

INDUSTRIAL PHOTOCHEMISTRY

III: INFLUENCE OF THE STIRRING OF REACTANTS ON THE KINETICS AND SELECTIVITY OF CONSECUTIVE LONG-CHAIN PHOTOCHEMICAL REACTIONS

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Summary

Under industrial conditions it is chlorine which, after absorption of light, gives free atoms which generate chlorination chains. In the particular case of the photochemical chlorination of toluene where several successive chlorination reactions are involved we show that the presence of an intense exciting light flux can be responsible for a reduction in the selectivity of the reaction; indeed, under such conditions the chlorination reaction does not occur in a homogeneous manner in the liquid phase (kinetic regime) but rather in the vicinity of the chlorine bubbles entering the reactor (diffusion regime). Thus successive chlorination reactions occur in a region in which chlorine can diffuse; each bubble then constitutes a kind of plug flow reactor which is independent of the buffer medium. This phenomenon is responsible for a modification of the selectivity of the reaction.

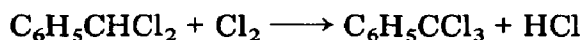
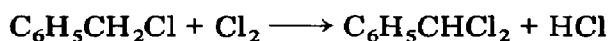
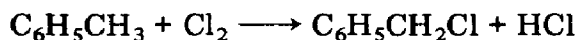
1. Introduction

In the two previous papers in this series [1, 2] we have demonstrated the effects that light distribution and stirring processes have on the initial and near-initial kinetics of long-chain reactions. In particular, in the case of the photochlorination of benzyl chloride we have been able to show that the spatial distribution of the free-radical chain carriers was defined by the absorption profile of the light in the photoreactor.

Under industrial conditions free chlorine atoms which generate the chain are produced when the chlorine molecules absorb suitable photons.

Thus if the rate of replacement of chlorine in the absorption zone is inadequate, high concentrations of the product to be photochlorinated, local impoverishment of chlorine leading to light absorption in deeper regions and eventually, when the consumption of chlorine is very rapid, almost complete disappearance of chlorine in the solution resulting in a reaction localized at the gas-liquid interface will occur. These different conditions can be obtained experimentally during a study of the photochlorination of toluene ($C_6H_5CH_3$) benzyl chloride ($C_6H_5CH_2Cl$) and benzylidene chloride ($C_6H_5CHCl_2$).

The following series of reactions is observed in the formation of benzyl chloride from toluene:



where $C_6H_5CCl_3$ is phenyl chloroform.

We show here, both theoretically and experimentally, that the spatial distribution of the absorbed light is likely to influence the selectivity of the conversion of toluene to benzyl chloride.

2. Mass transfer between gases and liquids

If we consider only physical absorption, that is the dissolution of a gas in a liquid when no chemical reaction occurs, we observe experimentally that the mean rate \bar{R} of gas absorption can be represented by the relation

$$\bar{R} = k_L S(A^* - A^0)$$

where A^0 is the mean concentration of gas dissolved in the liquid, A^* is the concentration of gas dissolved corresponding to the equilibrium with its partial pressure at the gas-liquid interface, S is the specific interfacial area and k_L is the mass transfer coefficient.

Numerous simplified models have been proposed to describe these absorption phenomena including those of Higbie [3] (surface renewal model) and Whitman [4] (film model) which were developed to examine the influence of chemical reactions on gas-liquid absorption. These models, which are generally not very realistic, have led to the determination of the coefficient k_L which is written

$$k_L = D/\delta$$

for the film model and

$$k_L = 2 \left(\frac{D}{\pi \theta} \right)^{1/2}$$

for the surface renewal model. D is the diffusivity of gas in the solution, δ is the thickness of the diffusion film and θ is the mean gas-liquid contact time of each element of the exchange surface.

Some workers have determined the coefficient k_L experimentally. In particular, Calderbank and Moo-Young [5] have established that in a bubble column where the bubble diameter is greater than 2.5 mm k_L can be calculated from the semiempirical formula

$$k_L = 0.42(g\nu)^{1/3} \left(\frac{D}{\nu} \right)^{1/2}$$

where ν is the kinematic viscosity of the liquid and g is the acceleration due to gravity. We have used this equation in the present work.

2.1. Saturation of a stirred solution in a half-closed reactor

If S is the specific surface area, c_g is the mean concentration in the chlorine bubbles, c_∞ is the equilibrium concentration expected in the absence of photochlorination and c_1 is the concentration in the liquid, we can describe the variation in the concentration of chlorine dissolved in a stirred solution in the absence of a reaction by

$$\frac{dc_1}{dt} = k_L S (c_\infty - c_1)$$

from which

$$c_1 = c_\infty \{1 - \exp(-k_L S t)\} = c_\infty \left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}$$

where $\tau = 1/k_L S$. When we make the substitutions

$$D = 5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

$$\nu = \frac{\text{viscosity}}{\text{volume mass}} = 1 \text{ cP g}^{-1}$$

$$g = 9.81 \text{ m s}^{-2}$$

$$k_L = 3.3 \times 10^{-2} \text{ cm s}^{-1}$$

we obtain the following results: extent of retention, 0.3; bubble diameter, 5 mm; $S = 3.6 \text{ cm}^{-1}$. These lead to a value of 8.4 s for τ . The saturation of the solution by chlorine is therefore not instantaneous. This effect is shown in Fig. 1.

2.2. Influence of a photochemical reaction

If the reaction is sufficiently slow to take place in the whole volume of the reactor (low optical density) and yet is sufficiently rapid for the concentration c_1 at equilibrium to be noticeably different from c_∞ , the rate of absorption of chlorine can be represented by the following relation:

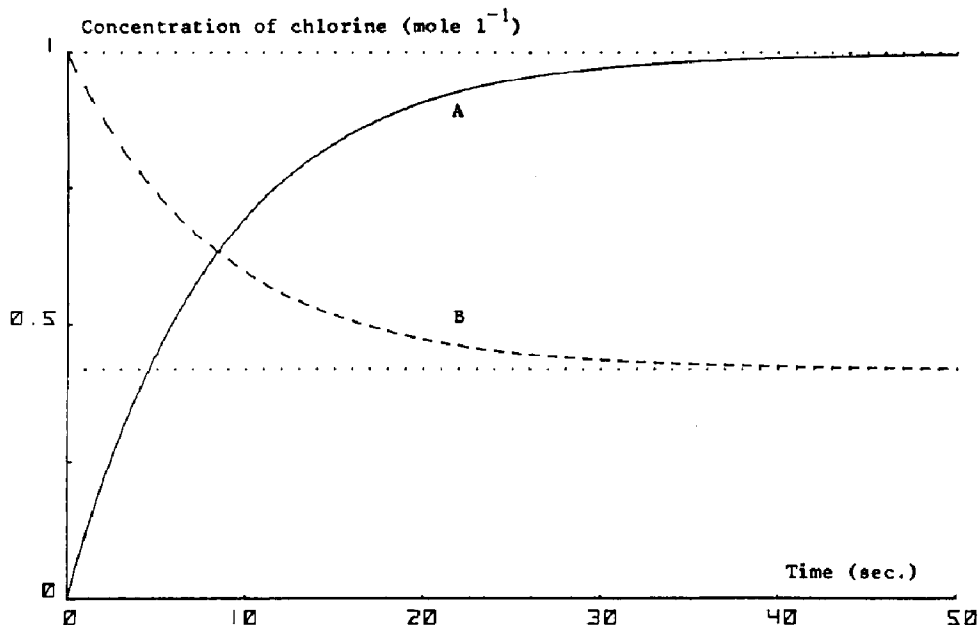


Fig. 1. Variation in the concentration of chlorine dissolved in toluene with time: curve A, in the absence of a reaction; curve B, after saturation of the solution and in the presence of irradiation under the standard laboratory conditions for photochlorination.

$$\bar{R} = k_L S (c_\infty - c_1) = \frac{dc_1}{dt} + k[RH]I_a^{1/2}$$

where RH is the substance to be photochlorinated, I_a is the intensity of light absorbed and $k = (\phi/k_t)^{1/2}k_p$ (mechanism A defined in ref. 2). ϕ is the primary quantum yield of initiation and k_p and k_t are the rate constants of the most important processes of propagation and termination of the chains. Therefore

$$c_1 = c_\infty - \frac{R_0}{k_L S} \left\{ 1 - \exp\left(-\frac{t}{\tau}\right) \right\}$$

where $R_0 = k[RH]I_a^{1/2}$. At the end of a time long with respect to τ we obtain the limiting value

$$c_1 = c_\infty - \frac{R_0}{k_L S}$$

For the photochlorination of toluene carried out in the laboratory where $R_0 = 6.2 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$ and $c_\infty = 1 \text{ mol l}^{-1}$ we obtain $c_1 = 0.42 \text{ mol l}^{-1}$ (see Fig. 1).

It should be noted that this relation only holds for $R_0 < c_\infty k_L S$. At higher values of R_0 the mean concentration of chlorine in the solution must be zero and the photoreaction will be limited to the vicinity of the bubbles (see Section 3.2).

3. Concentration profile of chlorine in the photoreactor

3.1. Kinetic regime

The kinetic regime exists when the reaction in the liquid is sufficiently slow to take place far from the gas-liquid interface in such a way that the bubbling ensures a continuous supply of chlorine to the whole of the reactor. However, because of the high molar extinction coefficient of chlorine ($\epsilon = 160 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 313 nm) the photochemical reaction is essentially localized in the region where the light enters the reactor.

To demonstrate the complexity of these phenomena of mass transfer, let us assume that a bubble of chlorine is irradiated directly without any previous absorption taking place (Fig. 2(a)). The regions close to the photon source must lead to larger reaction rates than the dark regions; therefore the diffusion of chlorine in these zones must be less rapid. The theoretical description of such reaction systems is almost impossible at present as we would have to take into account regions illuminated indirectly by reflection of the light not absorbed by the walls of the reactor, reflection by the chlorine bubbles etc. It is therefore necessary to introduce simplifying hypotheses into the analysis of the system. For example, the illumination is assumed to be the mean of the exciting fluxes arriving in the dark and irradiated zones. It is then possible to express semiquantitatively the variations in the chlorine concentration in the liquid phase near the gas-liquid interface.

We must now solve the equation

$$\frac{K}{D} (\mu c)^{1/2} = \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r}$$

for the liquid phase where D is the diffusion coefficient (physical and chemical), c is the concentration of chlorine, r is the distance of a given point from the centre of a bubble, μ is the absorption coefficient of chlorine, K is a coefficient equal to $\{(\phi I_0)^{1/2}/k_t^{1/2}\}k_p[\text{RH}]$ and I_0 is the incident luminous flux.

This approximation leads us to believe that the light intensity absorbed is essentially proportional to the chlorine concentration. The assumption that the exponential attenuation of the absorbed light is negligible appears reasonable when the strong absorption of light at $r > r_b$ (see Fig. 2(b)) is taken into account. Since the chlorination rate is very fast, there will be a very rapid consumption of chlorine in these zones and hence the diffusion of chlorine in the neighbourhood of the interface will be limited.

In the light of these remarks and approximations we can assume that the photoreactor is made up of two zones (see Fig. 2(c)): an irradiated zone between 0 and α which absorbs 99% of the exciting light; a dark zone between α and r_p from which the chlorine can migrate towards the irradiated zone by diffusion.

If, for simplicity, we choose a planar reactor for which we can obtain a simple analytical solution (instead of a modified Bessel equation which

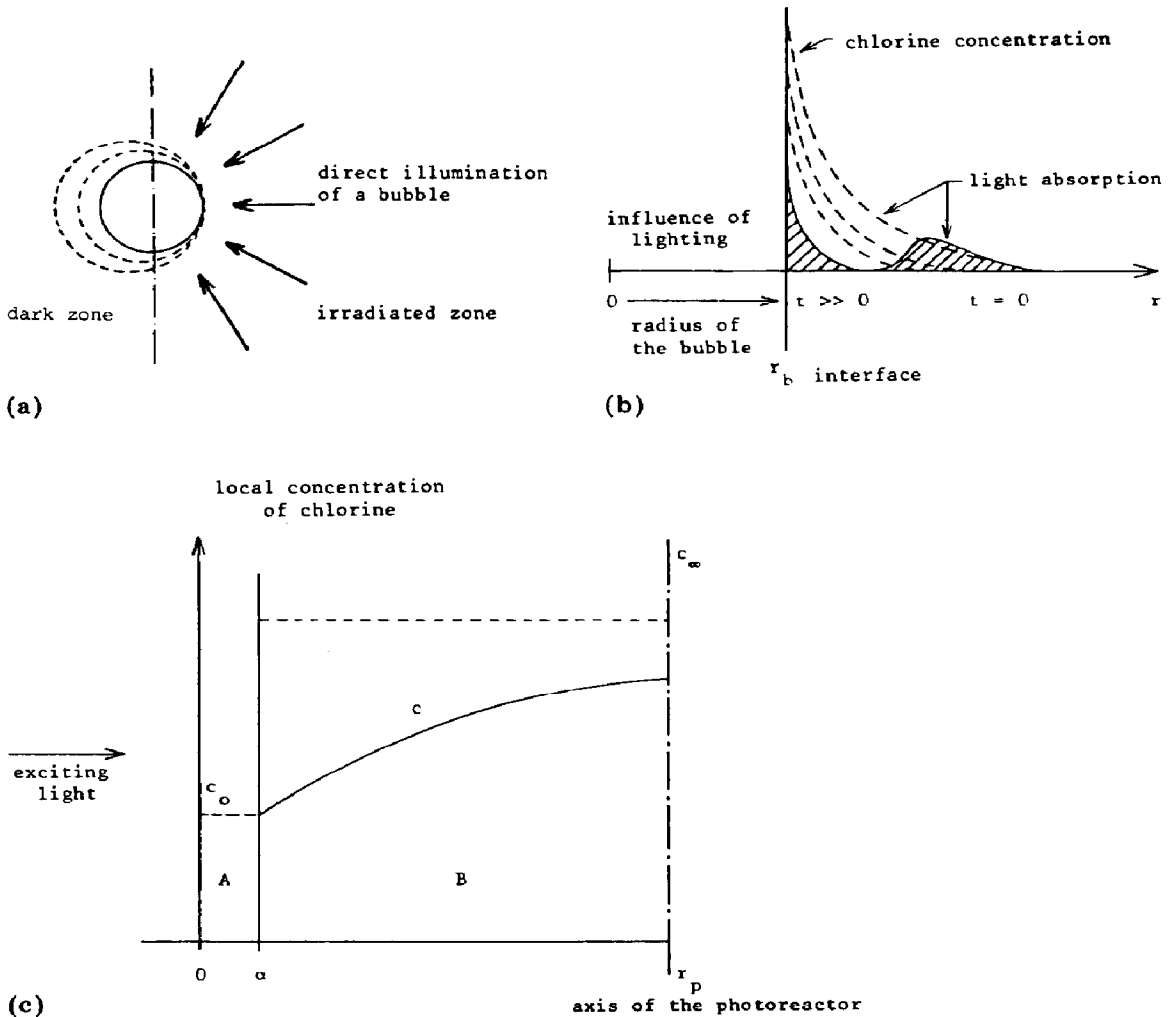


Fig. 2. (a) Schematic representation of the non-homogeneous diffusion of chlorine for non-homogeneous irradiation around a bubble (---, isoconcentration curve of chlorine); (b) evolution of the absorption profiles of the light (see text); (c) separation of the photoreaction into two zones (A, irradiated zone; B, dark zone from which mass transfer occurs).

would give no information on the semiquantitative description of the phenomena studied here), we have to solve

$$K(I_a)^{1/2} = k_L S(c_\infty - c_0) + D \left(\frac{\partial c}{\partial r} \right)_\alpha$$

between 0 and α , and

$$k_L S(c_\infty - c) + D \frac{\partial^2 c}{\partial r^2} = 0$$

between α and r_p . The solution is of the form

$$c = c_\infty + A \exp(-ar) + B \exp(ar)$$

where $a = (k_L S/D)^{1/2}$. (Under our experimental conditions and from calculations of the D coefficients carried out in ref. 2, a is of the order of 0.63.) A and B are two constants defined by the preceding equations when $(\partial c/\partial r)_{r_p} = 0$, so that

$$B = A \exp(-2ar_p)$$

$$A = -\frac{K}{D} \left(\frac{I_0}{\alpha} \right)^{1/2} \frac{1}{a[\alpha\{1 + \exp(-2ar_p)\} + \{1 - \exp(-2ar_p)\}]}$$

The calculation of α is performed using the simplifying hypothesis of an absorption limit of 99%, *i.e.*

$$\mu \frac{c\alpha}{c_\infty} = 4.6$$

or

$$\frac{c\alpha}{c_\infty} = 2.65 \times 10^{-2} \text{ cm}$$

We then obtain the following value for a chlorine concentration c_0 between 0 and α :

$$c_0 = \frac{1}{4} \left\{ -\frac{K}{D} \left(\frac{I_0}{2.65 \times 10^{-2} c_\infty} \right)^{1/2} \frac{1}{a\{a + \tanh(a\alpha)\}} + \left[\left(\frac{K}{D} \left(\frac{I_0}{2.65 \times 10^{-2} c_\infty} \right)^{1/2} \frac{1}{a\{a + \tanh(a\alpha)\}} \right)^2 + 4c_\infty \right]^{1/2} \right\}^2$$

These results allow us to calculate α and hence $c(r)$ as shown in Fig. 3 for $0 < r < r_p$. The standard conditions (mean rate, $6.2 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$ for $\langle J_a \rangle = 2 \times 10^{-8} \text{ einstein l}^{-1} \text{ s}^{-1}$; $K = 4.4 \times 10^{-2}$; $I_0 = 2 \times 10^{-9} \alpha \text{ einstein dm}^{-2} \text{ s}^{-1}$; $K/D = 2.2 \times 10^3$; $a = 0.63$) (see curve 3) correspond to experiments reported in ref. 2.

During the study of the photochlorination of benzyl chloride, a correction related to the light absorption profile shown in Table 1 should be made; the value obtained for $c = c_\infty$ at the corrected rate at 254 nm differs markedly from that obtained at 313 nm. The latter absorption wavelength is that used for chlorine in solution, the mean concentration c_0 of which in the irradiated zone is less than c_∞ and therefore corresponds to a corrected value. We can thus explain the difference between the results obtained by irradiation at 254 nm and at 313 nm.

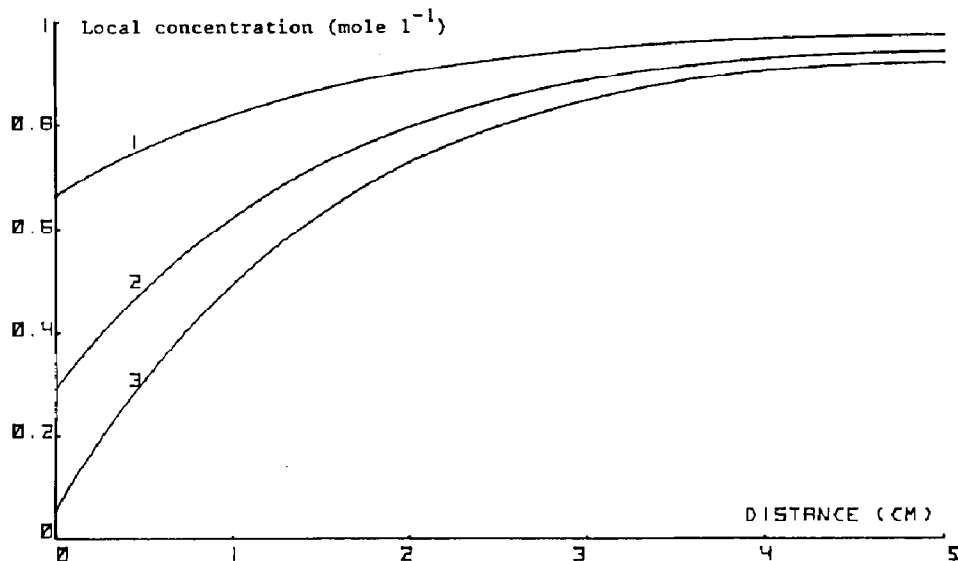


Fig. 3. Effect of the intensity of the incident light on the concentration profile of chlorine in the photoreactor: curve 1, $I_0/I_0^* = 0.01$; curve 2, $I_0/I_0^* = 0.1$; curve 3, $I_0/I_0^* = 1$. I_0^* is the intensity of the incident light under standard conditions [2].

TABLE 1

Excitation wavelength (nm)	$R_0/I_0^{1/2}$ (mol ^{1/2} l ^{-1/2} s ^{-1/2})	μ [2] (cm ⁻¹)	P_L [2]	$R_0/I_0^{1/2} P_L$ (mol ^{1/2} l ^{-1/2} s ^{-1/2})
254	13.9	3950	0.063	221
313	60	196	0.200	300

3.2. Diffusion regime

As already discussed, the diffusion regime exists at high incident light intensities. If this regime limits the reaction to the vicinity of the chlorine bubbles (see Fig. 4), it will be of interest to industry as it allows a high transformation rate, the absence of gaseous chlorine in the hydrochloric acid formed and recovered at the reactor exit and the elimination of the thermal addition reactions to the benzene ring between the chlorine and the compounds to be chlorinated.

If c is the chlorine concentration and if, for simplicity, we assume that the absorption is proportional to the concentration of chlorine dissolved near a bubble and that the hydrocarbon concentration is high, the chlorine concentration is defined by a law of the type

$$\frac{\partial c}{\partial t} = D \nabla^2 c - Kc^{1/2}$$

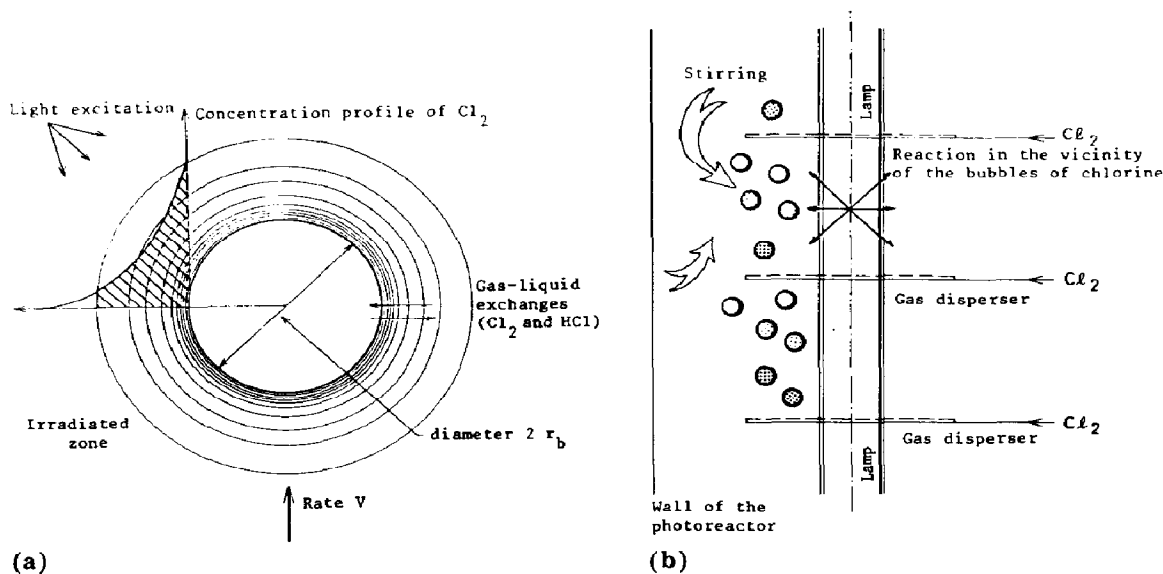


Fig. 4. Schematic representation of (a) a reaction in the diffusion regime near a bubble and (b) a photoreactor used for chain photoreactions.

where D is the diffusion coefficient of chlorine in the medium and K is a coefficient dependent on the reaction kinetics. Moreover, a limiting condition exists at the interface, which can be written

$$SD \left(\frac{\partial c}{\partial r} \right)_{r_b} = k_L S (c_\infty - c_0)$$

where r_b represents the radius of the bubble. This series of equations cannot be integrated, except numerically, and in order to visualize the distribution of the chlorine reactant near the bubble we make the following simplifying hypotheses: the lifetime of the bubble is sufficiently long and the bubble is sufficiently large to assume that

$$\frac{\partial c}{\partial t} = 0$$

inside the bubble; if c_0 represents the mean concentration, corresponding for example to an absorption of 90%, we assume

$$c^{1/2} \approx \frac{c}{c_0^{1/2}}$$

When these conditions are assumed the following very much simplified equation, which can be solved, is obtained:

$$\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} - \frac{K}{Dc_0^{1/2}} c = 0$$

which leads to

$$c \approx \frac{c_{\infty} k_L S}{(D/r_b^2)(1 + sr_b) + k_L S/r_b} \exp\{-s(r - r_b)\}$$

where

$$s = \left(\frac{K}{Dc_0^{1/2}} \right)^{1/2}$$

When we substitute the values given above, *i.e.*

$$D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

$$r_b \approx 0.5 \text{ cm}$$

$$k_L S \approx 5 \times 10^{-2} \text{ cm}^3 \text{ s}^{-1}$$

$$c_0 \approx 0.1 \text{ mol l}^{-1}$$

and the chlorination rates determined for toluene in the kinetic reaction regime, we obtain

$$K = 0.33 \left(\frac{1}{c_{\infty}} \right)^{1/2} \left\{ \frac{(I_0)_D}{I_0} \right\}^{1/2} \text{ mol l}^{-1} \text{ s}^{-1}$$

where I_0 and c_{∞} are the light intensity and the concentration corresponding to the conditions of the kinetic regime and $(I_0)_D$ is the incident light intensity corresponding to the diffusion regime.

For $(I_0)_D/I_0 = 100$, a condition which is easily obtained in an industrial reactor, we obtain

$$s \approx 100$$

from which, when the numerical values are taken into account,

$$c \approx c_{\infty} \exp\{-100(r - r_b)\}$$

Thus the chlorine concentration at the gas-liquid interface approaches the maximum concentration defined by Henry's law. The thickness of the useful layer, in which 90% of the reaction occurs, is obtained from

$$\exp\{-100(r - r_b)\} \approx 0.01$$

and is

$$r - r_b \approx 2 \times 10^{-2} \text{ cm}$$

Thus the reaction takes place in a thin layer of liquid very close to the chlorine bubble. In practice this liquid layer is a few tenths of a millimetre thick.

The influence of the absorbed light intensity on the reactor volume in which the photochlorination reaction takes place is shown schematically in Fig. 5. At low light intensities this volume, which is limited to the absorption

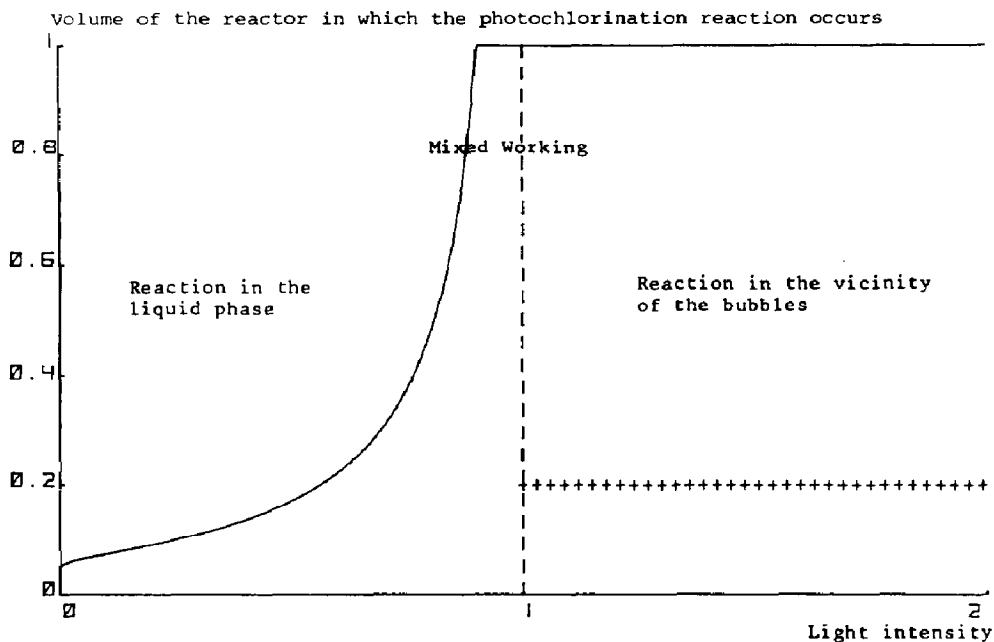


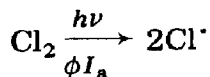
Fig. 5. Influence of the absorbed light intensity on the volume fraction of the reactor in which photochlorination occurs.

zone, does not depend on c_{∞} . When the intensity is increased, the kinetic regime is maintained but the absorption takes place deeper in the liquid and the volume where the reaction takes place is increased. At very high intensities the reactive zone is restricted to a limiting layer near the chlorine bubbles.

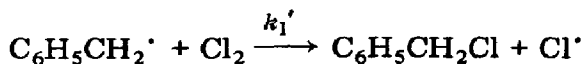
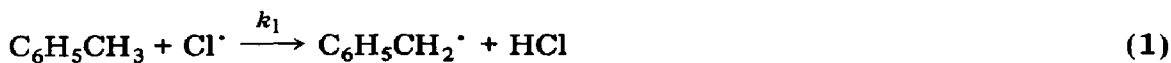
4. Influence of the reaction regime on the selectivity

4.1. Kinetic regime

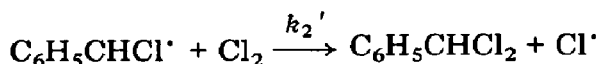
The mechanism of the photochemical chlorination of toluene can be represented by the following processes [6, 7]: initiation,



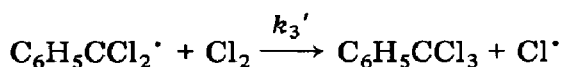
propagation (I),



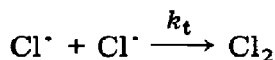
propagation (II),



propagation (III),



termination,



In a homogeneous solution the variations in the concentrations of the reactants as a function of time can be expressed as follows:

$$\frac{d[\text{C}_6\text{H}_5\text{CH}_3]}{dt} = - \left(\frac{\phi I_a}{k_t} \right)^{1/2} k_1 [\text{C}_6\text{H}_5\text{CH}_3]$$

$$\frac{d[\text{C}_6\text{H}_5\text{CH}_2\text{Cl}]}{dt} = \left(\frac{\phi I_a}{k_t} \right)^{1/2} (k_1 [\text{C}_6\text{H}_5\text{CH}_3] - k_2 [\text{C}_6\text{H}_5\text{CH}_2\text{Cl}])$$

$$\frac{d[\text{C}_6\text{H}_5\text{CHCl}_2]}{dt} = \left(\frac{\phi I_a}{k_t} \right)^{1/2} (k_2 [\text{C}_6\text{H}_5\text{CH}_2\text{Cl}] - k_3 [\text{C}_6\text{H}_5\text{CHCl}_2])$$

$$\frac{d[\text{C}_6\text{H}_5\text{CCl}_3]}{dt} = \left(\frac{\phi I_a}{k_t} \right)^{1/2} k_3 [\text{C}_6\text{H}_5\text{CHCl}_2]$$

We have used the experimental values for the rate constants of processes (1), (2) and (3) at 50 °C, which are given in Table 2 [6], to determine the variations in the concentrations of the reaction products as a function of the irradiation time (Fig. 6).

4.2. Diffusion regime

Each chlorine bubble which rises to the surface of the liquid in the photoreactor brings partially photochlorinated reactants with it. We can therefore assume that the photoreactor consists of two regions (see Fig. 7): a region where the photochemical reaction occurs during the lifetime T of a bubble and a second region which serves as a buffer reservoir and where no chemical reaction takes place (absence of chlorine). Under these conditions we can assume that the successive reactions occur in the chlorine penetration zone. At the end of the mean time T the reaction products are mixed throughout the reactor and the new mixture obtained is photochlorinated

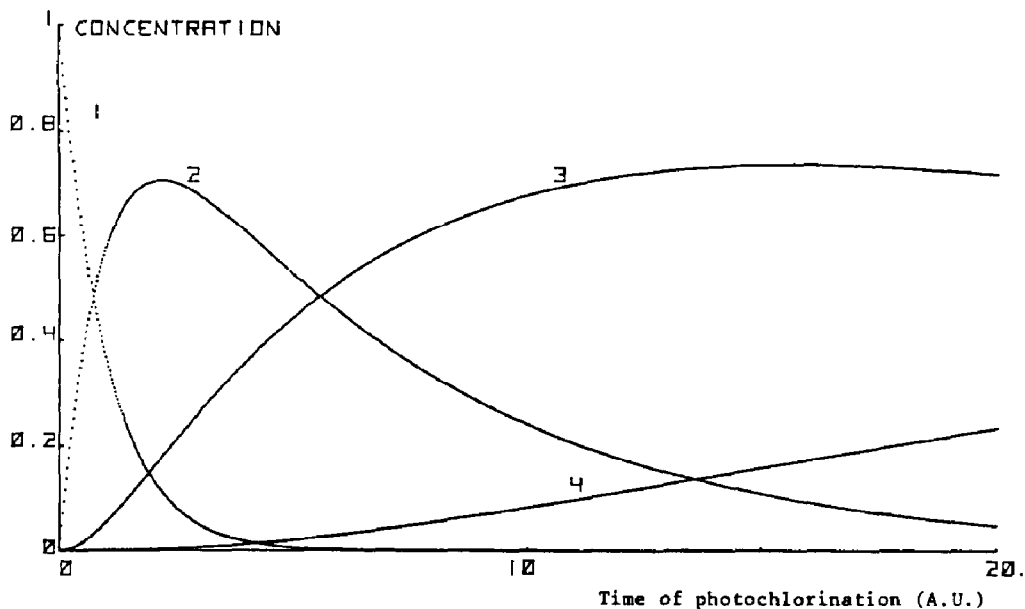


Fig. 6. Variation in the concentration of toluene and its chlorinated derivatives on the chain as a function of the irradiation time at 313 nm and 50 °C: curve 1, $\text{RH} \equiv \text{C}_6\text{H}_5\text{CH}_3$; curve 2, $\text{RH} \equiv \text{C}_6\text{H}_5\text{CH}_2\text{Cl}$; curve 3, $\text{RH} \equiv \text{C}_6\text{H}_5\text{CHCl}_2$; curve 4, $\text{RH} \equiv \text{C}_6\text{H}_5\text{CCl}_3$.

TABLE 2

Product	$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$\text{C}_6\text{H}_5\text{CHCl}_2$
k_i ($\text{mol}^{-1} \text{l s}^{-1}$)	$k_1 = 10^{7.4}$	$k_2 = 10^{6.6}$	$k_3 = 10^{5.7}$

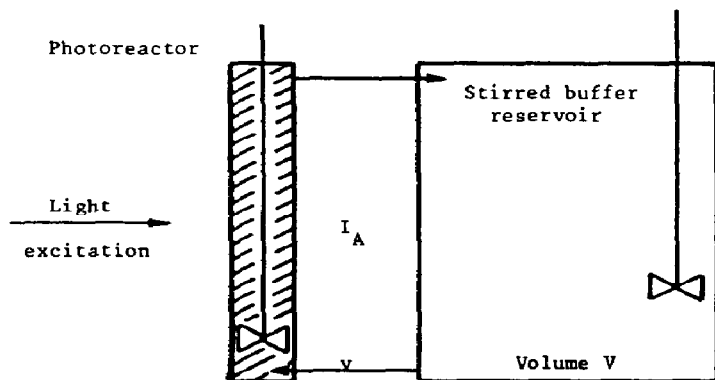


Fig. 7. Schematic representation of a gas-liquid photoreactor working in the diffusion regime.

around the next chlorine bubble. Figure 8 shows that when the solution is not stirred, as is the case around bubbles of gaseous reactants, there is likely to be a decrease in the selectivity of benzyl chloride and an increase in the kinetics of formation of the trichlorinated compound.

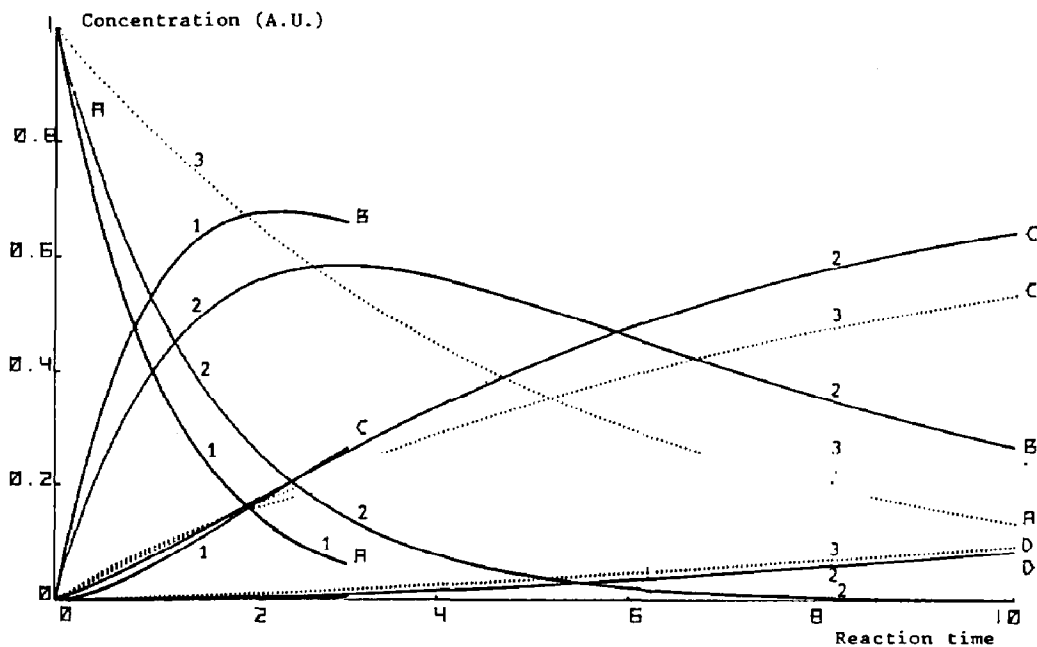


Fig. 8. Influence of the lifetime T of a chlorine bubble on the selectivity of photochlorination of $C_6H_5CH_3$ (curves A), $C_6H_5CH_2Cl$ (curves B), $C_6H_5CHCl_2$ (curves C) and $C_6H_5CCl_3$ (curves D): curves 1, $T = 0.2$ s; curves 2, $T = 1$ s; curves 3, $T = 5$ s.

So far we have assumed that the concentrations of the liquid reactants are very much larger than those of the dissolved reactant, *i.e.* chlorine, as these conditions are closer to those existing in industrial processes.

On a laboratory scale we can demonstrate this loss of selectivity in benzyl chloride by choosing a concentration of dissolved chlorine which is much larger than that of the reactants. We must then maintain a diffusion regime such that the liquid reagents move towards the walls where the photochemical reaction occurs and the subsequent change in the selectivity with respect to the first chlorination product can be detected.

5. Experimental verification

5.1. Kinetic regime

Figure 9 shows the distribution of the reaction products as a function of the degree of chlorination from 0 to 3 at a temperature of $50^\circ C$. In order to achieve a diffusion regime and to reproduce industrial conditions more closely the temperature of the liquid phase was increased to $80^\circ C$. The results obtained are shown in Fig. 10, curve I.

5.2. Diffusion regime

When the intensity of the lamp was increased the conditions of the diffusion regime were obtained and, as predicted in Section 4, a decrease in the selectivity of benzyl chloride was observed (Fig. 10, curves II). However,

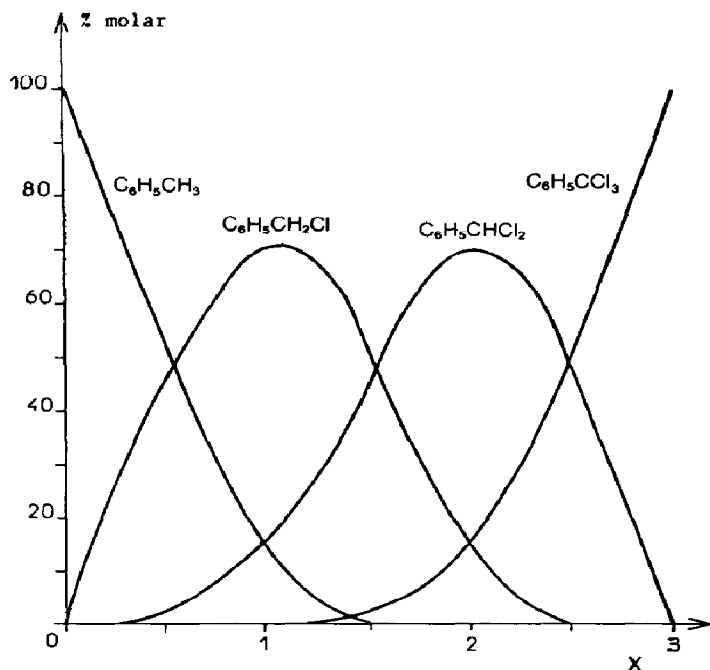


Fig. 9. Distribution of the products of toluene photochlorination as a function of the extent x of chlorination at 50 °C and 254 nm.

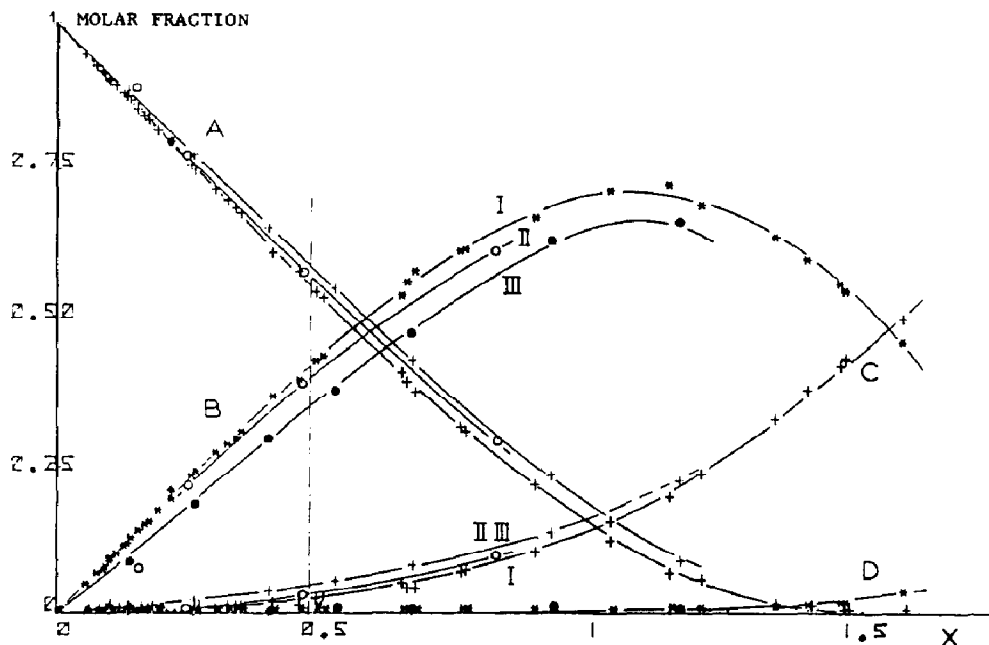


Fig. 10. Influence of the reaction regime on the distribution of the products of toluene photochlorination as a function of the extent x of chlorination at 80 °C and 313 nm: curves A, $C_6H_5CH_3$; curves B, $C_6H_5CH_2Cl$; curves C, $C_6H_5CHCl_2$; curves D, $C_6H_5CCl_3$; curves I, kinetic regime with $[RH] = 9.42 \text{ mol l}^{-1}$; curves II, diffusion regime with $[RH] = 9.42 \text{ mol l}^{-1}$; curves III, diffusion regime with $[RH] = 0.094 \text{ mol l}^{-1}$ (solvent, tetrachlorethylene).

when the extent of chlorination approached 0.5 the yellow coloration denoting the presence of chlorine in the solution reappeared. This phenomenon is interpreted as follows: the reactivity of the partially chlorinated products with respect to the free chlorine atom decreases with the degree of chlorination; thus as soon as the extent of the reaction exceeds 0.5 (under our experimental conditions) the rate of photochlorination at the same intensity becomes insufficient to consume all the chlorine entering the reactor.

These effects are demonstrated in Fig. 11 which shows the effects of both the extent of chlorination and the intensity of the absorbed light on the concentration of chlorine in the solution.

As predicted in Section 4 we should also expect a change in selectivity for very low concentrations of liquid reagent. As is shown in Fig. 10, curves III, this is in fact the case.

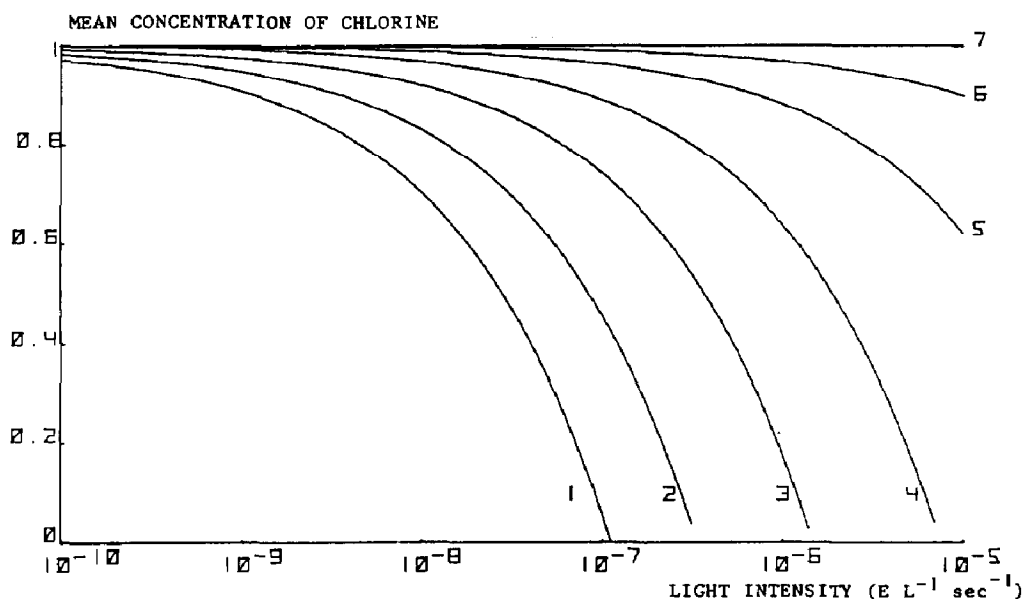


Fig. 11. Influence of the extent of chlorination and of the absorbed light intensity on the concentration of chlorine in the solution: curve 1, $x = 0$; curve 2, $x = 0.5$; curve 3, $x = 1$; curve 4, $x = 1.5$; curve 5, $x = 2$; curve 6, $x = 2.5$; curve 7, $x = 3$.

6. Conclusion

In the first three papers of this series we have shown the complex influence that the distribution and intensity of the light, the lifetime of the free-radical chain carriers, the stirring process and the homogeneity of the solution with respect to the free radicals and the reactants can have on the kinetics of long-chain photochemical reactions. In order to summarize this work the influence of these macroscopic parameters on the kinetics of chlorination of toluene to benzyl chloride is shown in Table 3.

It should be possible to extrapolate these results to a large number of photochemical reactions of industrial interest.

TABLE 3

<i>Parameter</i>	<i>Effect on the kinetics of a positive variation in the parameter</i>	<i>Comments</i>
Temperature	Increase in rate	Stirring is easier Lower limiting concentration of chlorine (Henry's law) Local boiling Decrease in the selectivity of benzyl chloride, made worse by the change from a kinetic regime to a diffusion regime
Light intensity	Increase in rate	Increase in the temperature (ΔH) Change from the kinetic regime to the diffusion regime; decrease in the selectivity of benzyl chloride
Gas flow	Increase in rate followed by a decrease	Heat exchanges and stirring are easier in the diffusion regime Eases the creation of the gas-liquid interface, with passage through a maximum related to the phenomenon of coalescence in the diffusion regime
	No change	No effect in the kinetic regime
Chlorine pressure	Decrease in rate	Chain lengths decrease owing to a more localized absorption Eases substitutions on the ring which results in a loss of selectivity

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Appendix A: nomenclature

- A^0 mean concentration of a gas dissolved in a liquid (mol l^{-1})
 A^* concentration of gas dissolved corresponding to thermodynamic equilibrium in the absence of a reaction (mol l^{-1})
 c concentration (mol l^{-1})
 c_g mean concentration of chlorine in a chlorine bubble (mol l^{-1})
 c_1 mean concentration of dissolved chlorine (mol l^{-1})

c_0	concentration of chlorine dissolved in the illuminated zone of the reactor (mol l^{-1})
c_∞	concentration of chlorine dissolved at thermodynamic equilibrium in the absence of a reaction (mol l^{-1})
D	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
g	acceleration due to gravity (m s^{-2})
I_a	absorbed light intensity (einsteins $\text{l}^{-1} \text{s}^{-1}$)
I_0	incident light intensity (einsteins $\text{s}^{-1} \text{cm}^{-2}$)
$(I_0)_D$	incident light intensity leading to the diffusion regime of photo-chlorination (einsteins $\text{s}^{-1} \text{cm}^{-2}$)
k	constant
k_i, k_i'	rate constants of the i th propagation process ($\text{mol}^{-1} \text{l s}^{-1}$)
k_L	mass transfer coefficient (cm s^{-1})
k_p	rate constant of a propagation process ($\text{mol}^{-1} \text{l s}^{-1}$)
k_t	rate constant of a biradical termination process ($\text{mol}^{-1} \text{s}^{-1}$)
P_L	coefficient defined in ref. 2
r	distance between a given point and the centre of a bubble (cm)
r_b	radius of a bubble (cm)
r_p	radius of a cylindrical photoreactor (cm)
\bar{R}	mean rate of absorption of a gas in a liquid ($\text{mol l}^{-1} \text{s}^{-1}$)
RH	hydrocarbon to be chlorinated
R_0	mean rate of chlorination ($\text{mol l}^{-1} \text{s}^{-1}$)
S	specific surface area (cm^{-1})
t	time (s)
x	extent of chlorination
α	thickness of the reactor zone corresponding to 99% absorption of the exciting light (cm)
δ	thickness of the diffusion film (cm)
ΔH	enthalpy of reaction (kJ mol^{-1})
ϵ	molar extinction coefficient ($\text{l mol}^{-1} \text{cm}^{-1}$)
θ	mean time of gas-liquid contact (s)
μ	absorption coefficient (cm^{-1})
ν	Stokes kinematic viscosity
ϕ	quantum yield of photolysis at the irradiation wavelength