

## COMPUTER ANALYSIS OF MIXING PROBLEMS ARISING IN CONSECUTIVE PHOTOCHEMICAL REACTIONS

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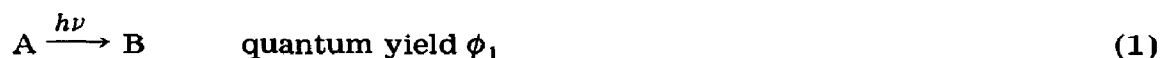
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### Summary

The importance of agitation processes, particularly molecular diffusion, in the kinetics of formation of products of consecutive photoreactions is demonstrated and some types of photoreactors adapted to the simplified study of such reactions are proposed.

### 1. Introduction

Simmons [1] and Erler and Tyler [2] have recently reviewed the equations for consecutive photochemical reactions, which are first order with respect to the intensity of the absorbed light, in a stirred batch reactor. The following processes are involved in these reactions:



It is assumed that A and B are unchanged in the absence of these reactions.

In refs. 1 and 2 the reactor is assumed to be perfectly stirred such that the composition of reactants and products is uniform and independent of the position ( $x, y, z$ ) in the reactor. Under these conditions, the equations derived by Simmons [1] are perfectly rigorous and can be used to determine the relative efficiencies of reactions (1) - (3). However, in addition to mistakes in the formulae given in ref. 2, no indication as to whether the photochemical reactor was stirred is given although this factor is of crucial importance as shown in refs. 3 and 4. Despite these difficulties the kinetic

problem discussed in ref. 2 is very interesting and in this paper we give an extended treatment of the problem, including the effects of stirring, in the reactor which is illustrated using data from ref. 2.

## 2. The case of a perfectly stirred batch reactor

In order to simplify the mathematical treatment of such reactors, an example of which is shown in Fig. 1, we assume that the light is monochromatic and is perpendicular to the front of the photoreactor.

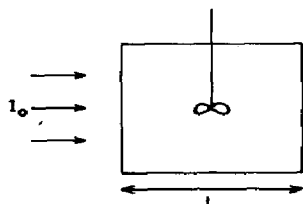


Fig. 1. Schematic representation of a perfectly stirred photochemical reactor.

If the reactor is perfectly stirred the kinetic rate equations describing the variations in the bulk concentration  $\bar{C}_i$  can be written as follows:

$$\frac{d\bar{C}_A}{dt} = I(L) \frac{-\phi_1 \epsilon_A \bar{C}_A + \phi_1' \epsilon_B \bar{C}_B}{\epsilon_A \bar{C}_A + \epsilon_B \bar{C}_B + \epsilon_C \bar{C}_C} \quad (4)$$

$$\frac{d\bar{C}_B}{dt} = I(L) \frac{\phi_1 \epsilon_A \bar{C}_A - (\phi_1' + \phi_2) \epsilon_B \bar{C}_B}{\epsilon_A \bar{C}_A + \epsilon_B \bar{C}_B + \epsilon_C \bar{C}_C} \quad (5)$$

$$\frac{d\bar{C}_C}{dt} = I(L) \frac{\phi_2 \epsilon_B \bar{C}_B}{\epsilon_A \bar{C}_A + \epsilon_B \bar{C}_B + \epsilon_C \bar{C}_C} \quad (6)$$

where  $I(L)$  is the light intensity in einsteins per second per centimetre cubed absorbed in a reactor of length  $L$  and the  $\epsilon_i$  are the molar extinction coefficients.  $I(L)$  is given by

$$I(L) = I_0 \bar{F} / V \quad (7)$$

where  $I_0$  is the intensity of the irradiating light at the entrance window,  $\bar{F}$  is the fraction of light absorbed which can be written

$$\bar{F} = 1 - 10^{-(\epsilon_A \bar{C}_A + \epsilon_B \bar{C}_B + \epsilon_C \bar{C}_C)L} \quad (8)$$

and  $V$  is the volume of the reactor.

The variation in the concentrations of A, B and C with time can be calculated from the data for  $\epsilon_i$ ,  $\bar{C}_i$  at  $t = 0$ ,  $I_0$  and  $L$ .

## 3. The case of a non-stirred reactor

In a non-stirred reactor the concentrations  $C_i$  are not constant. For parallel irradiation as shown in Fig. 1 they are a function of the distance  $x$

from the entrance window. In the absence of external stirring the effects of molecular diffusion and thermal convection, which are negligible in the stirred reactor, must be taken into consideration.

We denote by  $D_i$  the coefficients of molecular diffusion of the products. The kinetic rate equations for a layer of solution at a distance  $x$  from the entrance window can be written

$$\frac{\partial C_A}{\partial t} = D_A \nabla^2 C_A + i(x) \frac{-\phi_1 \epsilon_A C_A + \phi_1' \epsilon_B C_B}{\epsilon_A C_A + \epsilon_B C_B + \epsilon_C C_C} \quad (9)$$

$$\frac{\partial C_B}{\partial t} = D_B \nabla^2 C_B + i(x) \frac{\phi_1 \epsilon_A C_A - (\phi_1' + \phi_2) \epsilon_B C_B}{\epsilon_A C_A + \epsilon_B C_B + \epsilon_C C_C} \quad (10)$$

$$\frac{\partial C_C}{\partial t} = D_C \nabla^2 C_C + i(x) \frac{\phi_2 \epsilon_B C_B}{\epsilon_A C_A + \epsilon_B C_B + \epsilon_C C_C} \quad (11)$$

$i(x)$  is the local absorbed light intensity in einsteins per second per cubic centimetre at  $x$  and is given by

$$i(x) = \frac{L}{V} I_0 \frac{dF(x)}{dx} \quad (12)$$

where

$$F(x) = 1 - 10^{-\int_0^x (\epsilon_A C_A + \epsilon_B C_B + \epsilon_C C_C) dx} \quad (13)$$

*i.e.*

$$\frac{i(x)}{\epsilon_A C_A + \epsilon_B C_B + \epsilon_C C_C} = \frac{L}{V} I_0 \ln(10) \times 10^{-\int_0^x (\epsilon_A C_A + \epsilon_B C_B + \epsilon_C C_C) dx} \quad (14)$$

It should be noted that the bulk concentrations (as measured by spectrophotometry for instance) are given by

$$\bar{C}_i = \frac{1}{L} \int_0^L C_i(x) dx \quad (15)$$

This new set of differential equations can only be solved by a numerical calculation. However, a simple solution can be obtained for the following limiting conditions.

(1) When the intensity of the absorbed light is very low, diffusion becomes a very important factor in homogenization and the reactor can be considered as a stirred batch reactor. These conditions can easily be achieved when the reactants and the products are gases ( $D \approx 1 \text{ cm}^2 \text{ s}^{-1}$  [5] at atmospheric pressure), but the case for a liquid is quite different. For example, with  $D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (cyclohexane),  $\phi = 1$  and  $L = 10 \text{ cm}$  (where  $L$  is the length of the reactor), the mixing time is  $L^2/D \approx 10^7 \text{ s}$ . This is much longer than the time required for homogenization which is assisted by thermal stirring from the temperature gradient or than the photochemical reaction time.



TABLE 1

Data for the computer analysis of the photoreactions at 366 nm of  $Mn_2(CO)_{10}$  in acetonitrile and  $W(CO)_6$  with pyridine<sup>a</sup>

	$Mn_2(CO)_{10}$	$W(CO)_6$
$\phi_1$	0.43	1.0
$\phi_1'$	0.07	0.0
$\phi_2$	0.40	0.06
$I_0$ (einsteins $min^{-1}$ )	$3 \times 10^{-6}$	$7 \times 10^{-7}$
$\epsilon_A$ ( $M^{-1} cm^{-1}$ )	8900	400
$\epsilon_B$ ( $M^{-1} cm^{-1}$ )	10000	6500
$\epsilon_C$ ( $M^{-1} cm^{-1}$ )	400	7900
Cell path length (cm)	0.10	0.010
Initial concentration (M)	$6.1 \times 10^{-3}$	$1.0 \times 10^{-2}$
Cell volume (l)	$2.5 \times 10^{-5}$	$2.5 \times 10^{-5}$

<sup>a</sup>The data are taken from ref. 2 and references cited therein.

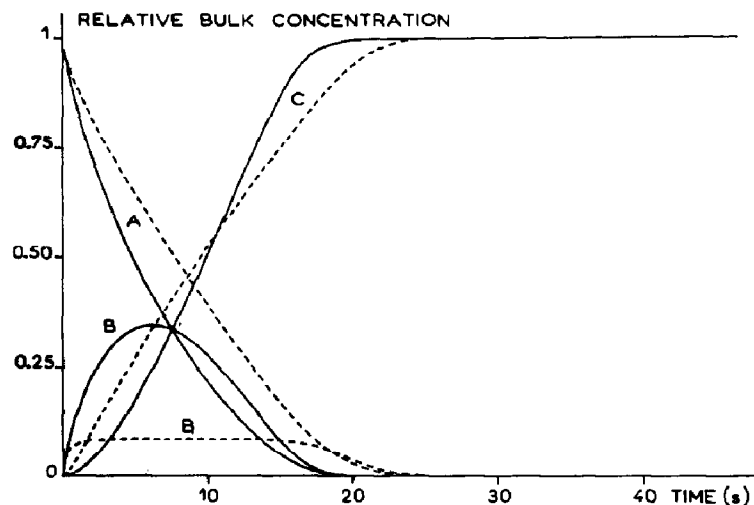


Fig. 2. Bulk concentrations  $\bar{C}_A$ ,  $\bar{C}_B$  and  $\bar{C}_C$  vs. time for a perfectly stirred reactor (—) and an unstirred reactor (---) (see text for details).

In order to illustrate this behaviour we have plotted in Fig. 4 the time dependence of the concentration profiles along the cell path for  $D = 0$  (perfectly unstirred reactor) and  $D = 10^{-4} cm^2 s^{-1}$  (rapid molecular diffusion;  $D$  is of the order of  $10^{-5} cm^2 s^{-1}$  in the solvent used in this example). It appears that mass transfer plays an important role in the apparent kinetics of the reaction.

## 5. Intermittent irradiation

It is quite usual in photokinetic studies to stop the irradiation for a time to allow the measurement of concentrations by a spectrophotometric

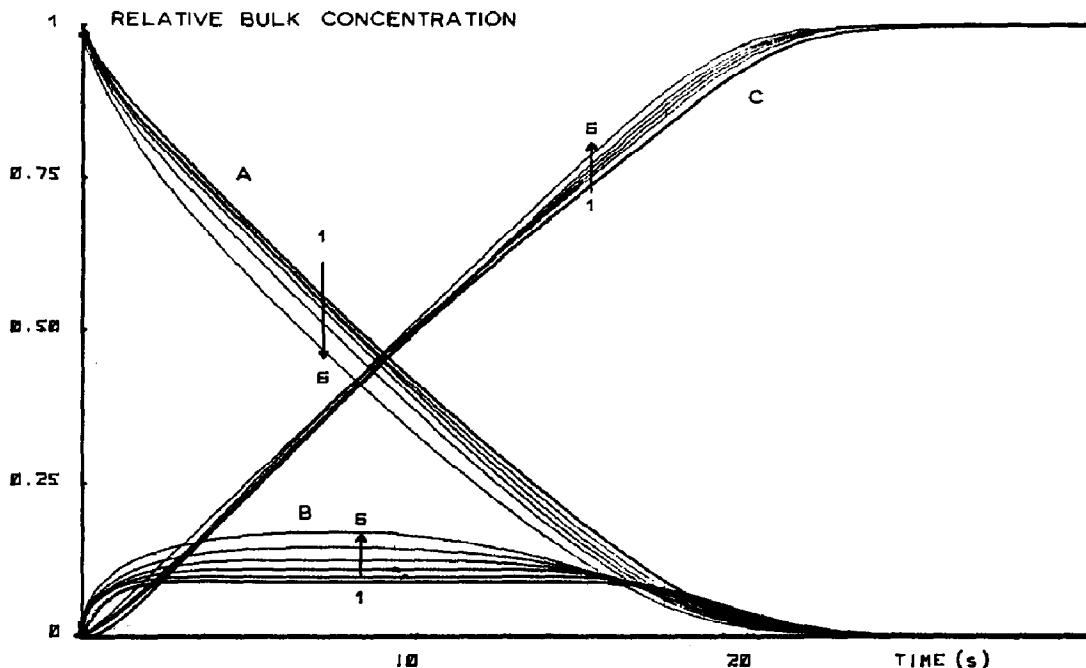


Fig. 3. Bulk concentrations  $\bar{C}_A$ ,  $\bar{C}_B$  and  $\bar{C}_C$  vs. time for an unstirred reactor in which diffusion occurs ( $D_A = D_B = D_C = D$ ): curves 1,  $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ; curves 2,  $D = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ; curves 3,  $D = 4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ; curves 4,  $D = 6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ; curves 5,  $D = 8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ; curves 6,  $D = 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ .

technique applied to the reaction cell itself. For a short irradiation experiment, these periods can be much longer than the irradiation itself. This may have two consequences: a dark reaction which modifies the chemical conditions may occur, or the solution may be homogenized by diffusion, convection or agitation.

We have illustrated the latter case in Fig. 5 where the reaction is assumed to take place during an irradiation period of 3 s and to be perfectly stirred during the recording of the concentrations which requires several minutes in darkness. The conditions are the same as in Fig. 2. It can be seen that although the concentration measurements are rigorous (the bulk concentration does not change during the dark period) the recording of the kinetics is strongly perturbed.

## 6. Reactors adapted to the study of consecutive reactions where the photo-products also absorb the exciting light

It is possible to carry out significant measurements in a reactor where the absorbances of the products are low. As an example Fig. 6 shows a plot of the time dependence of the bulk concentrations in the photosubstitution of CO by pyridine (py) in  $W(\text{CO})_6$ :

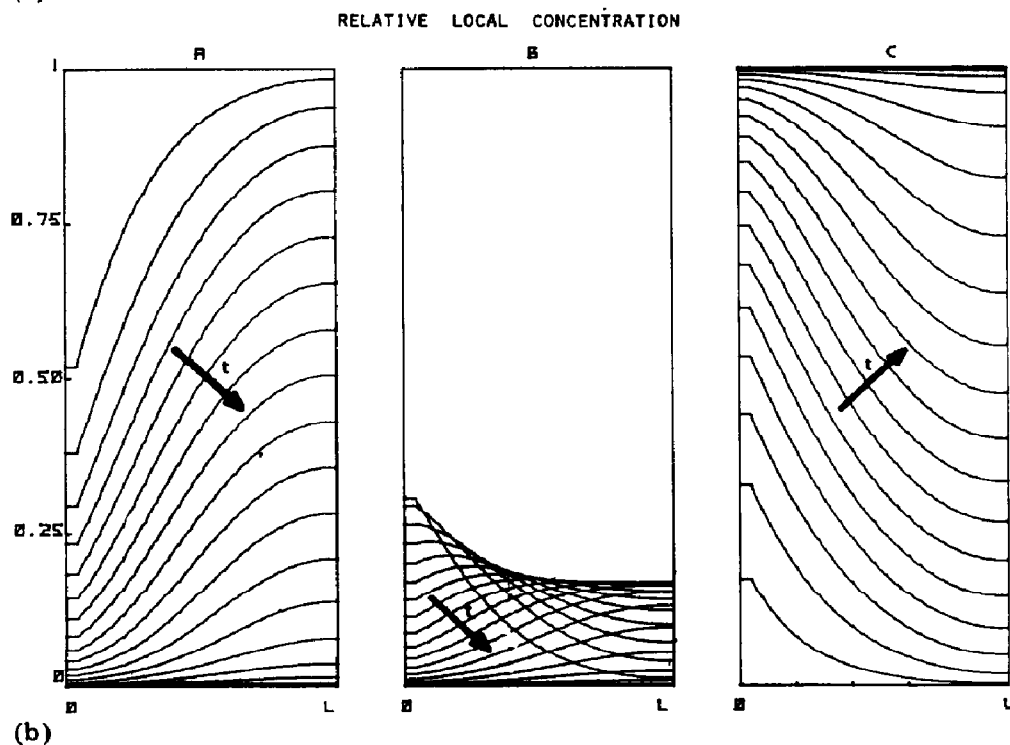
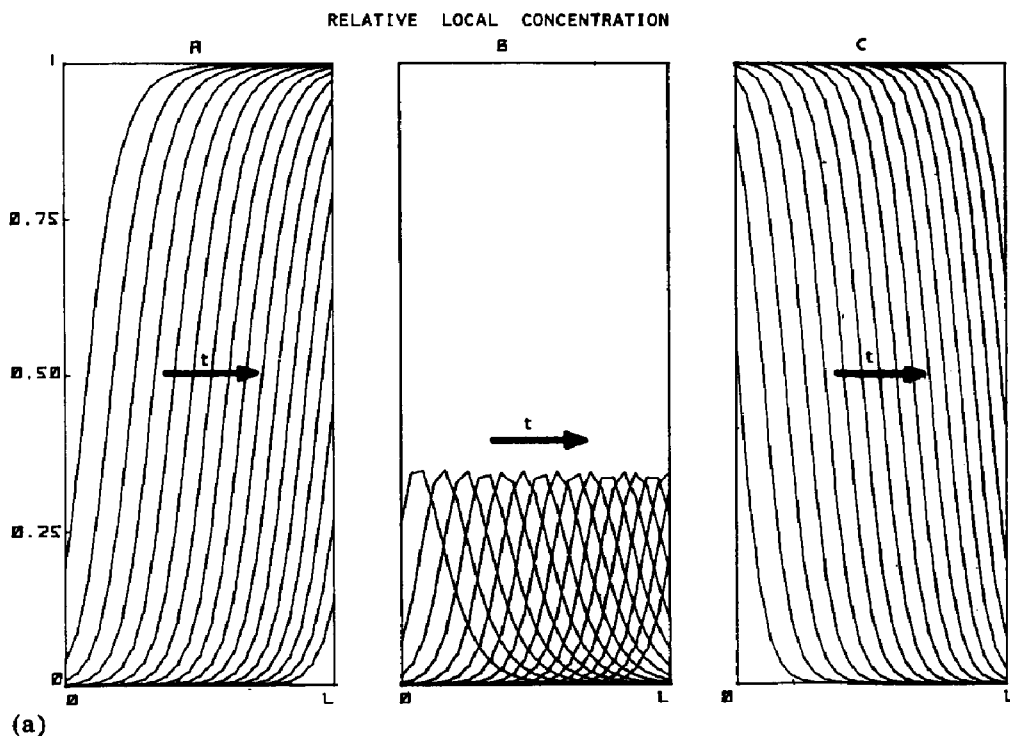


Fig. 4. Time dependence of the profiles of the local concentrations  $C_A$ ,  $C_B$  and  $C_C$  along the cell path in an unstirred reactor (conditions as in Table 1): (a)  $D = 0$ ; (b)  $D = 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ . The time interval between each curve is 1.1 s and the arrows indicate increasing time.

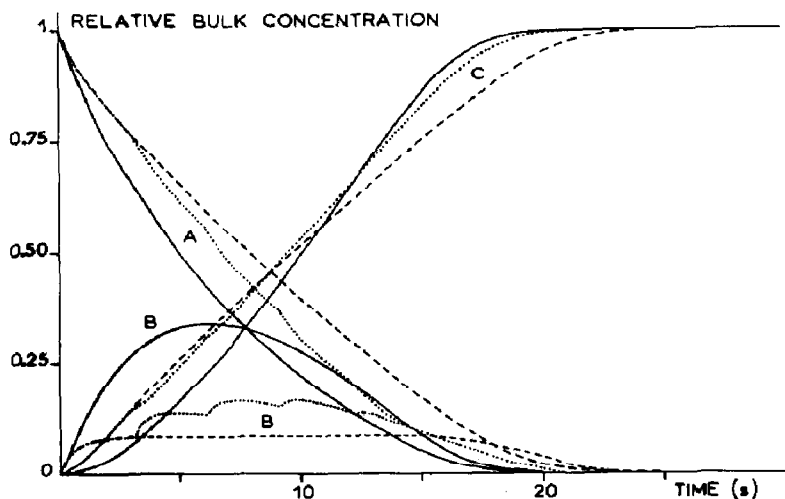


Fig. 5. Effect of intermittent irradiation of a reactor under the conditions given in Table 1: —, perfectly stirred reactor under continuous irradiation; ---, perfectly unstirred reactor under continuous irradiation without diffusion; ·····, perfectly unstirred reactor with no diffusion under intermittent irradiation but with complete homogenization every 3 s.

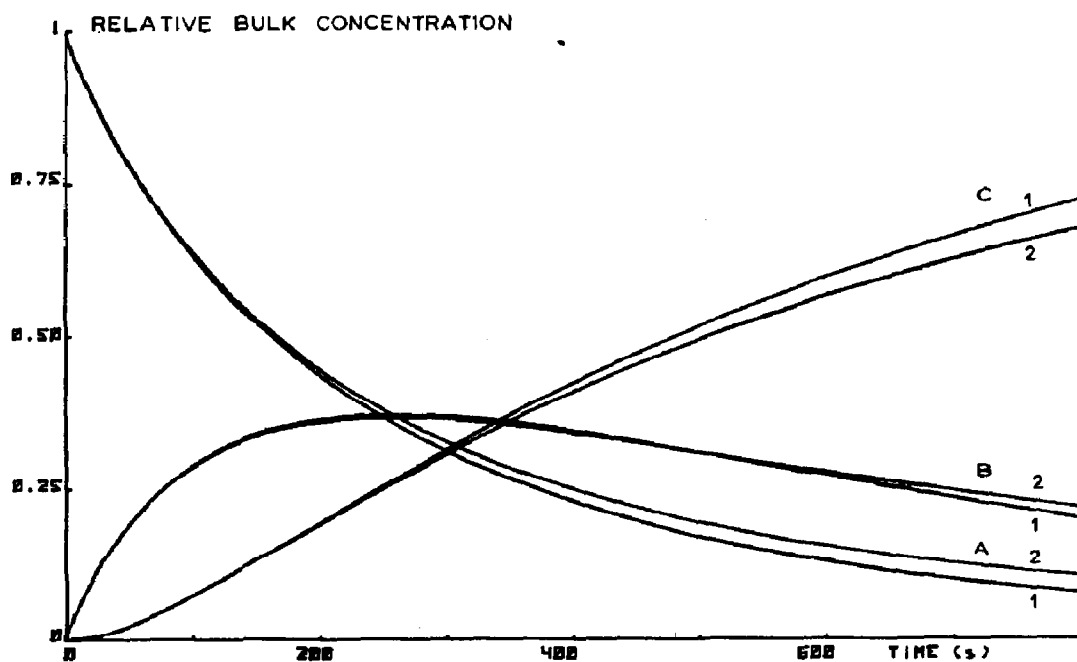
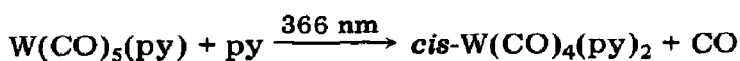
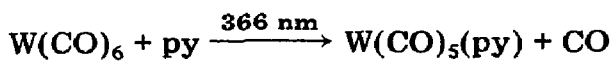


Fig. 6. Time dependence of the bulk concentrations  $\bar{C}_A$ ,  $\bar{C}_B$  and  $\bar{C}_C$  for products with low absorbance: curves 1, perfectly stirred reactor; curves 2, perfectly unstirred reactor.





The data reported in ref. 2 and summarized in Table 1 were used to compute the curves. Figure 6 shows that the absence of stirring has almost no effect on the kinetics of formation of B and C.

It is also possible to use perfectly stirred reactors, but these are rather difficult to design when small path lengths  $L$  are required. However, measurements can be made in a reactor with external mixing such as that shown schematically in Fig. 7 if no significant dark reaction occurs during the mixing time.

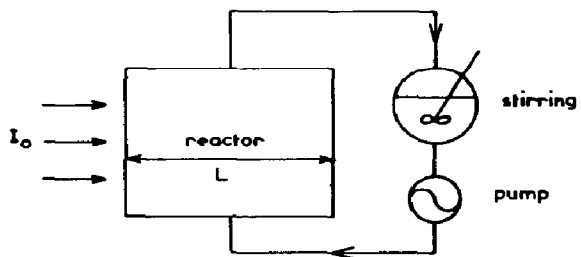


Fig. 7. Schematic representation of a photoreactor with external mixing.

## 7. Conclusion

The apparent kinetics of consecutive photoreactions can be significantly affected by the presence or absence of mixing of the solution. The experimental cases modelled in this paper show that the experimental arrangement and modelling procedure must be specified and coherent if significant kinetic parameters are to be obtained.

## References

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