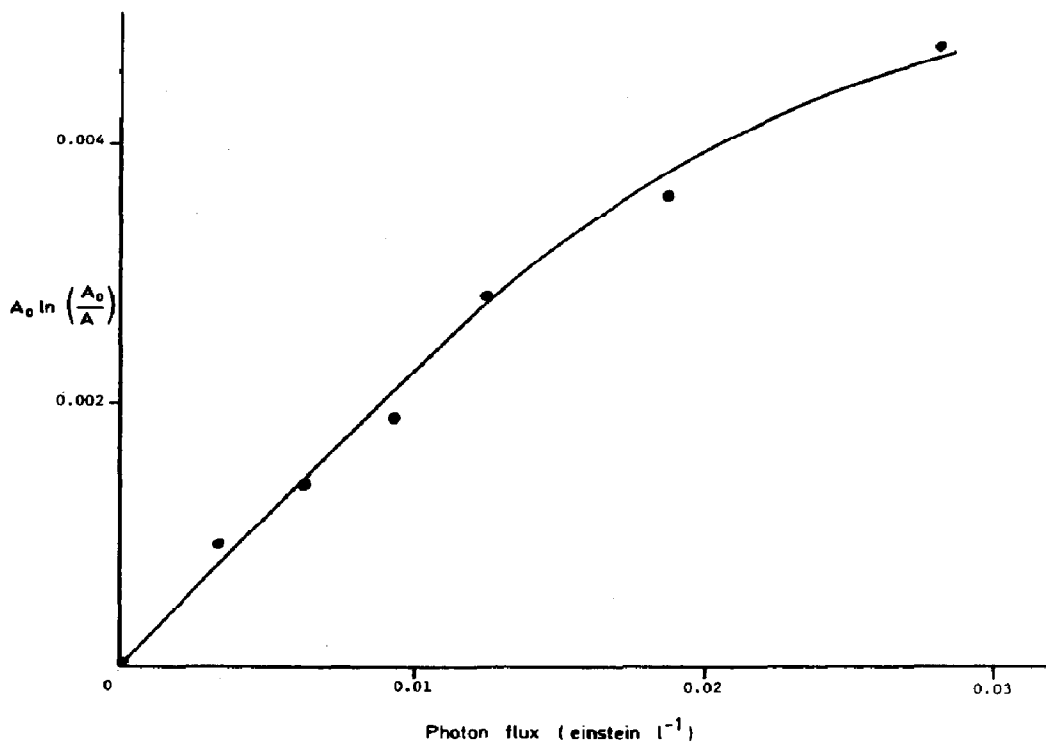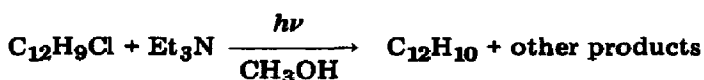
Fig. 4. Photodechlorination of 2,4,6-trichlorobiphenyl plotted according to eqn. (9).

TABLE 1

Photolysis of 4-chlorobiphenyl with 0.103 M triethylamine in methanol

Initial $[C_{12}H_9Cl]$ (M)	Amount consumed (M)	$[A]_0$ ln $([A]_0/[A])$ (M)	ϕ_r[a]
9.6×10^{-4}	7.1×10^{-4}	1.29×10^{-3}	0.14
1.92×10^{-3}	8.7×10^{-4}	1.15×10^{-3}	0.12
3.36×10^{-3}	1.01×10^{-3}	1.20×10^{-3}	0.13
4.80×10^{-3}	1.19×10^{-3}	1.35×10^{-3}	0.14

$$C_{12}H_9Cl + Et_3N \xrightarrow[CH_3OH]{h\nu} C_{12}H_{10} + \text{other products}$$

[a]From eqn. (9).

and $[C_{12}H_9Cl]^{-1}$ is obtained, suggesting that an excimer intermediate is involved in the reaction. However, no excimer is in fact reactive; the apparent increase in reactivity is an illusion which occurs because the solutions of different concentration were irradiated to different conversions. Retardation of the reaction by the product biphenyl is more pronounced in the more dilute solutions. Since substrate and product have comparable absorptivities, eqn. (9) was applied, and it can be seen from Table 1, last column, that ϕ_r is invariant with the concentration of 4-chlorobiphenyl. This result can also be obtained by extrapolation at each initial concentration back to

zero conversion, but eqn. (9) provides a simpler test to rule out the involvement of excimers.

The photocyanation of naphthalene [4] presents a contrasting situation. We deduced [5] that this reaction involves the naphthalene excimer, and it would be expected therefore that ϕ_r^{-1} should be proportional to $[C_{10}H_8]^{-1}$.

$$C_{10}H_8{}^* + C_{10}H_8 \rightarrow (C_{10}H_8)_2{}^* \xrightarrow{\ CN^-\ } C_{10}H_7CN$$

A conventional extrapolation study will be reported elsewhere [5]. For the present purposes, solutions of naphthalene (variable concentration) and KCN (fixed concentration) in aqueous acetonitrile were illuminated simultaneously, affording the results of Table 2. As in the previous example, the amount reacted increases with concentration. Equation (9) was selected to analyse the results because absorption studies showed that, as the conversion increased, the absorbance of the solutions first increased slightly and then decreased. A monotonic increase of ϕ_r with concentration was thereby established, and a plot of ϕ_r^{-1} against $[C_{10}H_8]_0^{-1}$ was found to be linear (Fig. 5) in conformity with the proposed mechanism.

A similar approach was taken to demonstrate the suppression of the photoreactivity of chlorobenzene by competing excimer formation [6].
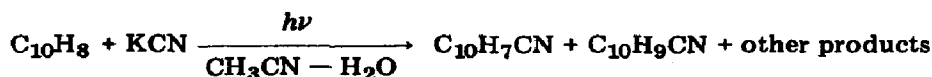
$$PhCl^* \rightarrow \rightarrow products$$

$$PhCl^* + PhCl \rightarrow excimer \rightarrow 2PhCl$$
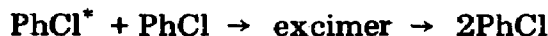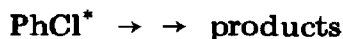
Such a scheme leads to a kinetic expression where ϕ_r^{-1} is proportional to [PhCl]. The validity of this scheme was first shown by the conventional extrapolation method [6]. It was also demonstrated by the use of eqn. (9) which was chosen because both chlorobenzene and the main reaction product benzene exhibit vibrational fine structure in their electronic spectra near 254 nm. Our photolysis equipment did not provide monochromatic radiation and, since the absorption profile of the reaction mixtures in the range 250 - 275 nm showed that the average absorbance over this range was only

TABLE 2

Photocyanation of naphthalene with 0.050 M KCN in 1:1 aqueous acetonitrile

Initial $[C_{10}H_8]$ (M)	Amount reacted (M)	$[A]_0 \ln ([A]_0/[A])$ (M)	$\phi_r{}^a$
1.0×10^{-3}	8.3×10^{-4}	1.84×10^{-3}	0.14
2.0×10^{-3}	1.50×10^{-3}	2.78×10^{-3}	0.22
5.0×10^{-3}	3.09×10^{-3}	4.81×10^{-3}	0.38
9.0×10^{-3}	4.41×10^{-3}	6.22×10^{-3}	0.45

$$C_{10}H_8 + KCN \xrightarrow[\ CH_3CN - H_2O\ ]{h\nu} C_{10}H_7CN + C_{10}H_9CN + other\ products$$

[a]From eqn. (9).
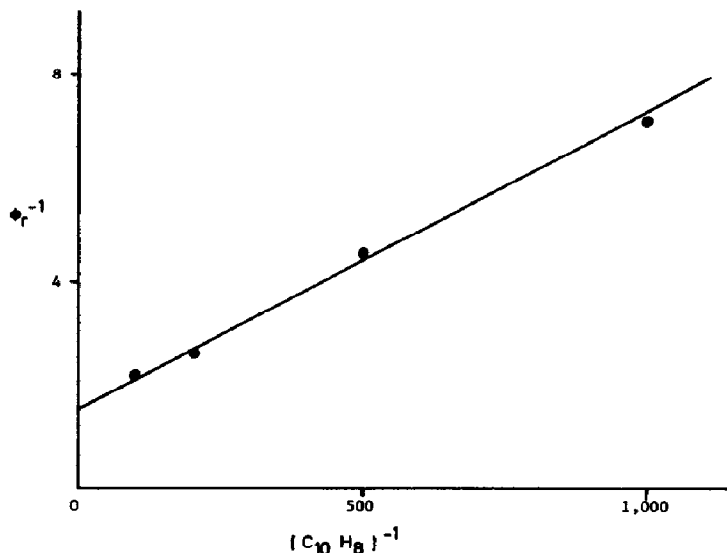
Fig. 5. Plot of ϕ_r^{-1} against $[C_{10}H_8]^{-1}$ in the photocyanation of naphthalene with 0.050 M KCN in equal volumes of water and acetonitrile.

slightly dependent on conversion, we concluded that eqn. (9) was the most appropriate expression to use.

The data are given in Table 3 and were obtained by simultaneous irradiation of cyclohexane solutions with different concentrations of chlorobenzene. They are calculated relative to [PhCl] = 0.020 M as its own actinometer. The proper relationship $\phi_r^{-1} \propto$ [PhCl] is shown to hold in Fig. 6. With ϕ_r determined as 0.41 for the 0.020 M solution, we find the limiting quantum yield at infinite dilution to be 0.58 from Fig. 6, compared with 0.54 obtained by the conventional method [6].

TABLE 3

Photodechlorination of chlorobenzene in cyclohexane

Initial $[C_6H_5Cl]$ (M)	Amount reacted (M)	$[A]_0 \, ln \, ([A]_0/[A])$ (M)	ϕ_{rel}[a]
0.010	8.60×10^{-3}	0.0197	1.13
0.020	1.17×10^{-2}	0.0175	1.00
0.031	1.22×10^{-2}	0.0154	0.88
0.051	9.61×10^{-3}	0.0106	0.61
0.071	8.60×10^{-3}	0.0093	0.53

$$C_6H_5Cl \xrightarrow[C_6H_{12}]{h\nu} C_6H_6 + \text{other products}$$
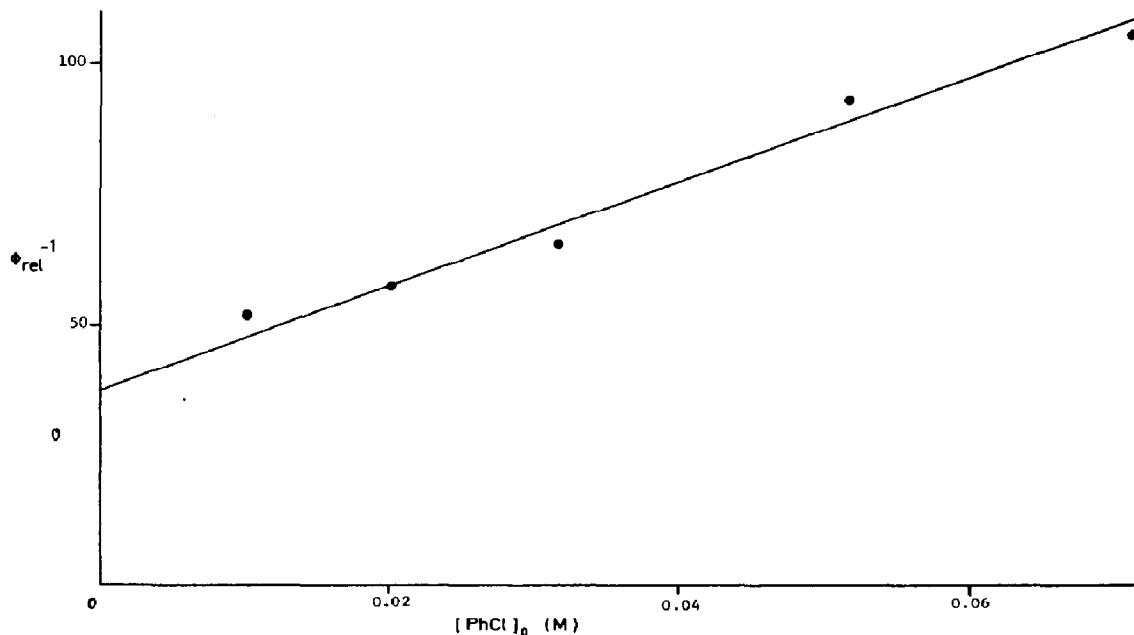
[a]Relative to 0.020 M solution.

Fig. 6. Dependence of ϕ_r on the concentration of chlorobenzene in the photodechlorination of chlorobenzene in cyclohexane. Data are relative to $\phi_{rel}(0.020\ M) = 1.00$.

4. Conclusions

We conclude that the expressions developed here for evaluating ϕ_r can be applied usefully to reactions where the product(s) compete with starting material for the incident radiation. However, a premise of the method is that the product(s) simply act as an internal filter. We must expect these expressions to be less useful if this is not the case; for example (i) if the products are themselves photolabile or (ii) if the products interact photochemically with the starting materials as, for example, by energy transfer or electron transfer processes.

5. Experimental

Full experimental details of the photochemical apparatus, methods for evacuating solutions, actinometry with correction for radiation at wavelengths absorbed by the sample, and gas–liquid chromatography (GLC) analysis are given in the papers cited in the reference list.

All photolyses were carried out in duplicate, using evacuated quartz ampoules 8 mm in outside diameter. Concentrations were adjusted so that all the incident light of wavelength 250 - 275 nm was absorbed. GLC analyses on each sample were carried out in at least duplicate, using the internal standard method. Absorption spectroscopy measurements were made on appropriately diluted photolysed solutions following the GLC analysis.

Acknowledgment

References

1 H. E. Zimmerman, R. C. Hahn, H. Morrison and M. C. Wani, *J. Am. Chem. Soc.*, *87* (1965) 1138.
2 N. J. Bunce, Y. Kumar, L. Ravanal and S. Safe, *J. Chem. Soc., Perkin Trans. II*, (1978) 880.
3 M. Ohashi, K. Tsujimoto and K. Seki, *J. Chem. Soc., Chem. Commun.*, (1973) 384.
4 J. A. J. Vink, P. L. Verheijdt, J. Cornelisse and E. Havinga, *Tetrahedron*, *28* (1972) 5081.
5 N. J. Bunce, J. P. Bergsma and J. L. Schmidt, submitted to *J. Chem. Soc.*
6 N. J. Bunce and L. Ravanal, *J. Am. Chem. Soc.*, *99* (1977) 4150.
   N. J. Bunce, J. P. Bergsma, M. D. Bergsma, W. de Graaf, Y. Kumar and L. Ravanal, *J. Org. Chem.*, *45* (1980) 3708.