INDUSTRIAL PHOTOCHEMISTRY
V: MODELLING AND TRIAL RUNS OF A REACTOR WITH SEPARATE PHOTOCHEMICAL AND THERMAL STEPS

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Summary

Annular reactors adapted to successive toluene chlorination have been described in the preceding papers in this series. In this paper a theoretical working model of a reactor in which the purely photochemical stage (initiation) is separated from the subsequent thermal stage (propagation) is reported. The model is in satisfactory agreement with experimental data obtained using the photochlorination of toluene as a reaction model. The advantages and disadvantages of this type of reactor are described.

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1. Introduction

The work reported in the preceding papers in this series [1 - 4] has improved our understanding of the mechanisms of cylindrical immersed lamp reactors and has enabled us to suggest improvements to these reactors. In this paper we examine a reactor of the type suggested by Lucas [5] and investigated briefly by Dworkin and Dranoff [6] to determine whether it could be used to modify the selectivity of successive photoreactors. This reactor is based on a principle similar to that proposed by Paneth some years ago in which the transfer of free radicals was demonstrated by the formation of a mirror. In this case the photochemical stage (initiation) is separated from the subsequent thermal stage by a physical barrier. In an attempt to clarify the numerous statements which have been made regarding this apparatus during national and international meetings we have modelled a photoreactor for gas–gas and gas–liquid applications, performed an experimental validation of the model for the photochlorination reaction of

toluene and analysed the advantages and disadvantages of the process with respect to the selectivity and the efficiency of transfer of radicals from the irradiated zone to the dark reaction zone.

Industrial photochemical reactors used for long-chain reactions appear to be classical reactors into which lamps have been introduced. However, the results presented here suggest that satisfactory results can only be obtained using plug flow reactors with improved illumination. However, we show in Appendix A that, in view of the risk of explosion when this type of reactor is used, the semiempirical solutions applied industrially cannot be abandoned at present.
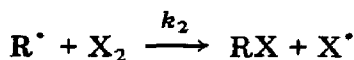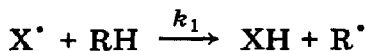
2. Model of a gas–gas long-chain radical reaction
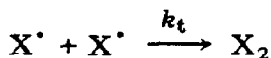
2.1. Perfectly stirred reactor

The reactor is shown schematically in Fig. 1. We can use the hypothesis of two perfectly stirred reactors to calculate the efficiency of transfer of radicals from the illuminated pre-reactor to the dark reactor. For example, if we assume a long-chain radical mechanism described by

$$X_2 \xrightarrow{h\nu} 2X^\bullet$$
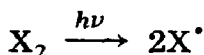
(formation of free radicals with a quantum yield ϕ)

$$X^\bullet + RH \xrightarrow{k_1} XH + R^\bullet$$
$$R^\bullet + X_2 \xrightarrow{k_2} RX + X^\bullet$$

(propagation)

$$X^\bullet + X^\bullet \xrightarrow{k_t} X_2$$

(chain termination) and if the flow at the entrance is q, we can calculate the mean concentration $\langle [X^\bullet] \rangle$ of $X^\bullet$ at the entrance of the reaction compartment from the relation
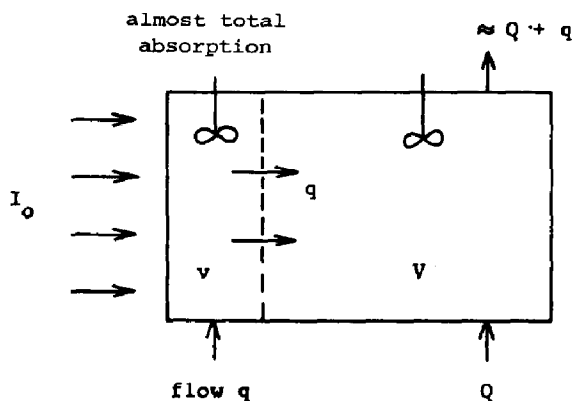

Fig. 1. Schematic diagram of a stirred reactor of the type proposed by Lucas.

$$k_t \langle [X^\bullet] \rangle^2 + \frac{q}{2v} \langle [X^\bullet] \rangle - I_a \phi = 0$$

which corresponds to an evaluation of $[X^\bullet]$ in the stationary regime. (If recombination occurs by a three-body collision, k_t is the product of the rate constant and the product concentration.) Under the most favourable transfer conditions, *i.e.* if the chain recombination processes are negligible, we obtain a maximum concentration $[X^\bullet]_0$ of $X^\bullet$ defined by

$$\frac{q}{2v} [X^\bullet]_0 - I_a \phi = 0$$

These two relations allow us to calculate the transfer efficiency η defined by

$$\eta = \frac{\langle [X^\bullet] \rangle}{[X^\bullet]_0}$$

$$\eta = \frac{(1 + 16 k_t I_a \phi v^2/q^2)^{1/2} - 1}{8 k_t I_a \phi v^2/q^2}$$

$$\eta = \frac{2}{(1 + 16 k_t I_a \phi v^2/q^2)^{1/2} + 1}$$

Thus η depends only on the value of the quantity

$$X = \frac{k_t I_a \phi v^2}{q^2}$$

or

$$X = k_t I_a \phi \tau^2$$

where I_a represents the light intensity absorbed per unit volume and τ is the residence time of the gas in the first compartment of the photoreactor.

The dependence of η on X is shown in Fig. 2. At low values of X the radicals have almost no time to recombine in the irradiated zone and η is close to unity; in contrast, at high values of X the radical recombination processes become more important and η tends to zero. The values of η calculated for $X_2 \equiv Cl_2$ and $X_2 \equiv NOCl$ ($k_t = 4.6 \times 10^9$ mol^{-1} l s^{-1} for $Cl^\bullet$ + $Cl^\bullet$ [7] and $k_t = 4.37 \times 10^{10}$ mol^{-1} l s^{-1} for NOCl [8]) are shown in Table 1. (Since the formation of NOCl has the highest rate constant of all the $NO^\bullet -$ $Cl^\bullet$ recombination processes, it is this which determines the kinetics. The rate constants for the three-body collision were recalculated as pseudo-two-body collision rate constants for an assumed pressure of 1 atm.)

These results show that under the ideal conditions of a perfectly stirred reactor the residence time in the irradiation compartment must be as small as possible so that the transfer efficiency is as large as possible. However, under these conditions these radicals are diluted in their carrier gas which is one of the reagents used in the dark zone.
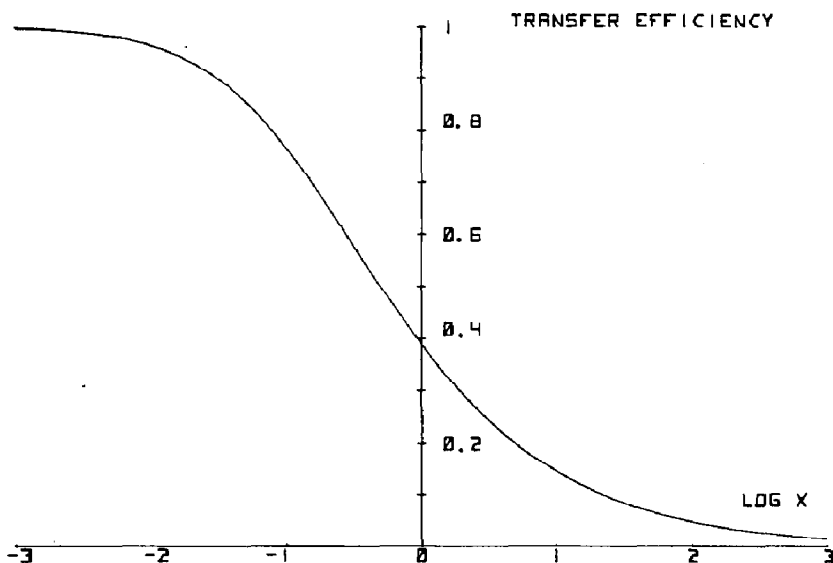
Fig. 2. Dependence of the transfer efficiency η on the ratio $X = k_t \phi I_a v^2 / q^2$.

TABLE 1

Variation of η with the residence time τ for Cl_2 and NOCl

τ (s)	η for the following irradiation conditions					
	$I_a = 0.5 \times 10^{-10}$		$I_a = 0.5 \times 10^{-8}$		$I_a = 0.5 \times 10^{-6}$	
	NOCl	Cl_2	NOCl	Cl_2	NOCl	Cl_2
10	0.03	0.099	0.003	0.011	0.0003	0.001
1	0.29	0.63	0.03	0.099	0.003	0.011
0.1	0.93	0.991	0.29	0.63	0.03	0.099
0.01	1	1	0.93	0.991	0.29	0.63

I_a is in units of einsteins per litre per second.

2.1.1. Extent of the reaction at the exit of the reactor

We assume that the radicals and the products are trapped at the exit of the dark reactor as no products are formed after the gas leaves this reactor. We can then use the transfer efficiency defined above together with the rate constants of the radical processes involved and the various residence times to calculate the extent of the reaction at the reactor exit.

If we denote by $[X^{\cdot}]_i$ and $[X^{\cdot}]_d$ the radical concentrations produced in the irradiated and dark zones respectively, we can as previously write

$$2k_t [X^{\cdot}]_d{}^2 + \frac{Q + q}{V} [X^{\cdot}]_d - \frac{q}{V} [X^{\cdot}]_i = 0$$

if the reaction between X_2 and RH is a long-chain reaction. Similarly, if we denote by $[RH]_0$ the concentration at the entrance to the reactor, then

$$Q[RH]_0 = Vk_1[RH][X^\cdot]_d + (Q + q)[RH]$$

The extent a_a of the reaction is then given by

$$a_a = \frac{k_1[X^\cdot]_d T}{1 + k_1[X^\cdot]_d T}$$

where $T = V/(Q + q)$, i.e.

$$a_a = \frac{(k_1/4k_t)([1 + 2\rho(T^2/\tau^2)\{(1 + 16k_t I_a \phi \tau^2)^{1/2} - 1\}]^{1/2} - 1)}{1 + (k_1/4k_t)([1 + 2\rho(T^2/2)\{(1 + 16k_t I_a \phi \tau^2)^{1/2} - 1\}]^{1/2} - 1)}$$

where $\rho = v/V$. Having established this relation we now calculate the value of a_a that is obtained if we use only one photoreactor of the same volume $V + v$ as that used when we require to separate the photochemical reactions from the subsequent thermal reactions. We obtain, with the same definitions,

$$\bar{a}_a = \frac{(1 + \rho)k_1[\bar{X}^\cdot]T}{1 + (1 + \rho)k_1[\bar{X}^\cdot]T}$$

where

$$[\bar{X}^\cdot] = \frac{\{1 + 16k_t \phi I_a T^2(1 + \rho)^2\}^{-1/2} - 1}{4k_t(1 + \rho)T}$$

so that

$$\bar{a}_a = \frac{(k_1/4k_t)[\{1 + 16k_t \phi I_a T^2(1 + \rho)^2\}^{1/2} - 1]}{1 + (k_1/4k_t)[\{1 + 16k_t \phi I_a T^2(1 + \rho)^2\}^{1/2} - 1]}$$

The variations in the ratio $a_a/\bar{a}_a$ at various values of the parameters are shown in Fig. 3 where the loss of efficiency due to the separation of the thermal and photochemical stages can be seen.

However, as has been emphasized by Dworkin and Dranoff [6], the products of side reactions can affect the transparency of the reactor. This occurs in the chlorination of chloroform when solid C_2Cl_6 is deposited on the walls of the photoreactor. It is also possible that light-absorbing substances which do not lead to the desired reaction, or which undergo reactions with a low yield, may be present in the dark reactor. In addition, a mixture of reactants and products which must be separated is formed at the exit (this problem also exists for other types of thermal and photochemical reactors).

2.2. The plug flow reactor

The reactor is shown schematically in Fig. 4. If it is assumed that the radicals produced in the irradiated zone are instantaneously mixed at the interface between the two compartments, it is possible to calculate the extent of the reaction at the exit of the reactor.
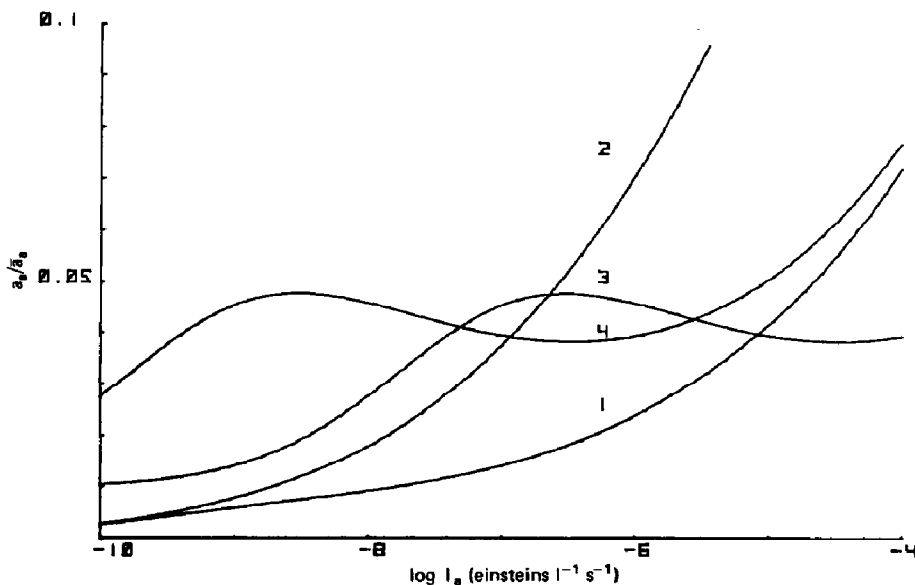
Fig. 3. Dependence of the ratio $a_a/\bar{a}_a$ on the absorbed light intensity I_a for the photochlorination of toluene at various values of ρ, τ and T: curve 1, $\rho = 0.0001$, $\tau = 0.1$ s, $T = 10$ s; curve 2, $\rho = 0.0001$, $\tau = 0.01$ s, $T = 10$ s; curve 3, $\rho = 0.01$, $\tau = 0.01$ s, $T = 0.1$ s; curve 4, $\rho = 0.01$, $\tau = 0.1$ s, $T = 1$ s.
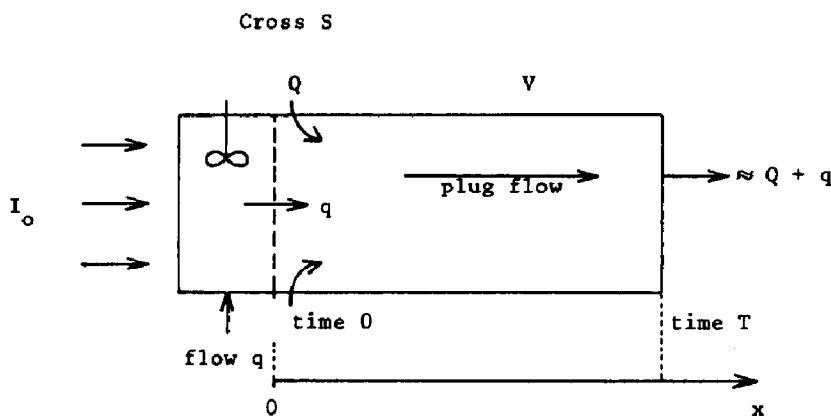

Fig. 4. Schematic diagram of a plug flow reactor of the type proposed by Lucas.

We can write the relation for the reaction being considered at any position x in the reactor:

$$\frac{Q+q}{S}\frac{d[X^\bullet]}{dx} = -2k_t[X^\bullet]^2$$

where S is the cross section of the plug flow reactor. Therefore the local concentration of $X^\bullet$ is given by

$$[X^\bullet] = \frac{[X^\bullet]_d}{1 + [X^\bullet]_d\{2k_tSx/(Q+q)\}}$$

The extent of the reaction can be calculated in the case where the reactant concentration remains reasonably constant along the reactor (if this is not so, the calculation is no longer directly possible and a result can only be obtained by numerical integration). We obtain

$$a_\text{p} = \frac{k_1}{2k_t} \, \log \left(1 + 2k_t [\text{X}^\bullet]_\text{d} \, \frac{V}{Q + q} \right)$$

which can easily be compared with the value obtained for a stirred reactor by substituting

$$[\text{X}^\bullet]_\text{d} = \frac{(1 + 16k_t I_\text{a} \phi \tau^2)^{1/2} - 1}{4k_t \tau}$$

The results of these calculations are shown in Fig. 5 where the behaviour of the different types of reactors can be seen.

At very low absorbed light intensities, we have

$$a_\text{p} = 2k_1 I_\text{a} \phi \tau T$$

i.e.

$$\frac{a_\text{p}}{a_\text{a}} = \frac{2\tau}{\rho T} = 2\frac{Q + q}{q}$$

which shows that under these conditions a plug flow reactor is preferable to a stirred reactor as far as the extent of the reaction is concerned.
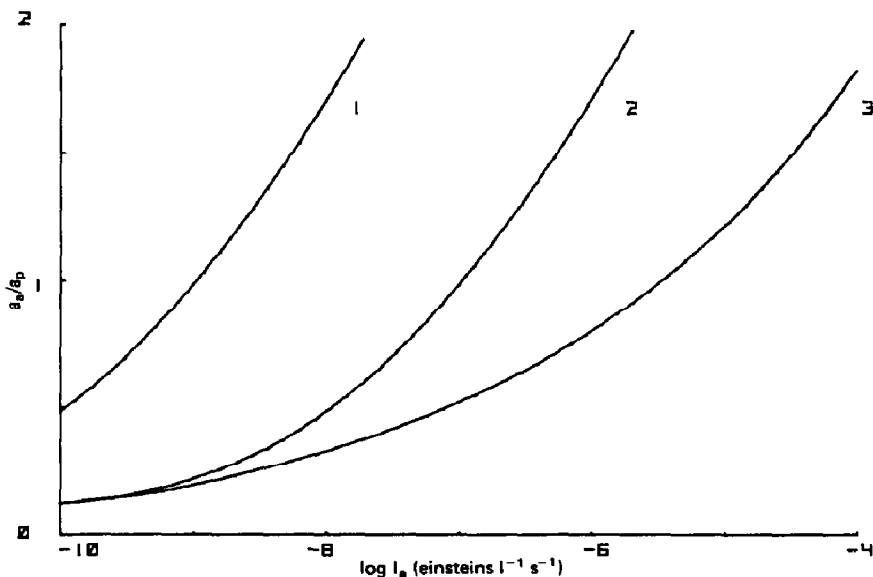

Fig. 5. Variation in the ratio a_a/a_p as a function of the absorbed light intensity I_a for the photochlorination of toluene at various values of ρ, τ and T: curve 1, ρ = 0.0001, τ = 0.1 s, T = 100 s; curve 2, ρ = 0.0001, τ = 0.01 s, T = 10 s; curve 3, ρ = 0.01, τ = 0.1 s, T = 1 s.

3. Model of a long-chain gas–liquid radical reaction

If we assume that the chemical reactor is a closed reactor stirred by chlorine bubbles containing free Cl˙ atoms formed in the pre-reactor under irradiation, it is possible to construct a model for the reaction kinetics of photochlorination (Fig. 6).

The chlorine bubbles which contain some of the Cl˙ atoms formed (the remainder are recombined in the pre-reactor) encourage mixing in the second reactor. However, the calculations presented in ref. 2 show that the Cl˙ radicals formed have a very short lifetime which is almost negligible in comparison with the mixing time in the chemical reactor. Thus we can consider each bubble as an independent system during its lifetime and we can state that the rate of reaction is equal to the sum of the rates obtained for each bubble, the radius of which is assumed to be almost constant.

Thus the reaction proceeds as follows: the irradiation of Cl_2 in the pre-reactor (which is assumed to be perfectly stirred) results in the formation of free chain-carrying Cl˙ atoms with an initial loss related to the Cl˙ + Cl˙ recombination in this reactor; bubbles of chlorine containing free Cl˙ atoms are formed almost instantaneously; Cl˙ and Cl_2 diffuse from the gas–liquid interface and initiate the chain radical reaction in competition with the recombination process

$$Cl˙ + Cl˙ (+M) \longrightarrow Cl_2 (+M)$$
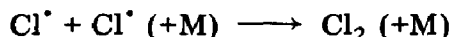
in the gas and liquid phases. Under laboratory test conditions we can arrange that the reaction kinetics are limited by the various transfer processes of the
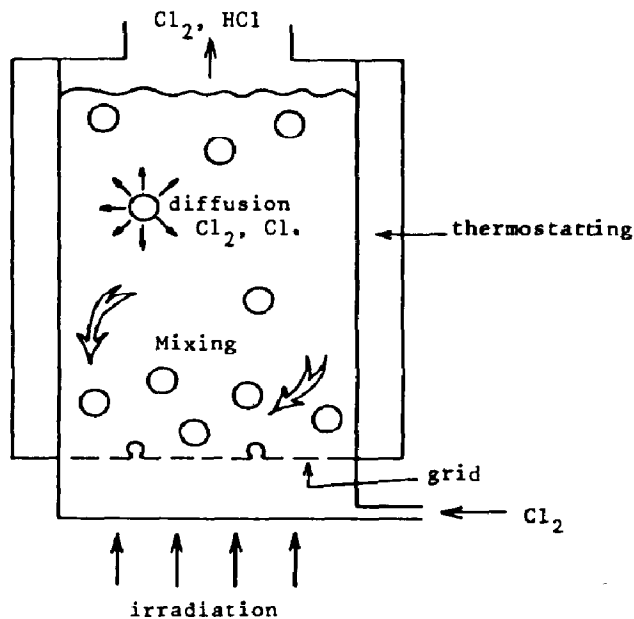

Fig. 6. Schematic representation of the working conditions of a stirred gas–liquid reactor of the type proposed by Lucas.

free Cl• atoms in the solution, and it is then unnecessary to take the diffusion of the chlorine molecules in solution into account.

3.1. Diffusion of Cl• atoms out of a bubble

The variation in the Cl• concentration inside a bubble is defined by

$$\frac{\partial[Cl^\bullet]}{\partial t} = D\,\nabla^2[Cl^\bullet] - 2k_t[Cl^\bullet]^2$$

Now the diffusion coefficient of Cl• in the gas phase [9] is approximately a factor of 10^5 greater than that of Cl• in the liquid phase. Thus, for simplicity, we assume that the concentration of Cl• in a bubble is almost uniform and depends only on the constant of recombination and the efficiency of transfer out of the bubble (Fig. 7). The Cl• concentration inside the bubble is defined by

$$\frac{d[Cl^\bullet]_g}{dt} = -2k_{t,g}[Cl^\bullet]_g{}^2 - K[Cl^\bullet]_g$$

where K is a coefficient which depends on the efficiency of gas–liquid transfer and which will be defined later and $k_{t,g}$ is the recombination constant of two Cl• atoms in the gas phase. The Cl• concentration in the liquid phase is given by

$$\frac{\partial[Cl^\bullet]_1}{\partial t} = D\,\nabla^2[Cl^\bullet]_1 - 2k_t[Cl^\bullet]_1{}^2$$

where k_t is the rate constant of recombination of two Cl• atoms in the liquid phase.

In the absence of a reaction between a gas X and a liquid, the concentration at the interface can be considered, for a very soluble gas, to be almost equal to the limiting concentration defined by Henry's law:
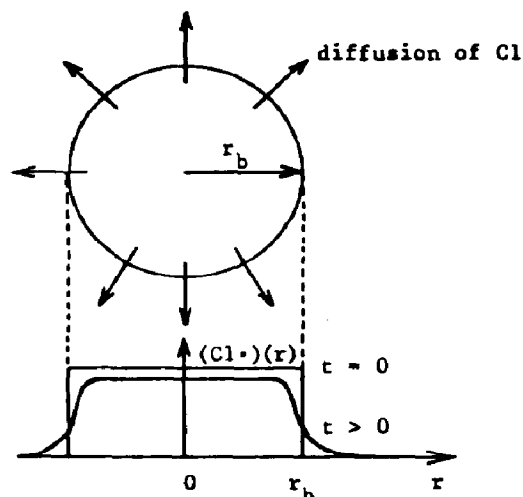

Fig. 7. Schematic representation of the diffusion of free Cl• atoms out of a bubble.

$$C_1 = HC_g$$

where C_1 is the concentration at the interface, C_g is the gas concentration and H is a proportionality constant. The variation in the concentration at the interface is a function of the diffusion in the liquid and of the volume of the gas enclosed in a bubble of radius r_b:

$$\text{flux} = 4\pi r_b^2 D \left(\frac{\partial[X]}{\partial r} \right)_{r_b}$$

In terms of Henry's law the variation in the concentration of X in the bubble as a result of the transfer is

$$\frac{4}{3}\pi r_b^3 \frac{\partial[X]_g}{dt} = 4\pi r_b^2 D \left(\frac{\partial[X]_l}{\partial r} \right)_{r_b}$$

i.e.

$$\frac{d[X]_g}{dt} = \frac{3D}{r_b} \left(\frac{\partial[X]_l}{\partial r} \right)_{r_b}$$

When the gas and the liquid react the concentration at the interface may be less than that defined by Henry's law because there is a marked reduction in the amount of gaseous reactant present which produces an apparent increase in the coefficient of transfer (the amplification factor E_i). E_i is defined by [10]

$$E_i \approx 1 + \alpha\beta^{1/2}$$

β is the ratio of the diffusion coefficient of the gaseous reactant to the diffusion coefficient of the liquid reactant in the liquid phase and $\alpha \approx C_{B1}/\eta C_{A_i}$ where C_{B1} is the concentration of the liquid reagent (in this case dissolved $Cl^{\bullet}$), C_{A_i} is the concentration of the dissolved reactant and η is the number of moles of the liquid reactant reacting with each mole of the gaseous reactant. Indeed, the only reaction which we have to take into account is the recombination reaction between two $Cl^{\bullet}$ radicals and not the chemical reaction $Cl^{\bullet} + RH \rightarrow HCl + R^{\bullet}$ as the chains regenerate the radicals (this would not be the case for a step reaction or for a molecular reaction). Under these conditions the expression for K is [10]

$$K \approx \frac{3DE_i}{r_b} \left(\frac{\partial[Cl^{\bullet}]_l}{\partial r} \right)_{r_b} \frac{1}{[Cl^{\bullet}]_g}$$

For the reaction under consideration

$$E_i \approx 2$$

If we assume $H = 1$ it is possible to calculate the variation in the efficiency of transfer of radical chain carriers outside a bubble as a function of the initial concentration of free $Cl^{\bullet}$ atoms (Fig. 8). Owing to the recombination processes taking place in the gas phase, the transfer efficiency is only satisfactory at very low initial concentrations, corresponding to very low
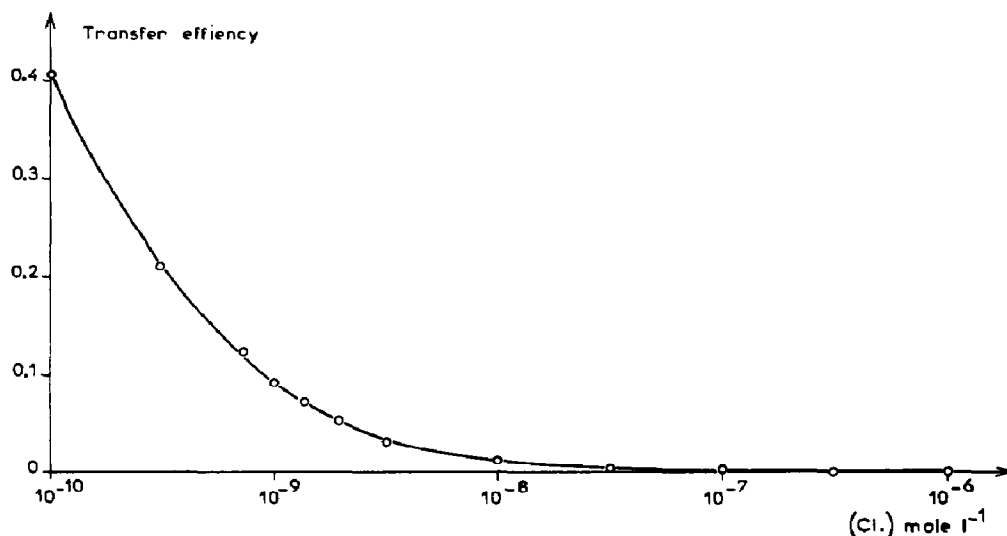
Fig. 8. The efficiency of transfer of Cl* atoms outside a bubble vs. the initial concentration of Cl* atoms.

exciting light intensities. Under our laboratory conditions the transfer efficiency is about 0.2 which is comparable with the value obtained in a classical photochemical reactor of the type discussed in previous work. Indeed, in the kinetic regime the light is absorbed near the point at which the light rays enter the photoreactor and hence there is a decrease in the mean yield of the reaction [3]. For a homogeneous distribution of the light in the reactor, the calculated rate V_c and the experimental rate V_e are related by

$$V_e = p V_c$$

At a high optical density

$$p \approx \frac{2}{(\epsilon C L)^{1/2}}$$

where ϵ is the molar extinction coefficient of Cl_2, C is the concentration of Cl_2 and L is the path length. Under our laboratory conditions p has a value of a few per cent. Thus in theory the efficiency of chlorination performed in this type of reactor on a laboratory scale should be close to that obtained using a classical photoreactor.

3.2. Extent of the photochlorination reaction

When the mechanism presented in refs. 2 - 4 is used, the local rate of reaction is expressed by

$$V(r, t) = k_1 [RH][Cl^*]$$

Thus the extent of a reaction in a series of chlorine bubbles containing free Cl* atoms which are assumed to be independent depends on the follow-

ing factors: the light intensity in the pre-reactor, the residence time in the pre-reactor, the number and size of the bubbles, the lifetime of the bubbles, the volume of the liquid reagent etc. These parameters will be used later to compare the model defined above with experiment.

4. Experimental validation

4.1. The photoreactor and the working conditions

The photoreactor used, which was built in the laboratory, is shown schematically in Fig. 6.

The following conditions were used in the experiments: temperature, 50 °C; liquid volume, 15 cm^3 (i.e. 0.141 mol toluene); irradiated volume, 5 cm^3; irradiation wavelength, 313 nm; chlorine flow rate, 8.3 cm^3 s^{-1}; bubble diameter, 2 mm; diameter of holes in the poly(vinyl chloride) grid, 0.5 mm; number of holes, 43 (total surface area of the grid, 844 mm^2); retention, about 0.3; optical density in the photochemical reactor, about 6 (the non-illuminated region of the reactor is assumed to be almost dark).

4.2. Results

The theoretical study presented above demonstrates the marked influence of the light intensity on the efficiency of transfer towards the liquid phase of radicals or free atoms formed by irradiation in the pre-reactor. We used the chromatographic technique to investigate the effect of the intensity of the exciting light on the rate of the photochemical reaction. The main results of our measurements are presented in Table 2.

If the reaction had been carried out in the kinetic regime under the same experimental conditions but using a classical annular reactor, we would

TABLE 2

Experimental results

I_a (×10^{-7} einsteins l^{-1} s^{-1})	Initial rate V_0 (×10^{-2} mol l^{-1} s^{-1})		$R = V_0/I_a^{1/2}$ [b] (mol$^{1/2}$ l$^{-1/2}$ s$^{-1/2}$)
	This work	Annular reactor in kinetic regime[a]	
11	1.0	37	9.5
5	2.5	25	35.3
2.3	2.66	17	55.4
1.2	3.0	12.3	86.6
0.6	1.6	8.7	65.3
0.08	0.80	3.2	89.4
0.019	0.37	1.5	84.2

[a]V_0 was calculated from the relation $V_0 = pk_1[RH](I_a/k_t)^{1/2}$ where $k_1 = 10^{8.2}$, $k_t = 10^{10.2}$ mol^{-1} l s^{-1} and $p \approx 0.03$ (p is dependent on the reactor used).
[b]This work.

have obtained results depending on the absorbed light intensity I_a but such that $V_0/I_a^{1/2}$ is a constant. In fact, in agreement with the theoretical study presented above, we show that the efficiency of radical transfer is a decreasing function of I_a which is not unreasonable as we expect high rates which could be of the order of those obtained under identical conditions in a classical reactor.

4.3. Comparison of the results obtained using a simplified model

If we assume that the illuminated pre-reactor is perfectly stirred, that the formation of bubbles is instantaneous, that the coefficient of Henry's law is about unity and that each bubble is independent, it is possible to calculate the theoretical variation of R with I_a from the simplified model.

The results of the diffusion calculations are in reasonable agreement with the results of the kinetic measurements. Doubtless better agreement would be obtained if H were known. However, the following trends can be identified. If H increases the concentration of free $Cl^\bullet$ atoms must increase near the interface which favours the local reaction kinetics but does not favour the diffusion of $Cl^\bullet$ atoms out of the bubble. We must then expect a slight increase in R with respect to that shown in Fig. 9. If the pre-reactor is not perfectly stirred (which is probably the case), we can expect the formation of bubbles containing variable concentrations of $Cl^\bullet$ atoms. Since the systems are non-linear, it is unlikely that the mean effect observed is the sum of the individual mean effects. Thus, depending on the nature of the regime in the pre-reactor, values of R which are greater or less than those shown in Fig. 9 can be obtained. These results suggest that
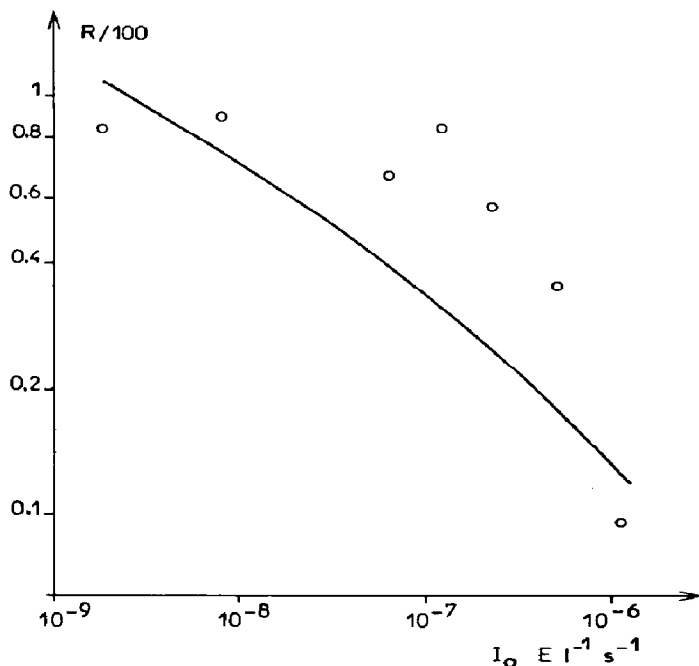

Fig. 9. $R = V_0/I_a^{1/2}$ vs. I_a for the chlorination of toluene.

the modelling of a reactor of this type for a gas–liquid chain reaction is satisfactory.

5. Industrial application of the reactor for a long-chain gas–liquid reaction

The measurements carried out using the laboratory reactor demonstrate an efficiency close to that obtained using classical photochemical reactors. Apart from the case when absorbing secondary products are produced which limit the absorption of light and lead to the formation of free radicals (tarring) where this type of reactor can be used to advantage, for the following reasons its performance does not appear to be sufficiently good to warrant its replacing classical reactors for radical chain reactions of chlorination.

(1) Its efficiency depends on stirring in the pre-reactor during illumination. The development of this reactor on an industrial scale would require the use of a pre-reactor of much larger dimensions than those used in the laboratory which could no longer be considered as perfectly stirred. Thus the radical transfer efficiency would be limited.

(2) The flow rate of chlorine in this pre-reactor must be as large as possible to ensure that free $Cl^\cdot$ atoms are transferred into the reaction zone. This result has two consequences: the presence of excess chlorine in the medium can lead to secondary thermal reactions and a mixture of chlorine and HCl, which must be separated, is produced at the reactor exit. In the diffusion regime the chlorine concentration is almost zero and thus these two problems are avoided.

(3) The requirement to build a grid in resistant material (*e.g.* nickel) produces a substantial increase in the cost of building the reactor.

(4) This type of reactor cannot be used to modify the selectivity of consecutive reactions such as those which participate in the photochlorination of toluene and its chlorinated derivatives. Indeed, the only application of interest is the separation of the photochemical steps from the thermal steps, which leads to the same selectivity.

(5) The efficiency decreases with increasing light intensity in contrast with the classical reactor working in the kinetic or diffusion regime for which absorption occurs in deeper regions when the light intensity is increased. (At very high intensities, the absorption will also occur in chlorine bubbles, which ought to lower the efficiency of the reactor). However, the efficiency of the reactor is not really important for long-chain radical reactions provided that the chain is long enough (greater than 100 units in general). The problems that the engineer must overcome are essentially the mastering and improvement of the selectivity of the reaction and the elimination of the excess heat produced by the reaction (see Appendix A).

Under these conditions we cannot easily see how this type of reactor could replace the classical reactors used in industry for photochemically initiated long-chain radical reactions, provided that tarring phenomena are not important.

Acknowledgment

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Appendix A

A.1. Is there an ideal reactor for the industrial photochlorination of toluene?

As has been shown in the previous papers in this series, the technology of photochemical systems is in its infancy and is little different from the technology of thermal reactions. In general photoreactors are only classical reactors into which a light source has been introduced.

Although this type of photoreactor has some advantages, such as simple operation, tested technology and limited construction costs, and performs satisfactorily in some photochemical syntheses (*e.g.* long-chain reactions), the specificity of the photoreaction is not taken into account and the industrialization of certain syntheses is not possible. The size and the geometry of the reactor are generally determined by the requirements of thermal transfer processes.

In order to illustrate the lack of photochemical specificity we first describe an industrial photoreactor for the chlorination of toluene, then examine an alternative type of photoreactor to determine whether it can be adapted to this industrial application and finally to compare the advantages and disadvantages of these two types of photoreactor.

A.1.1. Classical reactor for the photochlorination of toluene

The industrial photochlorination of toluene is carried out in a continuously stirred gas—liquid photoreactor with residence times ranging from 30 min to several hours.

A photoreactor which produces benzyl chloride at a rate of the order of 1.63 kmol h^{-1} (*i.e.* 1000 t year^{-1}) is shown in Fig. A1. The residence time is 2 h 40 min, and the irradiation is performed using five 400 W lamps
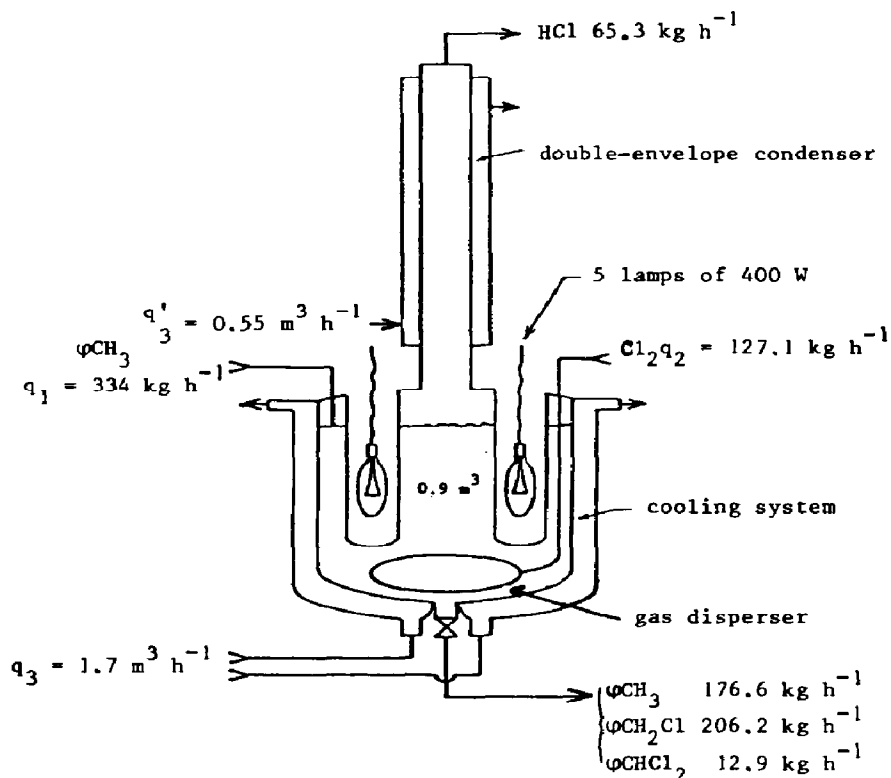
Fig. A1. Industrial reactor for the photochlorination of toluene ($\varphi \equiv C_6H_5$).

at a working temperature of 110 °C with a toluene reflux. The extent of chlorination is fixed at 0.5, and the non-transformed toluene at the reactor exit is separated by distillation, cooled and recycled to the reactor entrance. This type of reactor works in the diffusion regime [3]. The rate of the reaction is limited by the rate of chlorine supply and as a consequence there is a very low stationary concentration of chlorine in the liquid phase.

The thermal energy produced by the reaction is

$$\phi_R = 45\,640 \text{ kcal h}^{-1}$$

It is dissipated by three processes: via the specific heat (increase in the temperature of the entrant mass flux), by convection across the double envelope and via the latent heat (vaporization and condensation of toluene in the cooling coil). The removal of the heat of reaction does not cause major problems in this type of reactor. Since the number of parameters on which we can act is relatively large, control of the reaction does not present us with great difficulties and allows us to predict each local overheating rapidly. In contrast, when a reduced rate of reaction (limited by the chlorine supply) is used, such that there is a long residence time, the risk of secondary reactions which will cause a loss in selectivity is substantially increased.

Therefore the only improvement possible at present, bearing in mind the work carried out using this type of reactor, is a decrease in the residence time.

A.1.2. Reactor with low residence time: is this an ideal reactor?

It is not possible to obtain residence times of less than 10 min in the reactor described above (continuous stirring type) by simply increasing the light intensity and decreasing the reactor volume. Indeed, as the reaction rate is increased and the reaction volume is decreased the phenomenon of frothing becomes predominant and finally becomes uncontrollable, whereupon the liquid phase is blown out by the gas current. The search for very short residence times, of the order of 1 min, must therefore be directed towards other types of reactor.

An annular plug flow reactor with a cooling double envelope working under pressure is a possible technological solution for this type of synthesis. This reactor is shown schematically in Fig. A2.
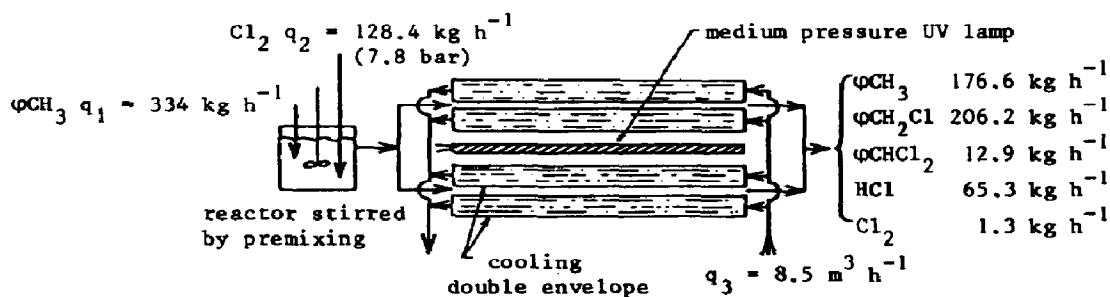

Fig. A2. Plug flow reactor adapted to the photochlorination of toluene ($\varphi \equiv C_6H_5$).

The following assumptions were used to determine the length and working conditions of this plug flow reactor.

(1) The reactor works continuously and isothermally at 110 °C. The heat of reaction is exchanged with a cooling fluid counterflow along the two walls.

(2) The lamp emits uniformly at 313 nm all along the reactor and the absorption of light is assumed to be complete at each point in the reactor.

(3) We neglect the variations in volume that occur during the reaction.

(4) The total thermal capacity of the reactant mixture is constant during the reaction and the chlorine and HCl solubilities are equal.

Thus the reactor comprises a continuously stirred reactor working at a pressure of 7.8 bar to ensure premixing of the reactants and to raise the temperature of the mixture to 110 °C, an isothermal plug flow reactor consisting of an annular space 20 cm in diameter and 1 mm thick in which the reaction mixture circulates at a pressure of 7.8 bar and a central zone with transparent Pyrex walls at the exit of a series of medium pressure UV lamps (with a power of about 40 W) in a central sheath which is cooled by a fluid counterflow.

Since the solubility of chlorine in toluene at 110 °C and atmospheric pressure is 0.61 mol l^{-1} [A1] the chlorine pressure necessary to dissolve 4.76 mol l^{-1} is 7.8 bar. The temperature of the reaction is fixed at 110 °C to limit the photochemical chlorination reactions on the ring, which are predominant

at low temperature, and to avoid problems during the reduction to atmospheric pressure. A 1% chlorine excess with respect to the extent of chlorination required is introduced into the plug flow so that the light absorption is essentially complete all along the reactor; the extent of the reaction is therefore determined by the residence time. The pressure gradient $\Delta\hat{p}$ is of the order of 600 Pa so that the circulation of toluene in the annular space does not obstruct the working of the reactor.

A.1.3. Conclusion

In order to summarize this work, we have assembled in Table A1 some comments on the advantages and disadvantages of the two reactors described with respect to the criteria of selectivity, security and control.

TABLE A1

Parameter	Stirred reactor	Plug flow reactor	Comment
Volume	—	+	A limited volume and residence time ensure a
Residence time	—	+	better selectivity and increase productivity
[Cl$_2$]	+	—	A high chlorine concentration is unfavourable to the selectivity and brings about risks of explosion
Selectivity	+	+	A large buffer volume dampens the thermal
Regulation	+	—	fluctuations. A very short residence time imposes the use of a system of rapid control

The comments given in this table enable the following conclusions to be drawn.

(1) Although the reactors are of different designs the dimensions of both of them are largely functions of the processes of thermal transfer.

(2) Although the plug flow reactor allows the stages of the reaction to be differentiated and some of the parameters to be controlled, there is not much improvement in the selectivity.

(3) Although the very short residence time of the plug flow reactor allows an increase in the productivity, the high chlorine concentration makes the control of the reaction much more complicated.

The example given here thus suggests that the choice of a classical reactor can lead to satisfactory results and that an increase in the productivity can only be obtained by using more complicated technology, particularly with respect to control techniques.

It is clear, however, that minor modifications to classical reactors will not result in significant progress being made in the industrialization of complex photochemical syntheses. Since the rate of the reaction is no longer completely described by the same state variables of the reaction mixture, it is desirable to adopt a new approach to photoreactor design in order to ensure better control or to take into account additional

parameters such as the light absorption profile, the lifetime of the reacting species, the homogenization processes, the stability of the reaction products under irradiation, the quantum yield of photolysis of the reactants and the order of the rate with respect to the intensity of absorbed light. Since photochemical reactions are very diverse, the geometry and the working conditions of the new photoreactors must take into account the variation of these new parameters from one reaction to another. It is therefore unlikely that an all-purpose photochemical reactor is feasible. Rather the industrialization of each photoreaction will necessitate the design of a specific photoreactor. However, the development of these new photoreactors can only be undertaken when the variables of each industrializable photoreaction have been defined and studied and when the photochemical engineer knows how to take them into account.

Reference for Appendix A

A1 S. K. Fong, *Ph.D. Thesis*, University of New South Wales, 1970.

Appendix B: nomenclature

a_a extent of the reaction at the exit of a stirred reactor of the Lucas type

$\tilde{a}_a$ extent of the reaction at the exit of a stirred reactor

a_p extent of the reaction at the exit of a plug flow reactor of the Lucas type

C concentration (mol l^{-1})

C_g concentration in the gas phase (mol l^{-1})

D diffusion coefficient (cm^2 s^{-1})

E_i amplification factor

H coefficient defined by Henry's law

I_a total absorbed light intensity (einsteins s^{-1} l^{-1})

I_0 emitted light intensity (einsteins s^{-1} l^{-1})

k_1 propagation rate constant (mol^{-1} l s^{-1})

k_t termination rate constant (mol^{-1} l s^{-1})

$k_{t,g}$ termination rate constant in the gas phase (mol^{-1} l s^{-1})

L thickness of the falling film or the optical path length (cm)

p coefficient defined in ref. 2

q volume flow of the reactant in the irradiated compartment of a reactor of the Lucas type (l s^{-1})

Q volume flow of unirradiated reactant in the dark region of a reactor of the Lucas type (l s^{-1})

r radial coordinate (cm)

r_b radius of a gas bubble (cm)

R $V_0/I_a^{1/2}$

S cross section of the plug flow reactor (dm^2)

t time (s)

T residence time in the dark region of a reactor of the Lucas type (s)

v volume of the irradiated region of a reactor of the Lucas type (l)

V volume of the dark region of a reactor of the Lucas type (l)

V_c calculated reaction rate (mol l^{-1} s^{-1})

V_e experimental reaction rate (mol l^{-1} s^{-1})

V_0 initial reaction rate (mol l^{-1} s^{-1})

x abscissa (cm)

ϵ molar extinction coefficient (mol^{-1} l cm^{-1})

η radical transfer efficiency

ρ ratio of the volume of the irradiated region to the volume of the dark region in a reactor of the Lucas type

τ residence time in the irradiated region of a reactor of the Lucas type (s)

ϕ quantum yield of photolysis (initiation stage)