J Indian Inst. Sci., Sept.–Oct 1988, **68**, pp. 375–384.

# An analysis of mixing of chain centres in photochemical reactors*

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Received on April 13, 1988, Revised on July 20, 1988

**Abstract**

A theoretical analysis of mixing of chain centres in photochemical reactors has been made considering both the first-order wall termination and the bimolecular termination [in bulk] of chain centres. Mixing effects are found to be diametrically opposite in the two termination modes, being beneficial in the bimolecular termination regime and adverse in the wall-termination regime. For competing modes, the mixing effects are closer to those valid for one or the other mode depending on the relative values of the rate constants and degree of attenuation

**Key words:** Photoreactors, chain centre mixing, wall termination, bimolecular termination.

## 1. Introduction

In many photochemical reactions of industrial importance, reactive intermediates are formed following radiation absorption, which then set off a thermal chain reaction. The chain growth is stopped if the reactive chain centres are deactivated by any of a number of possible ways such as the bimolecular termination in the bulk and the first-order wall termination, in which case the intermediates are required to diffuse to the walls for termination. One may also encounter the first-order terminations in the bulk. In general, for a reaction system we are considering here, we have a certain steady rate of spatially non-uniform generation of chain centres, their diffusion, and finally their termination by one or more modes noted above–all three rate processes simultaneously governing the average chain-centre concentration; the latter, in turn, often controls the overall rate of production of the desired compound in the propagation step. Given the generation and termination mode and rate, the average chain-centre concentration would essentially be controlled by diffusion or mixing of chain centres, the analysis of which constitutes the subject matter of this paper.

## 2. Previous work

Two extremes of mixing states of chain centres have been generally recognised in literature. One extreme is the so called 'local stationary state' of the chain centres[1,2], which

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*NCL Communication No. 3348.

seems to be a valid approximation to the situations where the half-lives of the chain centres are much less than their mixing time In such cases, the chain centres are locally immobilised. The other logical extreme mentioned in the literature[3–5], which may be termed the 'global-stationary state', is where the chain centres are perfectly mixed in a time much less than their half lives.

Hill and Felder[3] and Felder and Hill[5] showed that the chain-centre concentration and hence the production rate can be more in the global than in the local stationary state, in the case of bimolecular termination in the bulk and that such mixing effects were absent in the case of the first-order termination mode. However, for the latter mode no distinctions were made as to whether the terminations took place in the bulk or at the wall.

Very few papers have appeared dealing with the question of intermediate states of mixing of chain centres. Noyes[6] considered the problem for linear attenuation of radiation, whereas Hill and Reiss[7], and Shendalman and Hill[8] tackled the case of exponential attenuation, both being concerned only with bimolecular termination in the bulk.

It is our purpose in this paper to analyse theoretically the effect of mixing of chain centres on the photoreactor performance in the context of wall-termination mode and competing-termination modes. These two cases possessing features contrasting with those established by Hill and Reiss[7] for the bimolecular-termination mode do not appear to have been worked out in the literature.

## 3. Analysis

### *3.1 General situation*

We consider an one-dimensional model of diffusion of chain centres, analogous to Hill and Reiss[7] [henceforth this reference which will make frequent reappearance will be termed as (I)], to which real reactions like two-centre regenerative chain reactions, chain photopolymerisations can be reduced, as shown therein, under certain conditions. Thus, for our purpose, we would consider the diffusion of only one kind of radical species or chain centre subject to, in general, three types of terminations, namely: (i) bimolecular in the bulk, (ii) first order in the bulk and (iii) first order at the wall. Exponential attenuation of radiation by a sensitiser will be assumed. Under these conditions, the governing differential equations and the associated boundary conditions can be written as:

$$D_x \frac{{}^{2} D_1}{\mathrm{d}z^2} - k_b D_1 - 2k' D_1^2 = -2k\mu I_0 e^{-\mu z} \tag{1}$$

$$D_x \frac{\mathrm{d}D_1}{\mathrm{d}z} = k_w D_1 , \; z = 0 \tag{2}$$

$$D_x \frac{\mathrm{d}D_1}{\mathrm{d}z} = -k_w D_1 , \; z = L \tag{3}$$

where $k_b$ and $k_w$ are the first-order rate constants for termination in the bulk and at the wall, respectively, and $k'$ the bimolecular-rate constant.

In order to put the results to be presented in this work in a proper perspective, we shall briefly refer to the case of the termination in the bulk alone (either first order or bimolecular) which had received some attention in the literature.

For the latter case, with $k_w = 0$, $k_b \neq 0$, $k' \neq 0$, the dimensionless forms for equations (1) through (3) are given by

$$\frac{d^2 D^*}{d\xi^2} - \zeta_b^2 D^* - \frac{\zeta_b^2}{2}[-1+\sqrt{1+16R}\,]D^{*^2} = -\frac{8\zeta_b^2 R e^{-B_s \xi}}{-1+\sqrt{1+16R}} \tag{4}$$

$$\frac{d D^*}{d\xi} = 0, \quad \xi = 0, 1 \tag{5}$$

where the chain-centre concentration is normalised by a fictitious concentration $D_{LS}$, defined as:

$$D_{LS} = \frac{k_b}{4k'}\,[-1+\sqrt{1+16k'(k\mu I_0)/k_b^2}\,]. \tag{6}$$

The ratio $R$ which is a measure of the effectiveness of the bimolecular termination over the first-order termination for a given generation rate can be varied between zero and infinity to simulate one or the other termination mode.

It is interesting to note that a general analytical expression of average chain-centre concentration at infinite mixing can be obtained from equations (4) and (5) without actually solving them (following Felder and Hill[5]):

$$D^*_\infty = \frac{-1+\{1+16R(1-e^{-B_s})/B_s\}^{1/2}}{-1+\{1+16R\}^{1/2}}. \tag{7}$$

It can be shown from equation (7) that, as $R \rightarrow \infty$

$$D_{1\infty} = \left(\frac{k\mu I_0}{k'}\right)^{1/2}\left(\frac{1-e^{-B_s}}{B_s}\right)^{1/2} \tag{8}$$

and as $R \rightarrow 0$

$$D_{1\infty} = \left(\frac{2k\mu I_0}{k_b}\right)\left(\frac{1-e^{-B_s}}{B_s}\right). \tag{9}$$

Under the bimolecular termination mode, equation (4) can be shown to reduce to equation (2) of (I) the solution of which produces the well-known infinite mixing asymptote as given by equation (8) above. Similarly, under the first-order termination mode, equations (4) and (5) had been shown[9] to possess an analytical solution that led to an expression for the average concentration of chain centre as follows:

$$\bar{D}^{*} = \frac{1-e^{-B_s}}{B_s} \,. \tag{10}$$

The identity of equations (9) and (10) confirms that there is no mixing effect in the first-order termination in the bulk mode.

With the above background we now proceed to consider the problem with bimolecular termination in the bulk and first-order termination at the wall. Substituting $k_b = 0$, and with $k_w \neq 0$ and $k' \neq 0$ equations (1) to (3) take the following form:

$$D_s \frac{\mathrm{d}^2 D_1}{\mathrm{d} z^2} - 2k' \, D_1^2 = -2k\mu \, I_0 \, e^{-\mu z} \tag{11}$$

$$D_s \frac{\mathrm{d} D_1}{\mathrm{d} z} = k_w \, D_1 \,, \; z = 0 \tag{12}$$

$$D_s \frac{\mathrm{d} D_1}{\mathrm{d} z} = -k_w \, D_1 \,, \; z = L. \tag{13}$$

With a scheme of normalisation as used in (I), one ends up with the same differential equation, only now subject to non-zero derivative boundary conditions:

$$\frac{\mathrm{d}^2 D^*}{\mathrm{d}\xi^2} - 2\psi_0 \, D^{*^2} = -2\psi_0 \, e^{-B_s \xi} \tag{14}$$

$$\frac{\mathrm{d} D^*}{\mathrm{d}\xi} = \zeta_w^2 D^* \tag{15}$$

$$\frac{\mathrm{d} D^*}{\mathrm{d}\xi} = -\zeta_w^2 D^*. \tag{16}$$

Numerical solution of this set of equations has been obtained routinely in this work, by a powerful method, to be described later, over the entire mixing range without slightest problem of convergence.

However, in order to bring out all the important asymptotic cases in an elegant manner, a slightly different normalising scheme was applied, in this work, to equations (11) through (13):

$$\frac{\mathrm{d}^2 D^*}{\mathrm{d}\xi^2} - 2\psi_N \, D^{*^2} = -2e^{-B_s \xi} \tag{17}$$

$$\frac{\mathrm{d}D^*}{\mathrm{d}\xi} = \zeta_w^2 D^* \tag{18}$$

$$\frac{\mathrm{d}D^*}{\mathrm{d}\xi} = -\zeta_w^2 D^* \tag{19}$$

where the chain-centre concentration has been normalised with respect to a fictitious concentration $(L^2/D_x)\,(k\mu I_0)$ and $\psi_N = \psi_0^2$.

Even without solving these equations, one can, as before, find out the general expression for chain-centre concentration at infinite mixing extreme:

$$D_\infty^* = \frac{\zeta_w^2}{2\psi_N}\left[-1+\left\{1+\frac{4}{\zeta_w^2}\left(\frac{\psi_N}{\zeta_w^2}\right)\left(\frac{1-e^{-B_s}}{B_s}\right)\right\}^{1/2}\right]. \tag{20}$$

From this expression, it is possible to show that:

$$\lim_{\psi_N\to\infty} D_\infty^* = \frac{1}{\psi_N{}^{1/2}}\left(\frac{1-e^{-B_s}}{B_s}\right)^{1/2} \tag{21}$$

such that

$$D_{1\infty} = \left(\frac{k\mu I_0}{k'}\right)^{1/2}\left(\frac{1-e^{-B_s}}{B_s}\right)^{1/2}. \tag{21a}$$

Also

$$\lim_{\psi_N\to 0} D_\infty^* = \frac{1}{\zeta_w^2}\left(\frac{1-e^{-B_s}}{B_s}\right) \tag{22}$$

such that

$$D_{1\infty} = \frac{1}{2}\left(\frac{2Lk\mu I_0}{k_w}\right)\left(\frac{1-e^{-B_s}}{B_s}\right). \tag{22a}$$

The solution (21a) corresponds to the chain-centre concentration at infinite mixing under bimolecular-termination mode. However, there is no expression for chain-centre concentration at infinite mixing under wall-termination mode, available in the literature to which the solution (22a) corresponds. In this work, we proceed to fill up that gap.

### *3.2 Wall-termination mode*

Under this mode, $\psi_N = 0$, $\zeta_w^2 \neq 0$. Equations (17) through (19) can then be analytically solved and the resultant average chain-centre concentration is given by:

$$\bar{D}^* = \bar{D}_1 / \left( \frac{2L k\mu I_0}{k_w} \right)$$

$$= \left[ \frac{1 - e^{-B_s}}{B_s} \right] \left[ \frac{1}{2} - \frac{\zeta_w^2}{B_s^2} \right] + \frac{\zeta_w^2}{2B_s^2} \left( 1 + e^{-B_s} \right). \tag{23}$$

In contrast to equation (10) in the case of first-order termination in the bulk, $\bar{D}^*$ is seen to be a function of mixing (as represented by $\zeta_w^2$) and one obtains equation (22a) at infinite mixing, *i.e.* as $\zeta_w^2 \rightarrow 0$. Numerical results of calculation of $\bar{D}^*$ at intermediate $\zeta_w^2$ values are shown in fig. 1.

### *3.3 Bimolecular-termination mode*

In this mode, we put $\zeta_w^2 = 0$, $\psi_N = 0$ in equations (17) through (19). No analytical solution having been possible, recourse to a powerful numerical method was taken which formed the backbone of all the computed results presented in this paper.

The numerical technique involved quasilinearisation of the equations[10], followed by solution of the resulting linear ODE by a six-point collocation technique, iteratively. The collocation points and the matrices for this non-symmetric problem have been obtained following Finlayson[11].

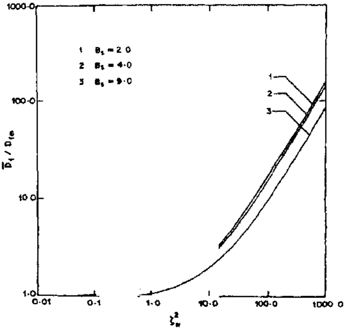

FIG. 1. Effect of mixing on average chain-centre concentration in the wall-termination controlling regime.

As a test of the method, it was first applied to the solution of equation (14) subject to zero-derivative boundary conditions, the case considered in (I). The entire fig. 2 of (I) could be reproduced without any convergence or other numerical difficulties mentioned by Hill and Reiss[7].

### 3.4 *Competing termination modes*

Next, the numerical method was applied to solving both equations (14) through (16) and (17) through (19). In either case, the entire mixing range characterised by a ratio of diffusion mean-free path to radiation mean-free path, $\Lambda = 0.01$ to $\Lambda = 100$ as covered in (I) was investigated. While in the former set of equations there was absolutely no convergence problem over the entire mixing range and for any value of optical thickness $B_s$, for the latter set convergence was slow for all $B_s$ at $\Lambda = 0.01$. Figure 2 shows a set of typical concentration profiles for the chain centres and demonstrates the effect of mixing on the profiles, and fig. 3 shows the characteristic mixing effect on the average chain-centre concentrations, where both termination modes are operative.

## 4. Discussion

In fig. 1, we observe that under the wall-termination regime for any optical thickness, the average chain-centre concentration is the lowest at the infinite mixing extreme and increases monotonically as the no-mixing regime is approached. The mixing effect is more at lower optical thickness than at higher values.

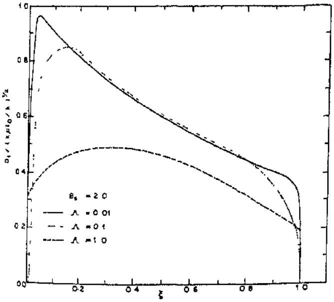

FIG. 2. Effect of mixing on the chain-centre concentration profiles under competing termination modes.

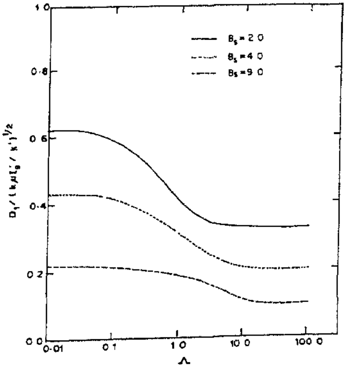

FIG. 3. Effect of mixing on the average chain-centre concentration under competing termination modes.

We know from the work of Hill and Reiss[7] that the mixing effect is just the opposite of the above in the case of bimolecular-termination regime.

In an intermediate regime where both the termination modes are competing, the mixing effect would be somewhere between the two extremes, as shown by fig. 3. If one compares this figure with fig. 2 of (I), one notices that irrespective of whether there is a simultaneous wall termination or not, given the rate of bimolecular termination in the bulk, the average chain-centre concentration is the same under conditions of no-mixing of chain centres characterised by a very low value of $\Lambda$. Secondly, unlike in the case of a purely bimolecular termination-controlling regime, the average chain-centre concentration falls with increase in mixing characterised by increase in $\Lambda$, when both termination modes are competing.

The results have a simple explanation. In a purely bimolecular termination-in-bulk regime, the chain centres are preserved from being deactivated by dispersing them towards the wall from the point of generation and hence the beneficial effect of mixing. But the same mixing will destroy the chain centres and hence will lower their average concentration when the wall termination is also there. Depending on the relative effectiveness of these two termination modes, especially when both the rate processes are comparable (as is the case treated here) complete reversal of mixing effect would take place. In the purely wall-termination regime qualitatively the same effect would be there, if only more accentuated.

It is worth emphasizing that in the literature, it is often loosely mentioned that a first-order termination process is insensitive to mixing of chain centres. Our work here clearly shows that this observation is correct only when a first-order termination takes place in the bulk. But a first-order wall-termination process admits a pronounced mixing effect.

To round off the results, fig. 2 shows some typical radical concentration profiles which are characterised by maxima somewhere within the diffusion path. Expectedly, the profiles become flatter as infinite mixing is approached.

## 5. Conclusions

A theoretical analysis of mixing of chain centres in photochemical reactors has been accomplished, in the context of either first-order wall-termination controlling regime or where both bimolecular termination in bulk and first-order wall termination modes are competing.

It has been shown that irrespective of whether there is any simultaneous wall termination of chain centres or not, for a given rate of bimolecular termination in the bulk, the average chain-centre concentration is identical at the no-mixing extreme.

On the other hand, as mixing is introduced its effect on the average chain-centre concentration is diametrically opposite in the two termination modes, namely, the bimolecular termination in bulk and by first-order wall termination. While for the first mode, mixing is known to increase the average chain-centre concentration, it is found here to reduce the concentration in the latter mode. For competing modes, the mixing effects are closer to those valid for one or the other mode depending on the relative values of rate constants and the degree of attenuation and can be calculated easily by a powerful numerical technique as used here.

It is only in the case of first-order termination in the bulk that there is no mixing effect.

### Nomenclature

$B_s$ = dimensionless optical thickness, $\mu L$

$D_x$ = diffusivity of chain centres

$D_1$ = concentration of the chain centres

$D^*$ = dimensionless chain-centre concentration; normalising parameter in each case defined in the text.

$\bar{D}^*$ = dimensionless average chain-centre concentration

$I_0$ = incident radiation intensity

$k$ = specific rate constant for the photosensitisation

$k'$ = bimolecular-termination rate constant

$k_b$ = rate constant for the first-order termination in the bulk

$k_w$ = rate constant for the first-order termination at the wall

$L$ = diffusion path length

$R$ = $k'(k\mu\ I_0)/k_b^2$

$z$ = spatial co-ordinate

*Greek letters*

$\mu$ = attenuation coefficient

$\xi$ = dimensionless spatial co-ordinate, $z/L$

$$\zeta_b^2 = \left(\frac{L^2}{D_x}\right) k_b$$

$$\zeta_w^2 = \left(\frac{L}{D_x}\right) k_w$$

$$h_0 = \left(\frac{L^2}{D_x}\right) (k' k\mu\ I_0)^{1/2}$$

$\psi_N = \psi_0^2$

$\Lambda = B_s/\psi_0^{1/2}$

*Subscript*

$\infty$ = infinite mixing

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