

INDUSTRIAL PHOTOCHEMISTRY

II: INFLUENCE OF THE STIRRING OF UNSTABLE RADICAL SPECIES ON THE KINETICS OF LONG CHAIN PHOTOCHEMICAL REACTIONS

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Summary

The experimental rate of a photochemically initiated long chain reaction seems to be a function of the absorption profile of the light, the mean lifetime of the free radical chain carriers and finally of all the processes of homogenization of the medium. The influence of these different factors is defined theoretically and illustrated with the aid of gas-liquid-type reactions, *i.e.* photooxidation of heptanal and benzaldehyde and photochlorination of benzyl chloride.

1. Introduction

As a rule an order n of a photochemical reaction can be defined with respect to the mean luminous intensity \bar{I}_a absorbed. If \bar{R} represents the mean rate of formation of a photoproduct, then

$$\bar{R} = k\bar{I}_a^n$$

where k is a constant of proportionality which is independent of \bar{I}_a but is a function of the macroscopic factors of the system. For long chain radical reactions n is found to be equal to 0.5. This value is due to the existence of processes of recombination of the chain carrier radicals.

In order to develop a photochemical reactor adapted to the study of long chain radical reactions in the laboratory, a certain number of conditions are necessary: (1) knowledge of the absorption profile of the light, which gives information about the rate of formation of the free radical chain carriers; (2) the mean lifetime of these radicals; (3) the stirring in the reactor with a view to a homogenization of the irradiated solution, which tends to render the local concentrations of unstable species (radicals) and molecular species

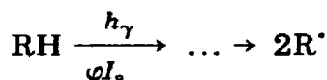
(in particular reagents) uniform. (This stirring can be natural (diffusion) or artificial.)

We present here a mathematical description of the influence of these parameters on the rate of a chain reaction and we also present some experimental results which enable us to illustrate the influence of these parameters.

2. Mean lifetime of a radical

Let us first consider a mechanism for a long chain radical reaction which can be as follows:

(a) photochemical initiation

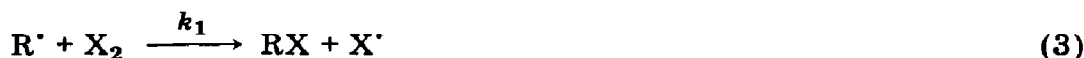


(formation of free radical chain carriers)

(b) mechanism A of propagation



(c) mechanism B of propagation



(d) termination



By adjusting the relative concentrations of RH and X₂ it is possible to obtain conditions where the processes of chain termination are essentially those described by scheme (d), *i.e.* corresponding to the existence of a much higher relative concentration of radical chain carrier. If, for example, the concentration of RH is sufficiently low, so that [RX₂[·]]/[R[·]] is much greater than unity, it becomes possible to define the lifetime of the radical present in the largest stationary quantity [1, 2].

If we assume a homogeneous distribution of the reagents RH and X₂ and of the light absorbed, we can, for example, specify a population of the radicals RX₂[·] as RX₂^{·*}, placed at distances that are sufficiently far apart that their encounter probability is practically zero during their lifetime. The rate of disappearance of the RX₂^{·*} radicals is then expressed by

$$\frac{d[\text{RX}_2^{*\cdot}]}{dt} = -k_2[\text{RX}_2^{*\cdot}][\text{RH}] + k_1[\text{R}\cdot][\text{X}_2] - k_3[\text{RX}_2^{\cdot}][\text{RX}_2^{*\cdot}]$$

As the reaction is a long chain reaction, then

$$\frac{d[\text{RX}_2^{*\cdot}]}{dt} = -k_3[\text{RX}_2^{*\cdot}][\text{RX}_2^{\cdot}].$$

under the chosen conditions (1) mechanism A of propagation and (2) reaction (II) as the preponderant termination reaction.

From this

$$[\text{RX}_2^{*\cdot}] = [\text{RX}_2^{*\cdot}]_{t=0} \exp(-k_3[\text{RX}_2^{\cdot}]t)$$

We can therefore define a mean lifetime of a free radical chain carrier by

$$\tau = \frac{1}{k_3[\text{RX}_2^{\cdot}]}$$

Thus

$$[\text{RX}_2^{\cdot}] = \left(\frac{\varphi \bar{I}_a}{k_3} \right)^{1/2}$$

which leads to

$$\tau = \frac{1}{(k_3 \varphi \bar{I}_a)^{1/2}} \quad (5)$$

Thus when all the radicals are in a homogeneous distribution in their surroundings, their lifetimes depend neither on the rate of initiation $\varphi \bar{I}_a$ nor on the rate constant of the preponderant process of recombination of the chains.

3. Stirring of radical chain carriers

However, as has been shown in ref. 3, the exciting light is absorbed according to non-flat profiles, which brings about an inhomogeneity in the concentration of the radical chain carriers. If the stirring is sufficiently good, we observe a homogenization of the reagents RH and X₂ and of the radical chain carriers in the solution. In this case, the measured lifetime will correspond to that presented here. On the contrary, if the radical lifetime is too short with respect to the processes of homogenization (diffusion, mechanical stirring, convection etc.) a mean value of τ must be used.

3.1. No stirring of the irradiated solutions

If we assume that the reactor used is an annular reactor of the same type as that described in ref. 3, the expression for the transmitted luminous intensity corresponds approximately to

$$I(r) = I(r_0) \frac{r_0}{r} \exp\{-k\epsilon c(r - r_0)\}$$

where k is a constant with a value greater than unity. We can justify the origin of k by the existence of rays emitted non-radially (and which as a consequence have an optical path that is longer than that corresponding to the rays emitted radially and which therefore have a larger probability of being absorbed). ϵ is the molar extinction coefficient of the absorbing substance at the concentration c , $r - r_0$ is the distance between a point r inside the reactor and a point r_0 on its entrance face and $I(r_0)$ is the flux of photons at the distance r_0 (Fig. 1). The luminous intensity absorbed between r and $r + dr$ then corresponds to

$$\begin{aligned} \frac{dI}{dr} &= I_a(r) = k\epsilon c I(r) \\ &= I(r_0) \frac{r_0}{r} \nu \exp\{\nu(r - r_0)\} \end{aligned}$$

with $\nu = k\epsilon c$.

Under these conditions, if there is no displacement of the radical chain carriers, their local lifetime must then be expressed by

$$\tau(r) = \frac{1}{\{k_3 \phi I_a(r)\}^{1/2}}$$

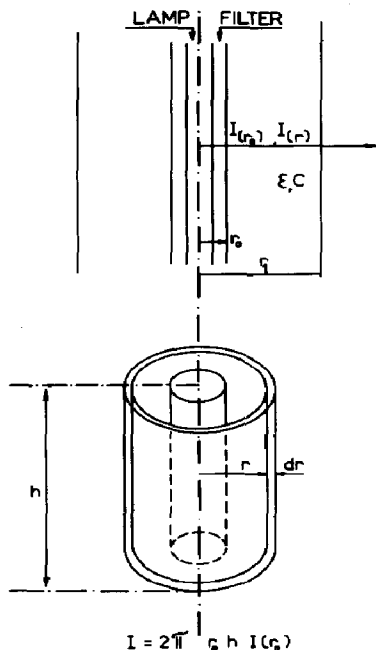


Fig. 1. The geometry of the photoreactor.

The mean lifetime (which has only a less significant meaning for radical species taken randomly in the reactor owing to a non-monoexponential mean decay) is obtained from this relationship by taking the mean local concentrations of these species into account:

$$[\text{RX}_2\cdot]_r = \left\{ \frac{\varphi I_a(r)}{k_3} \right\}^{1/2}$$

Thus

$$\begin{aligned} \langle \tau \rangle &= \frac{2\pi \int_{r_0}^{r_1} r [\text{RX}_2\cdot]_r \tau(r) dr}{2\pi \int_{r_0}^{r_1} r [\text{RX}_2\cdot]_r dr} \\ &= \nu^{1/2} (r_1^2 - r_0^2) \{16k_3\varphi I(r_0)r_0\}^{-1/2} \left[r_0^{1/2} - r_1^{1/2} \exp\left\{-\frac{\nu}{2}(r_1 - r_0)\right\} + \right. \\ &\quad \left. + \left(\frac{\pi}{2\nu}\right)^{1/2} \exp\left(\frac{\nu}{2}r_0\right) \left\{ \text{erf}\left(\frac{\nu r_1}{2}\right)^{1/2} - \text{erf}\left(\frac{\nu r_0}{2}\right)^{1/2} \right\} \right]^{-1} \quad (6) \end{aligned}$$

This value is necessary to compare with the lifetime $\bar{\tau}$ which we would have obtained with sufficient stirring such that the concentration of the radicals is considered as homogeneous. Then if

$$\begin{aligned} \langle I_a \rangle &= \frac{\int_{r_0}^{r_1} I_a(r) r dr}{\int_{r_0}^{r_1} r dr} \\ &= \frac{2r_0 I(r_0)}{r_1^2 - r_0^2} [1 - \exp\{-\nu(r_1 - r_0)\}] \end{aligned}$$

(corresponding to the mean luminous intensity absorbed), we can write

$$\bar{\tau} = \frac{1}{(k_3\varphi\langle I_a \rangle)^{1/2}}$$

We then define a coefficient P_c such that $P_c = \bar{\tau}/\langle \tau \rangle$ so that after calculation

$$\begin{aligned} P_c &= 8^{1/2} [r_0^{1/2} - r_1^{1/2} \exp\{-\nu(r_1 - r_0)\}] + \left(\frac{\pi}{2\nu}\right)^{1/2} \exp\left(\frac{\nu r_0}{2}\right) \left\{ \text{erf}\left(\frac{\nu r_1}{2}\right)^{1/2} - \right. \\ &\quad \left. - \text{erf}\left(\frac{\nu r_0}{2}\right)^{1/2} \right\} \{ \nu(r_1^2 - r_0^2) \}^{-1/2} [1 - \exp\{-\nu(r_1 - r_0)\}]^{-1/2} \quad (7) \end{aligned}$$

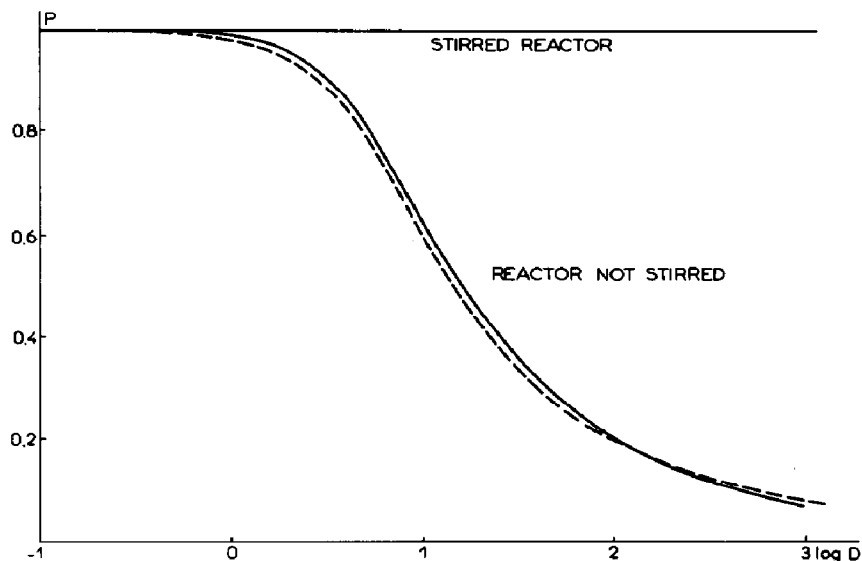


Fig. 2. The variation in the coefficient P as a function of the logarithm of the optical density D : —, planar reactor; ---, cylindrical reactor.

These different relationships are illustrated in Fig. 2 where we show a value of $\langle \tau \rangle$ that is always greater than that which would have been obtained if the solution had been perfectly stirred.

For a linear reactor P_L the expression for the local absorbed intensity is written as

$$I_a(x) = \nu I(x_0) \exp\{-\nu(x - x_0)\}$$

which leads to

$$P_L = \frac{2}{(\nu l)^{1/2}} \frac{1 - \exp(-\nu l/2)}{\{1 - \exp(-\nu l)\}^{1/2}} \quad (8)$$

for the mean rate in the absence of migration of the free radical chain carriers.

3.1.1. Consequences

If we suppose that the reaction obeys the proposed mechanism A with termination process (III), then the expression for the local rate of disappearance of RH is expressed by

$$R(r) = \left(\frac{d[\text{RH}]}{dt} \right)_r = k_2[\text{RH}] \left\{ \frac{\varphi I_a(r)}{k_3} \right\}^{1/2}$$

according to the irradiation profile. Thus, as in the preceding case, according to the mean lifetime of the radicals and to the stirring of the solution we shall define a mean rate by (1) making the assumption that the solution is not stirred (leading to $\langle R \rangle$) and (2) making, on the contrary, the assumption that the solution is perfectly stirred (leading to \bar{R}). Then

$$\langle R \rangle = \frac{2\pi \int_{r_0}^{r_1} rR(r) dr}{2\pi \int_{r_0}^{r_1} r dr}$$

and

$$\bar{R} = \frac{2\pi \int_{r_0}^{r_1} rk_2[\text{RH}](\varphi/k_3)^{1/2}\langle I_a \rangle^{1/2} dr}{2\pi \int_{r_0}^{r_1} r dr}$$

$$\bar{R} = \left(\frac{\varphi\langle I_a \rangle}{k_3} \right)^{1/2} k_2[\text{RH}]$$

with

$$\frac{\langle R \rangle}{\bar{R}} = \frac{\bar{\tau}}{\langle \tau \rangle} \quad (9)$$

As is shown by the results given in Fig. 2, the absence of stirring (in a time region that is less than the mean lifetime of the radical chain carriers) is responsible for the existence of a concentration gradient of the unstable species; this favours their recombination in the region of the entrance of the exciting light rays and, as a consequence, lowers the overall quantum yield of the phototransformation.

3.1.2. Stray absorption of the light

In an earlier article [4] we have used naphthalene, which is chemically inert, for the physical deactivation of the triplet states of aldehydes, precursors of free radical chain carriers in the photooxidation of these compounds. The presence of stray absorption in a perfectly stirred reactor or, on the contrary, in an unstirred reactor can modify the rate of a chain reaction, all other things being equal.

If we assume, for simplicity, an in-line reactor where the light enters axially in a cylindrical reactor, the axis of which is parallel to the direction of irradiation, the Beer-Lambert law enables us to calculate easily the values of the intensities of the light absorbed.

If $\nu = \epsilon c$ and $\nu' = \epsilon' c'$ corresponds to the stray absorption, then the luminous intensity absorbed at the distance x from the entrance face is expressed by

$$I_a(x) = I(0)\nu \exp\{-(\nu + \nu')x\}$$

and

$$\frac{\langle R' \rangle}{\langle R \rangle} = \frac{\nu}{\nu + \nu'} \frac{1 - \exp\{-(\nu + \nu')l/2\}}{1 - \exp(-\nu l/2)}$$

$$\frac{\bar{R}'}{\bar{R}} = \left(\frac{\nu}{\nu + \nu'} \right)^{1/2} \left[\frac{1 - \exp\{-(\nu + \nu')l\}}{1 - \exp(-\nu l)} \right]^{1/2}$$

The variations in $\langle R' \rangle \bar{R} / \langle R \rangle \bar{R}'$ versus $(\nu + \nu')l$ shown in Fig. 3 indicate the influence that stirring has on the correction to be made to take into account the stray absorption of light.

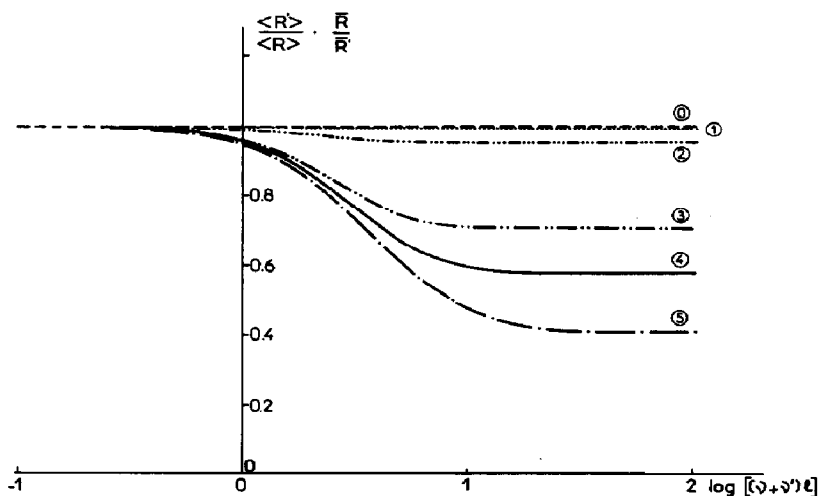


Fig. 3. $\langle R' \rangle \bar{R} / \langle R \rangle \bar{R}'$ vs. $\log(\nu + \nu')l$: curve 0, $\nu'/\nu = 0$; curve 1, $\nu'/\nu = 0.01$; curve 2, $\nu'/\nu = 0.1$; curve 3, $\nu'/\nu = 1$; curve 4, $\nu'/\nu = 2$; curve 5, $\nu'/\nu = 5$.

3.2. Stirring of solutions

Many chain reactions studied in the laboratory which have industrial importance call into play a liquid reagent RH and a gaseous reagent X_2 ($X_2 \equiv O_2, Cl_2$ etc.). In order to regenerate the X_2 in the solution, we must carry out a bubbling procedure adapted to the solution, which leads to stirring of the solution and as a consequence to partial or total mixing of the reagents and of the radicals present in the medium. The lowest concentration in general is that of the gaseous product. We suppose then that the concentration of RH is nearly constant in the medium.

In the next sections we analyse the different processes which produce partial or total mixing of the radical chain carriers. There are chemical and physical diffusion on the one hand and mechanical stirring (essentially by bubbling) on the other hand.

3.2.1. Physical and chemical diffusion

Apart from the specific problem of homogenization of the reagents in the irradiated solution, so far several workers [5 - 7] have treated the in-

fluence of the diffusional phenomena on the homogenization of the solutions. We are led, in theory, to solve the equation

$$\frac{\partial C}{\partial t} = D\nabla^2 C + 2\phi I(r) - 2k_3 C^2$$

where C is the concentration of radical chain carriers which determines the process of chain termination and D is the coefficient of diffusion for the radicals.

This system can only be solved numerically. However, according to Adda and Philibert [8] it is possible to calculate the mean displacement $\langle \bar{d} \rangle_t$ of a radical as a function of time t .

If $C(r, t)$ represents the mean concentration in a system of spherical symmetry, then

$$C(r, t) = \frac{b}{8(\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

where b is a constant. Since

$$4\pi \int_0^{\infty} C(r, t)r^2 dr = 1$$

we have

$$\begin{aligned} \langle \bar{d} \rangle_t &= \frac{\int_0^{\infty} r^3 \exp(-r^2/4Dt) dr}{\int_0^{\infty} r^2 \exp(-r^2/4Dt) dr} \\ &= \frac{4}{\pi^{1/2}} (Dt)^{1/2} \end{aligned}$$

The root-mean-square distance covered during the lifetime of a radical is expressed by

$$\begin{aligned} \langle \bar{d} \rangle &= \frac{4}{\pi^{1/2}} \frac{\int_0^{\infty} (Dt)^{1/2} \exp(-t/\tau) dt}{\int_0^{\infty} \exp(-t/\tau) dt} \\ &= 2(D\tau)^{1/2} \end{aligned} \tag{10}$$

Thus in a practically homogeneous medium, if we know D and τ , it is possible in theory to estimate whether the diffusional processes are able to explain homogenization of the solutions.

Having taken the values $D \leq 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [9] and $\tau \leq 10 \text{ s}$ into account, $\langle \bar{d} \rangle$ is always less than 10^{-2} cm , a value which is generally very much smaller than the dimensions of the reactors used in photochemistry. The solution of the differential equation is then not necessary, as it has been shown that, in the majority of the studies which have been carried out, the physical diffusion of the radicals can be considered as negligible.

3.2.2. Chemical diffusion

Independently of the processes of pure physical diffusion, the chain reaction itself can be responsible for a pseudomotion of the radicals as shown in Fig. 4 where we show qualitatively that the reaction from R^\cdot to R^\cdot via RX_2^\cdot is a means of chemical diffusion, in contrast with classical physical diffusion.

The calculation of the coefficient D_c of chemical diffusion can be carried out starting from elementary statistical theories of diffusion. If T represents the mean time between two reactions $R^\cdot \rightarrow \dots \rightarrow R^\cdot$ and if d is the elementary displacement undergone at each reaction, the random motion of a particle R^\cdot (or RX_2^\cdot) in the three directions of space is expressed by

$$D_c \approx \frac{d^2}{3T}$$

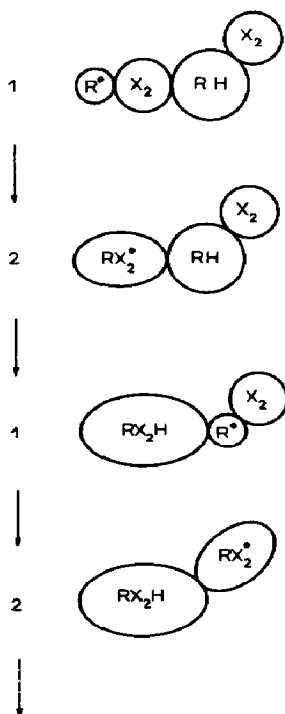
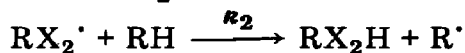


Fig. 4. The displacement of radicals by chemical reaction.

where the power 2 comes from the fact that two reactions are needed in order to go from one radical R^{\cdot} to another radical R^{\cdot} .

If we suppose that the reaction obeys mechanism A of propagation and process (II) of termination, then the time T is defined by the mean time of reaction of RX_2^{\cdot} with RH



which leads to

$$[RX_2^{\cdot}] = [RX_2^{\cdot}]_0 \exp(-k_2[RH]t)$$

and to

$$T \approx \frac{1}{k_2[RH]}$$

Under these conditions an estimation of D_c will correspond to

$$D_c \approx \frac{d^2}{3} k_2[RH] \quad (11)$$

3.2.2.1. Estimation of D_c . In the particular case of the photooxidation of heptanal under the conditions $[RH] \approx 7.5 \text{ mol l}^{-1}$, $k_2 = 3 \times 10^3 \text{ mol}^{-1} \text{ l s}^{-1}$ [10] and $d \approx 7 \text{ \AA}$ then $D_c \approx 0.4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, a value that is much smaller than that for D . Thus physical or chemical diffusion will not, in general, be able to bring about homogenization of the irradiated solutions, even if the mean lifetime of the radicals is long (several seconds).

On the contrary, in the case of the photochlorination of toluene, we have $[RH] \approx 9.42 \text{ mol l}^{-1}$, $k_2 \approx 10^{9.1} \text{ mol}^{-1} \text{ l s}^{-1}$ [11] and $d \approx 7 \text{ \AA}$ and $D_c \approx 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. This is about twice as large as the coefficient of physical diffusion in a fluid medium (heptane, water etc.).

3.2.3. Diffusion by mechanical stirring

The photoreactors used in industry, similar to those used in the laboratory, are generally of the bulbous column type with no mechanical stirring; their performances depend essentially on the hydrodynamic conditions, the specific interfacial area and finally on the lighting conditions. Although the optimization of the running conditions of these reactors is difficult to carry out, as we do not know the relative importance of these parameters very well, it is certain that the homogenization of the reactive phase must contribute to the improvement of the overall performances of the photoreactor by causing the non-active zones to disappear.

Having taken the industrial constraints into account, this partial or total homogenization can only be obtained by a modification of the hydrodynamic parameters (speed of the gas, volume and geometry of the reactor, mechanical stirring etc.) in order to provoke sufficient stirring for the homogenization of the unstable reagents such as the free radicals. During the past few years the

study of the mixing in bulbous columns has been the object of a large number of publications [12 - 27].

In this type of reactor the superficial speed of the liquid phase is generally negligible compared with that of the gas phase; the upward current of the bubbles of gas induces a downward movement of the liquid and, more generally, eddies all along the column, which cause a back-mixing effect. The mixing does not occur in the same manner in all directions and we must distinguish two modes of dispersion, axial dispersion and radial dispersion.

3.2.3.1. Axial mixing coefficient. Axial mixing in gas-liquid contactors is usually characterized by a dispersion coefficient which is based on the unidimensional diffusional model. In order to measure this coefficient, the majority of researchers [12 - 27] have used the "steady state tracer injection" technique, in which the tracer is continually injected into the liquid phase, and the analysis of the results of which is based on the differential equation

$$E_L \frac{d^2c}{dz^2} + V_L \frac{dc}{dz} = 0 \quad (12)$$

E_L is the coefficient of axial dispersion (in units of square centimetres per second) and V_L is the speed of the liquid (in units of centimetres per second), which leads to the limiting conditions appropriate to the solution

$$\log \left(\frac{c_z}{c_0} \right) = \frac{V_L}{E_L} z \quad (13)$$

and to the experimental determination of E_L .

Some researchers [19, 28] have also used "transient state measurements", which lead to the differential equation

$$\frac{\partial c}{\partial t} = E_L \frac{\partial^2 c}{\partial z^2} \quad (14)$$

with the limiting conditions $\partial c / \partial z = 0$ for $z = 0$ and $z = h$. The solution is then

$$\frac{c_z}{c_0} = \frac{1}{(\pi\beta)^{1/2}} \sum_{n=-\infty}^{+\infty} \exp \left\{ -\frac{(z/2h + n)^2}{\beta} \right\}$$

with

$$\beta = \frac{E_L t}{h^2}$$

The results obtained with these two experimental techniques are comparable, which confirms the validity of the theory. The determination of the coefficient E_L has then enabled us to study the influence of numerous parameters such as the diameter ϕ of the column, superficial speeds of the gas and of the liquid, viscosity of the liquid etc. on mixing. The studies have been carried out on columns of diameters varying from 2 to 106 cm with superficial speeds of the gas from 0.1 to 45 cm s⁻¹.

TABLE 1
Relationships for E_L

<i>Researchers</i>	<i>Reference</i>	E_L ($\text{cm}^2 \text{s}^{-1}$)
Joshi and Sharma	25	$0.31\phi^{1.5} V_G$
Cova	14	$V_G^{0.45} \rho_L^{0.40}$
Deckwer <i>et al.</i>	16	$2\phi^{1.5} V_G^{0.5}$
Towell and Ackerman	19	$1.32\phi^{1.5} V_G^{0.5}$
Reith <i>et al.</i>	18	$0.33\phi V_L$

According to the different relationships presented in Table 1, which relate the coefficient of axial dispersion E_L to the parameters of the bulbous column, it seems that the only important parameters for the axial mixing are the superficial speed of the gas and the diameter of the column; the physical properties of the liquid, the height of the column, the speed of the liquid and finally the geometry of the sprinklers play only a minor role.

The fact that the coefficient E_L depends on the diameter of the column indicates that the eddies produced by the motion of the bubbles are of the same dimensions as the diameter. Towell and Ackerman [19] have also shown that the movements of the liquid on a larger scale are added to these eddies.

The axial mixing in bulbous columns is more generally described using a Peclet number defined in the following way:

$$\text{Pe} = \frac{V_L \phi}{E_L}$$

This adimensional number evidently only has a value in a comparative sense and does not enable us to know the variations in the coefficient E_L with respect to other parameters.

3.2.3.2. Radial mixing coefficient. Although all the researchers concerned have studied axial dispersion, few of them [13, 18] have undertaken a study of radial dispersion, which is more difficult to demonstrate. With the aid of the tracer technique, on injection at the centre of the column and on analysis at different distances from the axis, Reith [18] has shown that the coefficients of radial dispersion E_r are smaller by a factor of 10 than the coefficients of axial dispersion, all other things being equal, *i.e.*

$$E_r \approx \frac{E_L}{10} \quad (15)$$

In conclusion, the mixing in bulbous columns is therefore essentially due to axial displacements. Now, if there is a photochemical reaction in the bulbous column on external irradiation, only radial dispersion could make the radical chain carriers migrate sufficiently quickly towards the centre of

the column: therefore we shall not take into account the coefficient of radial dispersion E_r in the model of the stirring in photoreactors.

3.2.3.3. Mixing time. By analogy with the root-mean-square displacement by diffusion of a radical during its lifetime $\bar{\tau}$, it is possible to define a mixing time θ such that during this time a molecule at the wall of the column travels the radius of the column in order to reach the centre of the reactor, *i.e.*

$$\frac{\phi}{2} = 2(E_r\theta)^{1/2} \quad (16)$$

With the relationship given by Deckwer *et al.* [16] for the coefficient E_r and eqn. (16) we have

$$\frac{\phi}{2} = 2(0.2\phi^{1.5}V_G^{0.5}\theta)^{1/2}$$

i.e.

$$\theta = 0.31 \left(\frac{\phi}{V_G} \right)^{1/2} \quad (17)$$

We see in Table 2 that, although it is easy to obtain mixing times of about 1 s, it is almost impossible to obtain values of less than 0.1 s. For example, it is impossible to maintain a superficial speed of the gas of the order of 1 m s⁻¹ in a reactor of diameter 1 cm without carrying some of the liquid phase into the vapour phase.

TABLE 2

Mixing times calculated from eqn. (17)

ϕ (cm)	θ (s)			
	$V_G = 0.1 \text{ cm s}^{-1}$	$V_G = 1 \text{ cm s}^{-1}$	$V_G = 10 \text{ cm s}^{-1}$	$V_G = 100 \text{ cm s}^{-1}$
1	1	0.3	0.1	0.03
10	3	1	0.3	0.1
10 ²	10	3	1	0.3

Thus for free radicals with mean lifetimes that are greater than 0.1 s in a laboratory reactor of restricted dimensions, it will always be possible to homogenize the concentration of the radicals in the reactor using the movement of the gas in the liquid phase. For radicals with shorter lifetimes, there will be either partial mixing or, for very short lifetimes (*e.g.* the chlorine radical), a concentration profile that is directly defined by the absorption profile of the light.

3.2.3.4. Demonstration of the processes of mechanical stirring. In order to visualize the different effects that we have described, we have thought of

constructing an experiment that is easy to run which is performed in the following way. The pseudo-photoreactor is made from a beaker into which nitrogen is bubbled through sintered glass. At the instant $t = 0$, we inject a waft of a fluorescent tracer (pyranine) and we monitor the evolution of the local concentrations of this tracer by taking a photograph every 0.7 s; the experimental system is submitted to irradiation at 365 nm (Wood lamp).

The results obtained are assembled in Fig. 5 where we show (1) the presence of a dead volume in the little-stirred zone at the bottom of the reactor and (2) back mixing.

4. Consequences

If D , D_c and E_L are known, the root-mean-square distance covered by a radical chain carrier is expressed by

$$\langle \bar{d} \rangle \approx 2 \{ (D + D_c + E_r) \tau \}^{1/2} \quad (18)$$

We can now try to schematize the working of a photoreactor in which a long chain reaction takes place, as is shown in Fig. 6.

The luminous excitation takes place in the vicinity of the entrance face of the photoreactor and all processes of homogenization defined in Section 3 intervene to render the reaction as homogeneous as possible. We can therefore propose a simplified working model of such a system, *i.e.* a photoreactor (where radical species are formed) and a stirred buffer reservoir are permanently interconnected. The rate of reaction is then related to the flow Q of the solution (see Fig. 6(b)) from one reactor to the other. If, for example, we assume mechanism A of propagation and eqn. (III) for termination and if v_1 is the volume of the photoreactor and v_2 that of the buffer reservoir, then

$$\varphi \bar{I}_a - \frac{Q}{2v_1} ([RX_2^\cdot]_1 - [RX_2^\cdot]_2) - k_3 [RX_2^\cdot]_1^2 = 0$$

and

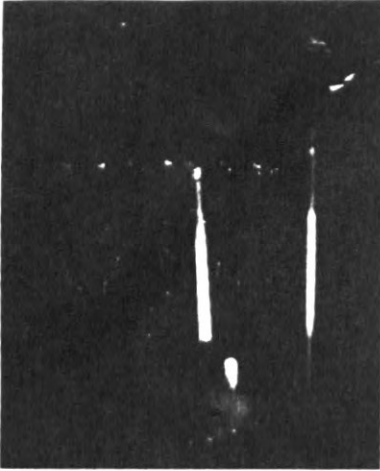
$$\frac{Q}{2v_2} ([RX_2^\cdot]_1 - [RX_2^\cdot]_2) - k_3 [RX_2^\cdot]_2^2 = 0$$

where the indices 1 and 2 characterize the species present in the photoreactor and in the buffer reservoir respectively. We take

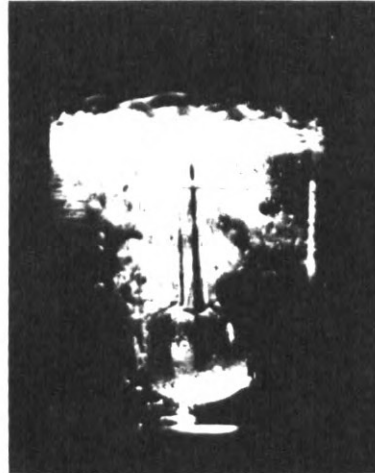
$$t_1 = \frac{v_1}{Q}$$

$$t_2 = \frac{v_2}{Q}$$

$$\alpha = 2k_3 t_2 [RX_2^\cdot]_{1,0}$$



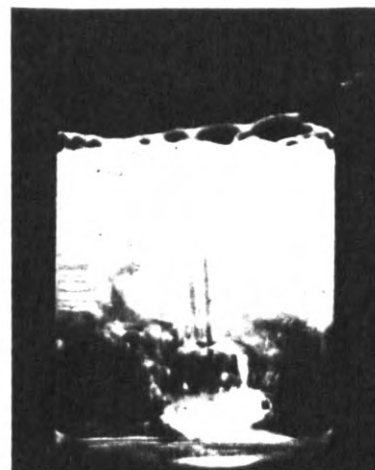
(a)



(b)



(c)



(d)



(e)



(f)

Fig. 5. Visualization of stirring in a reactor: (a) injection of the fluorescent tracer at $t = 0$; (b) - (f) photographs taken every 0.7 s.

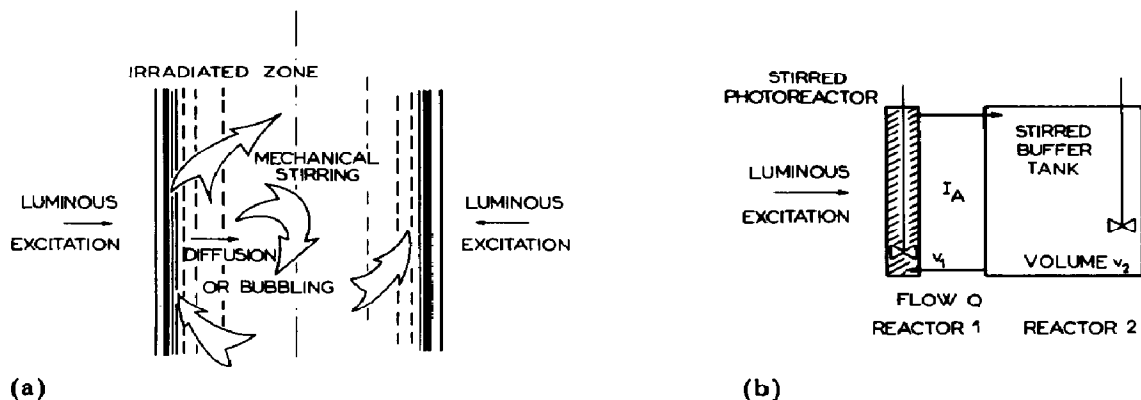


Fig. 6. (a) A representation of the different processes of homogenization; (b) a schematic representation of a partially stirred system.

$$[RX_2']_{1,0} = \left\{ \frac{\varphi I_a}{(1 + v_2/v_1)k_3} \right\}^{1/2}$$

and

$$y = \frac{[RX_2']_1}{[RX_2']_{1,0}}$$

which corresponds to an infinite flow (perfectly stirred system). Then

$$\left(1 + \frac{t_1}{t_2}\right)(1 - y^2) - 2\alpha y^3 - \alpha^2 y^4 = 0$$

and

$$x = \frac{[RX_2']_2}{[RX_2']_{1,0}}$$

$$x = y + \alpha y^2$$

The solution to these equations can easily be found by numerical techniques (the method of Newton, for example). The mean rate of reaction is expressed by

$$R = k_2[RH] \left(\frac{[RX_2']_1 v_1 + [RX_2']_2 v_2}{v_1 + v_2} \right)$$

If R_0 corresponds to the rate obtained in the case of a perfectly stirred reactor, we have shown in Fig. 7 the variations in R/R_0 with $\alpha = 10^M$, the coefficient α being inversely proportional to the mean rate of stirring. We have indicated three regions in Fig. 7.

(1) Region A is the region of small α , *i.e.* long radical lifetime with respect to the mean speed of stirring. The system behaves as if the exciting light was distributed in a homogeneous way throughout the reactor.

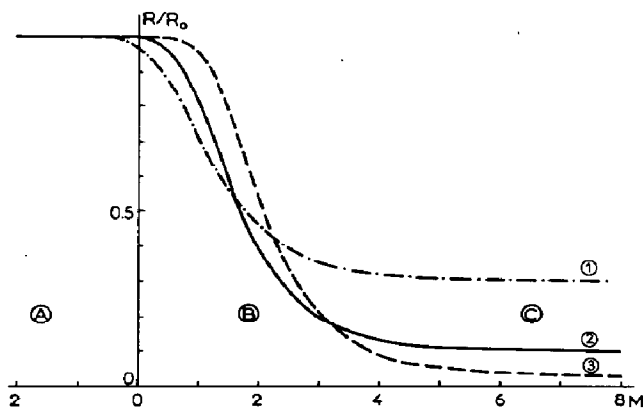


Fig. 7. The variation in the relative rate with α ($\alpha = 10^M$): curve 1, volume ratio = 10; curve 2, volume ratio = 100; curve 3, volume ratio = 1000.

(2) Region B is the region of intermediate α . There is a restricted participation of the buffer reservoir to the kinetics.

(3) Region C is the region of large α . The lifetime of the radical chain carriers is so short compared with the time of stirring that there is participation of the buffer reservoir. Its only role is to assure regeneration of the reagents.

5. Experimental results

We have just defined three regions, two of which correspond to lifetimes that are either long or, on the contrary, very short compared with the speed of stirring. These different cases are demonstrated with the aid of kinetic examples which are described in this section.

5.1. Photochlorination of benzyl chloride

The photochlorination of benzyl chloride is a long chain reaction the kinetic scheme for which is similar to that shown in Section 2 with mechanism B of propagation. The initiation step can be obtained either by photolysis of chlorine (with a wavelength λ in the range 280 - 450 nm) or by photolysis of the hydrocarbon (λ in the range 230 - 280 nm). The local rate of chlorination is then written as

$$R(r) = \left\{ \frac{\varphi I_a(r)}{k_3} \right\}^{1/2} k_2 [\text{RH}]$$

The experimental results and data of the kinetic study of the photochlorination of benzyl chloride at a temperature of 50 °C and at two wavelengths (254 and 313 nm) of irradiation are shown in Table 3.

For the two wavelengths of irradiation, the calculation of the lifetime of the chlorine radicals ($\varphi \approx 0.5$ [2] and $k_3 = 10^{10.2} \text{ mol}^{-1} \text{ l s}^{-1}$) shows that

TABLE 3
Photochlorination of benzyl chloride

λ (nm)	ν (cm^{-1})	$I_a \times 10^{-6}$ (einsteins $\text{s}^{-1} \text{l}^{-1}$)	τ (s)	P_L	$\langle R \rangle / I_a^{1/2}$ ($\text{mol}^{-1/2} \text{l}^{1/2}$ $\text{s}^{-1/2}$)	$\langle R \rangle / I_a^{1/2} P_L$ ($\text{mol}^{-1/2} \text{l}^{1/2}$ $\text{s}^{-1/2}$)
254 ^a	3466	0.96	10^{-2}	0.068	13.9	204
313 ^b	172	0.74	1.3×10^{-2}	0.250	60.0	240

$\varphi(\text{CH}_2\text{Cl}) = 8.7 \text{ mol l}^{-1}$.

^aAbsorption by $\varphi(\text{CH}_2\text{Cl})$.

^bAbsorption by Cl_2 .

there cannot be a homogenization of the radicals: the rate of chlorination is therefore related to the absorption profile of the light (see Table 3).

In order not to make the calculations too complex, for high optical densities we can compare our cylindrical reactor with a planar reactor (see Fig. 2) of the same irradiated area; the rate of reaction is then written as a function of the absorbed intensity \bar{I}_a determined experimentally:

$$\langle R_\lambda \rangle = \frac{2}{(\nu_\lambda l)^{1/2}} \frac{k_2}{k_3^{1/2}} (\varphi \bar{I}_a)^{1/2} [\text{RH}]$$

After correction of the rates by the factor P_L , the results obtained confirm the assumption of short lifetimes for the radicals as well as the influence of the absorption profile of the light on the rate of reaction.

Since the initiation steps are different at 254 and 313 nm, the quantum yields φ_λ of photolysis at the two wavelengths do not have to be rigorously equal, which would explain the difference between the two corrected rates. Our own measurements, however, lead to closely related values for these yields. Thus, having taken the precision of our measurements into account, there is good agreement between the experimental results and the model proposed.

5.2. Photooxidation of heptanal

Heptanal is oxidized photochemically with the kinetic scheme shown in Section 2 with propagation mechanism A. For pressures P_{O_2} of oxygen greater than 200 mmHg, the free radicals come from the singlet S_1^* and from the triplet T_1^* excited states of heptanal.

The local rate of photooxidation is written as

$$R(r) = \{\varphi I_a(r)\}^{1/2} f([\text{RH}], P_{\text{O}_2}, \theta)$$

The experimental results and the data related to the kinetic study of the photooxidation of heptanal at a temperature of 0 °C and at the wavelengths 254 and 313 nm of irradiation are given in Table 4.

Since we know that the primary quantum yield of decomposition of heptanal is a function of the concentration of the aldehyde [4] ($\varphi \approx 0.04[\text{RH}]$)

TABLE 4

Photooxidation of heptanal

λ (nm)	ν (cm^{-1})	$I_a \times 10^{-6}$ (einsteins $\text{s}^{-1} \text{l}^{-1}$)	τ (s)	P_L	$\langle R \rangle / I_a^{1/2}$ ($\text{mol}^{-1/2} \text{l}^{1/2} \text{s}^{-1/2}$)
254	3.8	7.7	0.4	0.99	2.8×10^{-2}
313	10.4	7.5	0.4	0.62	2.9×10^{-2}

[RH] = 0.74 mol l^{-1} ; solvent, *n*-decane.

and that $k_3 = 10^{7.4} \text{ mol}^{-1} \text{ l s}^{-1}$, the calculation of the lifetime of the radical chain carrier gives (see Table 4) $\tau = 0.4 \text{ s}$. By taking into account the technique of stirring used, this lifetime must be sufficiently large to allow homogenization of the concentration of the radical RO_2^{\cdot} throughout the volume of the reactor. The experimental results show that the rate of oxidation is practically independent of the absorption profile of the light (see Table 4) and thus confirm this homogenization.

5.3. Photooxidation of benzaldehyde

Benzaldehyde is oxidized photochemically with the same mechanism of photooxidation as for heptanal. The free radicals for initiation come essentially from the self-deactivation of the aldehyde to the triplet state, leading to a quantum yield of initiation of 0.5 [29].

The kinetics of oxidation of this aldehyde are well known (refs. 10, 30, and references therein); the constant of recombination at 0°C is equal to $10^{8.3} \text{ mol}^{-1} \text{ l s}^{-1}$ (according to Ingles and Melville [31]), leading to a mean lifetime of the radicals of about 10^{-2} s , which is intermediate between the two values given earlier. The results are assembled in Table 5.

The results obtained at 313 and 254 nm correspond to a chain reaction of which the transient radical species has such a small mean lifetime compared with the ensemble of the processes of homogenization that the reaction is considered as totally homogeneous (for heptanal). However, this lifetime is

TABLE 5

Photooxidation of benzaldehyde

λ (nm)	ν (cm^{-1})	$I_a \times 10^{-6}$ (einsteins $\text{s}^{-1} \text{l}^{-1}$)	τ (s)	P_L	$\langle R \rangle / I_a^{1/2}$ ($\text{mol}^{-1/2} \text{l}^{1/2}$ $\text{s}^{-1/2}$)	$\langle R \rangle / I_a^{1/2} P_L^{1/2}$ ($\text{mol}^{-1/2} \text{l}^{1/2}$ $\text{s}^{-1/2}$)
254 ^a	1731	8.3	3×10^{-2}	0.048	2.04×10^{-2}	42.5×10^{-2}
313	176	1.3	9×10^{-2}	0.48	3.18×10^{-2}	6.63×10^{-2}

[RH] = 0.98 mol l^{-1} ; solvent, *n*-decane.

^aA correction has been carried out on the calculations of I_a and $\langle R \rangle$ to take into account the stray emission of the lamp at 313 and at 366 nm.

sufficiently long that the effect of the stirring is sensitive to the kinetics of oxidation.

6. Experimental details

6.1. Products

Benzyl chloride, heptanal, benzaldehyde and decane were obtained from Fluka (greater than 99% pure) and were purified by vacuum distillation. Chlorine (greater than 99.7% pure) and oxygen (greater than 99.5% pure) from Air Liquide Co. were used without purification.

6.2. Instrumentation

The kinetic study has been carried out in a set-up composed of a thermostatted photoreactor, a measuring cell and a crushing pump used for recycling the gas. For the study of the photooxidation we have taken the measuring cell used by Carmier and Deglise [32]: the pressure of oxygen is maintained constant in the reactor and the volume of oxygen consumed is compensated for by the addition of the same volume of mercury contained in a manostat.

The consumption of chlorine is followed by an absorption spectrophotometer in the visible region [2]. The chlorine circulates in a Pyrex cell placed in the measurement compartment of a UV Perkin-Elmer spectrophotometer model 137. The rate of chlorination with time is measured by recording the optical density at 390 nm of the gaseous mixture contained in the cell.

The photoreactors used for the irradiation at 254 nm are of the immersion lamp type. The light source is a low pressure mercury vapour lamp (Hanau model TNN 15/32). For the irradiation at 313 nm, the photoreactors consist of a cylindrical reactor placed at one of the focal axes of an elliptical reflector and a medium pressure mercury vapour lamp [33] placed along the other focal axis. All these reactors possess a double envelope (used for thermostating) and a means of circulation for a chemical filter [34] for the study at 313 nm.

The chlorination of benzyl chloride has been studied at a temperature of 50 °C in a pure medium and with a pressure of 450 mmHg of pure Cl₂. The intensities absorbed by the liquid phase were 0.96×10^{-6} einsteins s⁻¹ l⁻¹ at 254 nm and 0.74×10^{-6} einsteins s⁻¹ l⁻¹ at 313 nm.

During the study of the photooxidations, the initial concentrations of heptanal and of benzaldehyde were 0.74 mol l⁻¹ and 0.98 mol l⁻¹ respectively in the solvent *n*-decane. The temperature was 0 °C and the pressure was 450 mmHg of pure O₂. The absorbed intensities were 7.7×10^{-6} einsteins s⁻¹ l⁻¹ at 254 nm and 7.5×10^{-6} einsteins s⁻¹ l⁻¹ at 254 nm for the photooxidation of heptanal and 8.3×10^{-6} einsteins s⁻¹ l⁻¹ at 254 nm and 1.2×10^{-6} einsteins s⁻¹ l⁻¹ at 313 nm for the photooxidation of benzaldehyde.

The absorbed luminous intensities have been measured by actinometry (photochemical decomposition of oxalic acid sensitized by uranyl sulphate). Finally, in each case we have verified that the rate of reaction was not diffusion limited and that we were in the kinetic regime.

Nomenclature

C	concentration (M)
$C(r, t)$	local concentration at a distance r from the axis of the lamp and at time t (mol l^{-1})
d	elementary displacement of a radical at each reaction (cm)
$\langle \bar{d} \rangle$	root-mean-square distance covered by a radical during its lifetime (cm)
$\langle \bar{d} \rangle_t$	mean displacement of a radical in the time t (cm)
D	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
E_L	axial diffusivity ($\text{cm}^2 \text{s}^{-1}$)
E_r	radial diffusivity ($\text{cm}^2 \text{s}^{-1}$)
h	height of an annular photoreactor (cm)
I_a	luminous intensity absorbed ($\text{einsteins s}^{-1} \text{cm}^{-3}$)
$I(r)$	luminous intensity transmitted at a distance r along the axis of the lamp ($\text{einsteins s}^{-1} \text{cm}^{-2}$)
k	constant of proportionality
k_i	rate constant of the elementary process i ($\text{mol}^{-1} \text{l s}^{-1}$)
Pe	Peclet number
Q	liquid flow (l s^{-1})
r	radial distance (cm)
r_0	interior radius of an annular reactor (cm)
r_1	exterior radius of an annular reactor (cm)
R	rate of reaction ($\text{mol l}^{-1} \text{s}^{-1}$)
R_0	rate of reaction in a perfectly stirred reactor ($\text{mol l}^{-1} \text{s}^{-1}$)
t	time (s)
t_1	residence time in reactor 1 (s)
t_2	residence time in reactor 2 (s)
T	mean time between two reactions (s)
v_1	reactor volume 1 (l)
v_2	reactor volume 2 (l)
V_L	linear speed of the liquid in a bubble column (cm s^{-1})
V_G	linear speed of the gas (cm s^{-1})
x	coordinate in a planar reactor (cm)
θ	mixing time in a bubble column (s)
λ	wavelength of irradiation (nm)
ν	absorption coefficient (cm^{-1})
ν_L	viscosity of the liquid phase (cP)
ρ_L	density of the liquid phase
τ	radical lifetime (s)
φ	quantum yield of photolysis
ϕ	diameter of the bubble column (cm)
$\langle \rangle$	mean value when the radical concentration is not homogeneous in the reactor
—	mean value when all the concentrations are homogeneous in the reactor

References

- 1 J. C. Andre, F. Baronnet, M. Niclause and J. Lemaire, *J. Chim. Phys.*, **68** (1971) 1177 - 1182.
- 2 A. Tournier, *Thèse d'Ingénieur-Docteur*, Nancy, 1978.

- 3 A. Tournier, J. C. Andre, X. Deglise and M. Niclause, *J. Photochem.*, 18 (1981) 47.
- 4 J. C. Andre, M. Bouchy and M. Niclause, *J. Photochem.*, 5 (1976) 1 - 12.
- 5 M. P. Ramage and R. E. Eckert, *Ind. Eng. Chem., Fundamen.*, 18 (1979) 216 - 221.
- 6 S. K. Fong and J. S. Ratcliffe, *Mech. Chem. Eng. Trans.*, 8 (1) (1972) 1 - 8.
- 7 J. G. van de Vusse, *Chem. Eng. Sci.*, 21 (1966) 631 - 643.
- 8 Y. Adda and J. Philibert, *La Diffusion dans les Solides*, Institut National des Sciences et Techniques Nucléaires and Presses Universitaires de France, Paris, 1966.
- 9 L. S. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973.
- 10 G. E. Zaikov, J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 47 (1969) 3017.
- 11 G. Russel, A. Ito and D. Hendry, *J. Am. Chem. Soc.*, 85 (1963) 2976.
- 12 S. H. Eissa, M. M. El-Halwasi and M. A. Saleh, *Ind. Eng. Chem., Process Des. Dev.*, 10 (1971) 31 - 36.
- 13 S. H. Eissa and K. Schügerl, *Chem. Eng. Sci.*, 30 (1975) 1251 - 1256.
- 14 D. R. Cova, *Ind. Eng. Chem., Process Des. Dev.*, 13 (1974) 292 - 296.
- 15 W. B. Argo and D. R. Cova, *Ind. Eng. Chem., Process Des. Dev.*, 4 (1965) 352 - 359.
- 16 W. Deckwer, U. Graeser, H. Langemann and Y. Serpemen, *Chem. Eng. Sci.*, 28 (1973) 1223 - 1225.
- 17 K. B. Bischoff and J. B. Phillips, *Ind. Eng. Chem., Process Des. Dev.*, 5 (1966) 416 - 421.
- 18 T. Reith, S. Renken and B. A. Israel, *Chem. Eng. Sci.*, 23 (1968) 619 - 629.
- 19 G. D. Towell and G. H. Ackerman, *Proc. 5th Eur.-2nd Int. Symp. on Chemical Reaction Engineering, Amsterdam, May 1972*, Elsevier, Amsterdam, Preprint B 3 - 1.
- 20 Y. Kato and A. Nishiwaki, *Int. Chem. Eng.*, 12 (1972) 182 - 187.
- 21 K. Akita and F. Yoshida, *Ind. Eng. Chem., Process Des. Dev.*, 12 (1973) 76 - 80.
- 22 K. T. Shah, S. Krishnamurthy, *Ind. Eng. Chem., Process Des. Dev.*, 18 (1979) 187 - 189.
- 23 E. Smith, M. Fidgett, J. Salek and J. Shayegan, *Proc. 2nd Eur. Conf. on Mixing, Cambridge, March 30, 1977*, British Hydromechanics Research Association, Cranfield, 1978, G2/15 - G2/30.
- 24 B. Koenig, R. Bucholz, J. Luecke and K. Schuegerl, *Chem. Ing. Tech.*, 49 (1977) 661.
- 25 J. B. Joshi and M. M. Sharma, *Can. J. Chem. Eng.*, 56 (1) (1978) 116 - 119.
- 26 J. Todt, J. Luecke, K. Schuegerl and A. Renken, *Chem. Eng. Sci.*, 22 (4) (1977) 369 - 375.
- 27 M. Hartman, *Collect. Czech. Chem. Commun.*, 41 (9) (1976) 2498 - 2509.
- 28 W. Siemes and W. Weis, *Chem. Ing. Tech.*, 29 (1957) 727.
- 29 H. L. J. Bäckström and U. Riiner, *Acta Chem. Scand.*, 20 (1966) 630.
- 30 T. Takeuchi and T. Osa, *Nippon Kagaku Kaishi*, 12 (1972) 2374 - 2378.
- 31 T. A. Ingles and H. W. Melville, *Proc. R. Soc. London, Ser. A*, 218 (1953) 175.
- 32 J. C. Carmier and X. Deglise, *C. R. Acad. Sci., Ser. C*, 277 (1973) 1187.
- 33 W. Frankenburger and H. Klinkhardt, *Z. Phys. Chem., Abt. B*, 15 (1932) 421.
- 34 J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1967, p. 732.