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Nonuniform Initiation of Photoreactions. III. Reactant Diffusion in Single-Step Reactions

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The influence of nonuniform initiation on conversion in single-step photoreactions is examined theoretically. Reaction types studied include reaction following absorption by reactant and photosensitized reaction. The batch slab reactor and the laminar flow tubular reactor with outside radiation are considered. In the case of reaction following absorption by reactant in the batch slab reactor, nonuniform initiation is found to have no influence on conversion, whereas for the other combinations of reaction and reactor its presence requires the specification of diffusion as well as kinetic parameters in order to characterize the conversion history unequivocally. The characteristics of conversion histories in the presence of nonuniform initiation are determined, and the influence of nonuniform initiation on chemical measurements of radiation and on tubular reactor performance in the neighborhood of laminar-turbulent flow transitions is discussed.

The complete determination of the kinetic behavior of isothermal photoreactions in the presence of strong absorption of radiation often requires a knowledge not only of chemical rates but also of rates of diffusion or mixing in the directions of radiation attenuation. The response to the nonuniform initiation resulting from strong absorption depends on the reaction mechanism and on the relative rates of mass transfer, reaction, and radiation absorption. When reactive intermediates disappear in pairs, the observed reaction rate will vary with the extent of movement of intermediates. When intermediates singly disappear, movement of intermediates has no effect on reaction rate. The influence of nonuniform initiation on photoreactions in which movement of reactive centers is important has been discussed in earlier papers in this series (*1, 2*).

In the present paper, reactions are considered in which the extent of movement of intermediates is unimportant, and attention is centered on the effect of reactant movement. We deal with reactions which may be represented by the single step,

$$A \rightsquigarrow B$$

While this reaction may actually proceed via a complex sequence of elementary reactions of reactants and intermediates, the kinetic features of present interest are nevertheless embodied in the single step shown. At the same time, examination of the influence of nonuniform initiation on this reaction may be helpful in understanding effects in complex mechanisms, since the reaction is of the nature of a reaction initiation step. Also, the results of the present analysis may be of use in assessing the importance of diffusion and mixing on chemical mea-

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surements of absorbed intensity. Photochemical and radiation chemical reactions used for this purpose may sometimes be representable effectively as single-step reactions.

Our objects in this paper are to set up equations for photoreaction with diffusion for interesting types of single-step reactions, to determine whether diffusion effects are predicted by these equations, to characterize the effects via the solutions of the equations, and to show some consequences which follow for kinetics experiments and for chemical dosimetry measurements.

EQUATIONS FOR REACTION WITH DIFFUSION

Two situations which are of interest in experiments are considered. These involve a batch reactor and a continuous reactor.

Batch Reactor

A common batch reaction vessel for kinetics experiments is a cell with flat parallel end windows, one of which admits a parallel beam of radiation. The radiation propagates in the x direction, normal to the plane of the windows, and produces in the reactant a distribution of absorbed intensities and a corresponding distribution of reaction rates. The reaction rate will generally depend on concentration and position and is therefore denoted mathematically by $R(c, x)$. If the cell is initially filled with the substance A, and if at time zero illumination of the reactant commences, then the subsequent reactant concentration history in the cell will be governed by the equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - R(c, x) \tag{1}$$

Diffusion is present as a result of spatially nonuniform consumption of reactant resulting in turn from the nonuniform absorbed intensity distribution.

The initial condition is

$$c(0,x) = c_0 \tag{2}$$

and boundary conditions for chemically inert end windows are

$$\frac{\partial c}{\partial x} = 0 \text{ at } x = 0, x_1 \tag{3}$$

Continuous Reactor

A flow reactor often used for photoreactor studies (*3* to *6*) is the tubular reactor with a uniform flux of radiation incident on the tube surface and directed radially and normal to the tube axis. The absorbed intensity distribution produced in the reactant results in a distribution $R(c,r)$ of reaction rates. The concentration history of reactant A flowing in laminar flow through the illuminated zone is governed by the equation

$$2\bar{u}\left(1 - \frac{r^2}{r_0^2}\right)\frac{\partial c}{\partial z} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) - R(c,r) \tag{4}$$

Initial and boundary conditions are

$$c(0,r) = c_0 \tag{5}$$

$$\frac{\partial c}{\partial r} = \lim_{r\to 0}\frac{1}{rD}\int_0^r R(c,r)\,r\,dr \quad \text{at } r = 0 \tag{6}$$

$$\frac{\partial c}{\partial r} = 0 \text{ at } r = r_0 \tag{7}$$

The boundary condition at the origin has been discussed by Schechter and Wissler (*7*).

In the description of these two reactors in the above equations, constant physical properties and a negligible heat of reaction are assumed or implied. Our objects are to calculate for certain forms of the reaction rate term, $R(c,x)$ or $R(c,r)$, the average concentration within the batch cell as a function of time or leaving the flow reactor, and to show how these averages depend on rates of diffusion and radiation absorption as well as chemical rates.

The forms of R of interest, as stated in the discussion above, are those which depend not only on concentration, as is usual for a chemical rate process, but also on position. The derivation of these forms follows from considering the differential form of the Beer-Lambert law. For the slab geometry and a monochromatic source

$$\frac{\partial I(t,x)}{\partial x} = -\alpha c(t,x) I(t,x) \tag{8}$$

The functional dependence of the intensity, I, and the concentration of absorber, c, on t and x is shown for emphasis. α is the molar absorptivity. On integrating this equation over x we obtain

$$\ln\frac{I(t,x)}{I_0} = -\alpha\int_0^x c(t,x)\,dx$$

or

TABLE 1. BATCH REACTOR EXPRESSIONS

	Absorption by photosensitizer	Absorption by reactant
I_a	$\mu I_0 e^{-\mu x}$	$\alpha c I_0 e^{-\alpha\int_0^x c\,dx}$
$R(c,x)$	$k\mu I_0 e^{-\mu x} c$	$\phi\alpha c I_0 e^{-\alpha\int^x c\,dx}$
t_1	$1/k\mu I_0$	$1/\phi\alpha I_0$
τ	μx_1	$\alpha c_0 x_1$
ψ	$x_1^2 k\mu I_0/D$	$x_1^2\phi\alpha I_0/D$
Λ	$(D/k\mu I_0)^{1/2}\mu$	$(D/\phi\alpha I_0)^{1/2}\alpha c_0$
$R(C,X)t_1/c_0$	$Ce^{-\tau X}$	$Ce^{-\tau\int_0^X C\,dX}$
Solution		
$\Lambda \to \infty$	$C(\theta) = \exp\{-[1-\exp(-\tau)\theta/\tau\}$	$C(\theta) = 1 - \theta/\tau + 1/\tau \ln[1 + e^{-\tau}(e^{\theta} - 1)]$
$\Lambda = 0$	$C(\theta,X) = \exp[-\exp(-\tau X)\theta]$ $C(\theta) = \int_0^1 C(\theta,X)\,dX$	$C(\theta) = 1 - \theta/\tau + 1/\tau \ln[1 + e^{-\tau}(e^{\theta} - 1)]$

$$I(t,x) = I_0\, e^{-\alpha \int_0^x c(t,x)dx} \tag{9}$$

The absorbed intensity, I_a, is

$$I_a(t,x) = -\frac{\partial I(t,x)}{\partial x} = \alpha c(t,x) I_0\, e^{-\alpha \int_0^x c(t,x)dx} \tag{10}$$

Two forms of the reaction rate term arise, depending on the identity of the absorber. If the absorber is the reactant itself, and decomposition with efficiency, ϕ, follows absorption, then, by using Equation (10) as it stands, we obtain

$$R(c,x) = \phi\alpha c I_0\, e^{-\alpha \int_0^x c dx} \tag{11}$$

On the other hand, the radiation may be absorbed by a photosensitizer, which transfers energy to the reactant which then decomposes. The photosensitizer is not consumed and its concentration remains constant in space and time. From Equation (10), the absorbed intensity is given by

$$I_a(x) = \mu I_0 e^{-\mu x} \tag{12}$$

and is a function only of position. The product of the molar absorptivity and the photosensitizer concentration has been written as μ, the linear absorption coefficient. The reaction rate is then proportional to the absorbed intensity and the concentration of reactant

$$R(c,x) = k\mu I_0 e^{-\mu x}\, c \tag{13}$$

where k is the proportionality constant.

The expressions for the absorbed intensity and the reaction rate for the two absorbers are summarized in Table 1. Corresponding terms for the tubular reactor geometry derived in the same way are given in Table 2.

In terms of dimensionless variables, Equation (1) with its initial and boundary conditions is

$$\frac{\partial C}{\partial \theta} = \frac{1}{\psi}\frac{\partial^2 C}{\partial X^2} - \frac{R(C,X)t_1}{c_0}$$

$$C(0,X) = 1$$

$$\frac{\partial C(\theta,0)}{\partial X} = \frac{\partial C(\theta,1)}{\partial X} = 0 \tag{14}$$

The corresponding equations for the tubular reactor are

$$2(1-\rho^2)\frac{\partial C}{\partial \theta} = \frac{1}{\psi}\left(\frac{\partial^2 C}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial C}{\partial \rho}\right) - \frac{R(C,\rho)t_1}{c_0}$$

$$C(0,\rho) = 1$$

$$\frac{\partial C(\theta,0)}{\partial \rho} = \lim_{\rho\to 0}\frac{\psi}{\rho}\int_0^\rho \frac{R(C,\rho)t_1}{c_0}\rho d\rho$$

$$\frac{\partial C(\theta,1)}{\partial \rho} = 0 \tag{15}$$

where

$$C = c/c_0$$
$$X = x/x_1$$
$$\rho = r/r_0$$
$$\theta = t/t_1$$

The dimensionless forms of the reaction rate terms and the definitions of the reference time, t_1, and the dimensionless parameter, ψ, are given in Tables 1 and 2. It is convenient to present solutions of the diffusion equations in terms of two other dimensionless parameters, τ and Λ, also defined in the tables. The three parameters are related by the equation

$$\Lambda = \tau/\psi^{1/2} \tag{16}$$

τ is the optical thickness of the reactor of interest. For direct absorption by the reactant it is based on initial reactant concentration. ψ is the ratio of a characteristic diffusion time to the chemical lifetime, t_1. Λ is the ratio of the reactant diffusion mean free path during the time t to the radiation mean free path. These same parameter with definitions appropriate for the kinetic scheme oi interest were used to describe the nonuniform initiation problem in which diffusion of intermediates is important (2).

Equation (15) was previously solved analytically for the photosensitized reaction by Schechter and Wissler (7).

TABLE 2. CONTINUOUS REACTOR EXPRESSIONS

	Absorption by photosensitizer	Absorption by reactant
I_a	$2\mu I_0(r_0/r)e^{-\mu r_0}\cosh(\mu r)$	$2\alpha c I_0(r_0/r)e^{-\alpha\int_0^{r_0} cdr}\cosh(\alpha\int_0^r cdr)$
$R(c, r)$	$2k\mu I_0(r_0/r)e^{-\mu r_0}\cosh(\mu r)c$	$2\phi\alpha c I_0(r_0/r)e^{-\alpha\int_0^{r_0} cdr}\cosh(\alpha\int_0^r cdr)$
t_1	$1/k\mu I_0$	$1/\phi\alpha I_0$
τ	$2\mu r_0$	$2\alpha c_0 r_0$
ψ	$r_0{}^2 k\mu I_0/D$	$r_0{}^2\phi\alpha I_0/D$
Λ	$(D/k\mu I_0)^{1/2}\mu$	$(D/\phi\alpha I_0)^{1/2}\alpha c_0$
$R(C, \rho)t_1/c_0$	$\dfrac{2C}{\rho}e^{-\tau/2}\cosh(\tau\rho/2)$	$\dfrac{2C}{\rho}e^{-\frac{\tau}{2}\int_0^1 Cd\rho}\cosh\left(\dfrac{\tau}{2}\int_0^\rho Cd\rho\right)$
Solution		
$\Lambda \to \infty$	$C(\theta) = \exp\{-[1-\exp(-\tau)]4\theta/\tau\}$	$C(\theta) = 1 - \dfrac{4\theta}{\tau} + \dfrac{1}{\tau}\ln[1 + e^{-\tau}(e^{4\theta} - 1)]$
$\Lambda = 0$	$C(\theta,\rho) = \exp[-\exp(-\tau/2)\cosh(\tau\rho/2)\dfrac{\theta}{\rho-\rho^3}]$	$\displaystyle\int_1^{(C\theta,\rho)} \frac{dC(\theta,\rho)}{C(\theta,\rho)e^{-\frac{\tau}{2}\int_0^1 C(\theta,\rho)d\rho}\cosh[\frac{\tau}{2}\int_0^\rho C(\theta,\rho)d\rho]} + \frac{\theta}{\rho-\rho^3} = 0$
	$C(\theta) = 4\int_0^1 (\rho-\rho^3)C(\theta,\rho)d\rho$	$C(\theta) = 4\int_0^1 (\rho-\rho^3)C(\theta,\rho)d\rho$

EXISTENCE OF DIFFUSION EFFECT

For the batch reactor let us integrate Equation (14) over X from 0 to 1. We obtain

$$\frac{dC(\theta)}{d\theta} = -\int_0^1 \frac{R(C,X)t_1}{c_0}\,dX \qquad (17)$$

where

$$C(\theta) = \int_0^1 C(\theta,X)\,dX$$

Diffusion terms are missing by virtue of the boundary conditions. Let us evaluate the right-hand side of Equation (17) using the reaction rate term corresponding to absorption by reactant. The version of Equation (17) of interest then is

$$\frac{dC(\theta)}{d\theta} = -\int_0^1 C \exp\left(-\tau\int_0^X C\,dX_1\right)dX$$

The derivative of the argument of the exponential is $-\tau C$. Hence after multiplying and dividing the right-hand side by τ the integrand may be written as the derivative of the exponential:

$$\frac{dC(\theta)}{d\theta} = \frac{1}{\tau}\int_0^1 \frac{d}{dX}\left[\exp\left(-\tau\int_0^X C\,dX_1\right)\right]dX$$

When we evaluate the exponential at the two limits we find

$$\frac{dC(\theta)}{d\theta} = -\frac{1-e^{-\tau C(\theta)}}{\tau} \qquad (18)$$

Equation (18) was derived without restriction on the diffusion rate and yet it contains no measure of the diffusion rate. At the same time the only concentration term present is the average concentration. Equation (18) is therefore integrable as it stands, and we conclude that for reaction following direct absorption in the batch slab reactor the history of the average concentration is independent of diffusion rate. This conclusion cannot be shown to be valid in similar ways for the other absorber-reactor combinations, indicating that a diffusion effect may be expected in the other cases.

SOLUTIONS AND THEIR CHARACTERISTICS

Extreme Diffusion Rates

Much can be learned about the influence of nonuniform initiation through examination of the solutions of Equations (14) and (15) for the cases in which diffusion rates are very rapid or when diffusion is absent.

For infinitely rapid diffusion, $\psi = 0$ and $\Lambda \to \infty$, and concentrations are uniform over the X- or ρ-coordinate. Reaction proceeds at a rate corresponding to the mean reaction rate. Thus, for example, for the batch reactor, Equation (14) becomes

$$\frac{dC(\theta)}{d\theta} = -\int_0^1 \frac{R(C,X)t_1}{c_0}\,dX \qquad (19)$$

identical with Equation (17). Solutions of this equation for the two absorbers are given in Table 1. Those corresponding to the continuous reactor are given in Table 2.*

In the absence of diffusion, $\psi \to \infty$ and $\Lambda = 0$, and Equation (14) becomes

$$\frac{\partial C(\theta,X)}{\partial\theta} = -R[C(\theta,X),X] \qquad (20)$$

If we separate variables and integrate we obtain

$$\int_1^{C(\theta,X)} \frac{dC(\theta,X)}{R[C(\theta,X),X]} + \theta = 0 \qquad (21)$$

This equation is to be solved for $C(\theta,X)$, and from this solution the average concentration is formed

$$C(\theta) = \int_0^1 C(\theta,X)\,dX \qquad (22)$$

Solutions of Equation (21) are given in Table 1 adjacent to the entry $\Lambda = 0$. A similar treatment can be given for the tubular reactor. The average concentration of interest is the mixed average effluent concentration. The resulting equations for the tubular reactor are given in Table 2. The solutions of Equations (19), (21), and (22) and of the corresponding equations for the tubular reactor were obtained numerically.

Graphical representations of the solutions for extreme diffusion rates are shown in Figures 1 and 2. Figure 1 is for the direct absorption reaction and Figure 2 is for the photosensitized reaction. The results for both reactors are shown in each figure for two values of optical thickness, $\tau = 1$ and 10. Mixed average fraction conversion is plotted against $\theta/\overline{R}$. For the slab reactor $\overline{R} = 1$. For the tubular reactor $\overline{R} = 1/4$. With this abscissa, the curves for both reactors are identical for $\Lambda \to \infty$.

Many of the consequences of nonuniform initiation of the single-step reaction are evident in these figures. First, for the reaction following absorption by reactant (Figure 1) one sees little or no effect of diffusion. For the batch slab reactor, as shown earlier, the indicated curves are valid for all rates of diffusion. For the continuous tubular reactor, the effect of diffusion is small, and smaller at $\tau =$

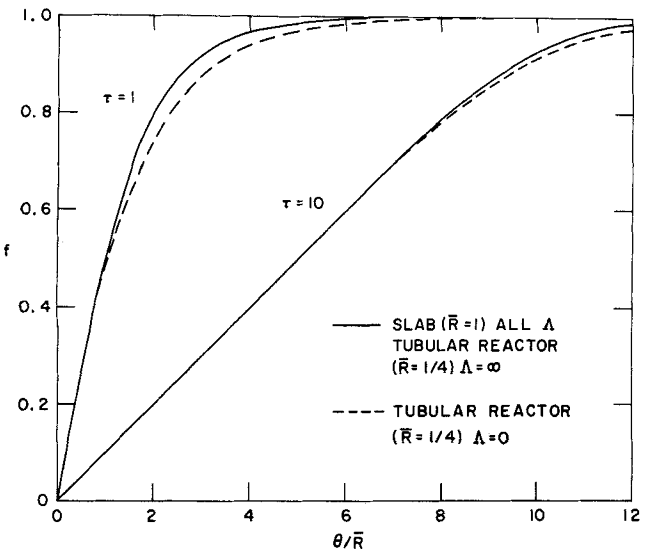

Fig. 1. Fraction conversion history for the reaction following absorption by reactant, for all diffusion rates for the batch slab reactor, and for extreme diffusion rates for the continuous tubular reactor.

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* Note that in obtaining the solution for the case of absorption by reactant in the batch reactor for both $\Lambda \to \infty$ and $\Lambda = 0$ one must solve the following equation:

$$\int_1^C \frac{dC}{1-e^{-\tau C}} + \frac{\theta}{\tau} = 0$$

The solution to this equation which one finds by reference to tables of integrals is the implicit relation

$$\tau - \tau C(\theta) - \ln\frac{1-e^{-\tau C(\theta)}}{1-e^{-\tau}} - \theta = 0$$

In this relation one recognizes that $-\tau C(\theta) = \ln e^{-\tau C(\theta)}$ and makes this substitution. Explicit solution of the resulting equation for $C(\theta)$ is then straightforward, and yields the relation given in Table 1. Exactly the same development is required in obtaining the equation for the tubular reactor for $\Lambda \to \infty$ given in Table 2 except that θ is replaced by 4θ throughout.

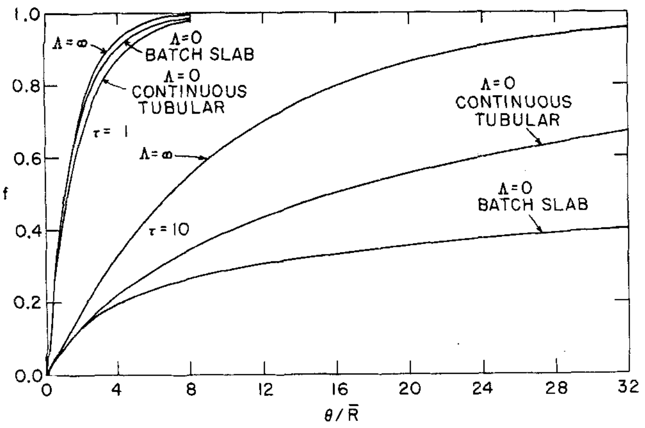

Fig. 2. Fraction conversion history for the photosensitized reaction, for extreme diffusion rates.

10 than at $\tau = 1$. Diffusion effects may be of any size in the photosensitized reaction (Figure 2). Thus, for very weak absorption, diffusion exerts little or no influence on the conversion history, but, as absorption becomes stronger and stronger, the influence of diffusion becomes correspondingly greater. For both reactions, diffusion is only influential at finite conversions. At sufficiently small conversions, regardless of optical thickness, diffusion has no effect on conversion. The effect of diffusion at high conversions is always to increase the rate of conversion. Thus, when the initiating radiation is effectively distributed at its average value over an optically dense reactant, the resulting average conversion rate is greater than when the radiation is absorbed in a more localized fashion.

Solution for All Diffusion Rates

In order to determine the relative values of rates of diffusion, radiation absorption, and chemical kinetics which correspond effectively to the curves for $\Lambda = 0$ and $\Lambda \rightarrow \infty$, and to define the intermediate region, the complete solution of Equations (14) and (15) for particular optical thicknesses must be obtained. This was done numerically for the photosensitized reaction in both reactors, that is, Equation (15) was solved. The solution was based on an implicit difference equation representation of Equation (15).

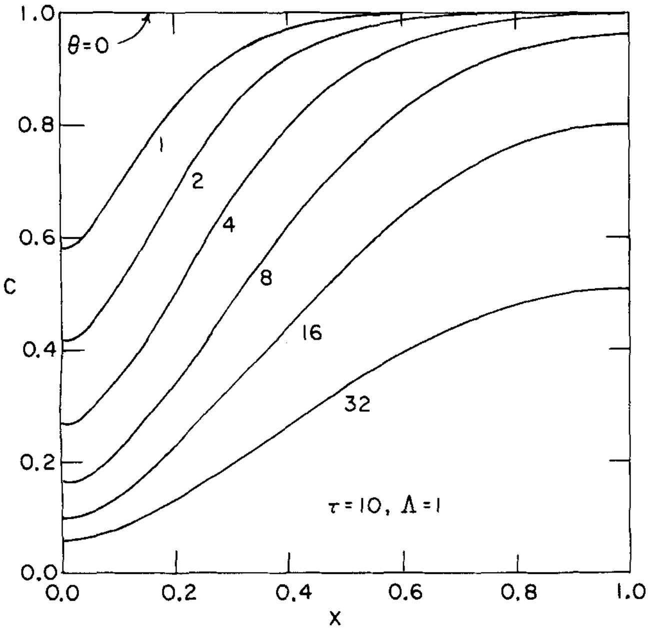

Fig. 3. Concentration profiles for the photosensitized reaction in the batch slab reactor.

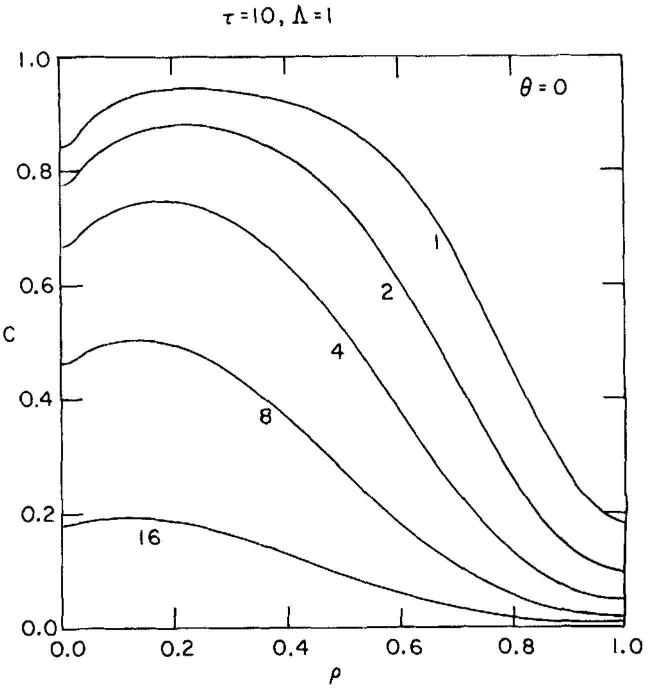

Fig. 4. Concentration profiles for the photosensitized reaction in the laminar flow tubular reactor.

Typical concentration profiles and their development in time are shown in Figures 3 and 4 for the two reactors. The calculations were made for $\tau = 10$, a moderately high optical thickness, and for a mean free path ratio, Λ, of unity, a value which, it will shortly be seen, corresponds roughly to the middle of the transition range between the absence of diffusion and the presence of infinitely rapid diffusion. In the batch reactor (Figure 3) consumption of reactant is greatest near the point of radiation entry and it proceeds in time toward the other end of the cell. The same situation is found in the continuous reactor (Figure 4), except that in addition concentration of the radiation at the center of the reactor leads to very high intensities there (infinite at $\rho = 0$) and to very rapid consumption of reactant there as well as at the reactor wall.

The history of the averages of such profiles for the batch reactor is shown for $\tau = 10$ and a range of values of Λ in Figure 5. There it is seen that the complete

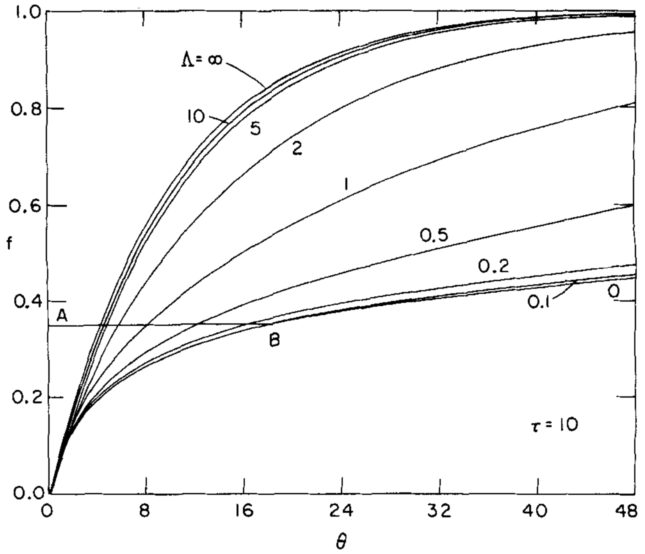

Fig. 5. Fraction conversion history for the photosensitized reaction in the batch slab reactor.

transition range from the effective absence of diffusion to the presence of effectively infinite rapid diffusion corresponds roughly to $0.1 < \Lambda < 10$. Thus, in terms of the definition of Λ as a ratio of mean free paths, when the diffusion mean free path corresponding to the mean life of the reactant at the incident intensity is one-tenth or less of the radiation mean free path, then the reaction proceeds as if diffusion were totally absent. The effective absorbed intensity at each location is the local absorbed intensity. On the other hand, when the same diffusion mean free path is ten times the radiation mean free path, the reaction proceeds as if diffusion were infinitely rapid and the effective absorbed intensity at each location is the average absorbed intensity.

The same transition range was found for Λ for the photosensitized reaction in the continuous tubular reactor. Also, in previous work (*2*) on initial rates in chain reactions where the movement of reactive centers in response to nonuniform initiation was studied, the same range of Λ was found to define the transition region. For the chain reaction the diffusion mean free path was defined as that corresponding to the mean chain lifetime.

DISCUSSION

The introduction of rapid diffusion in an optically dense reactant leads effectively toward a spreading of the absorbed radiation over the entire reaction volume at its mean value. The resulting average fraction conversion versus time relation equals or exceeds that for lower diffusion rates where the absorbed radiation acts more nearly at its local values. In this section we point out two areas in which nonuniform initiation may influence the outcome of experiments.

Chemical Measurements of Radiation

A prominent practical manifestation of nonuniform initiation lies in its influence on chemical actinometry and dosimetry. The Fricke ferrous sulfate dosimeter (*8*) used for ionizing radiations and energetic particles may approximate the case of the photosensitized reaction. The ferrous ion or the dissolved oxygen molecules (when present) may be the limiting diffusing reactant. The potassium ferrioxalate actinometer (*9, 10*) used for visible and ultraviolet light may correspond to the reaction which follows direct absorption. The ferrioxalate ion presumably is the photolyte. While systems such as these are well characterized for the purpose of chemical measurements of radiation in the presence of weak absorption and/or perfect mixing (rapid diffusion), their mechanisms are not always unequivocally known; and the assumption that they follow effectively the simple single-step mechanism of the present discussion may be incorrect. Thus it may be incorrect to assume that the uranyl oxalate actinometer system (*11*), which is often spoken of as a photosensitized reaction, is indeed of that nature as far as the nonuniform initiation problem is concerned, for the photolyte is evidently a uranyl oxalate complex in equilibrium with uranyl and oxalate ions (*11*).

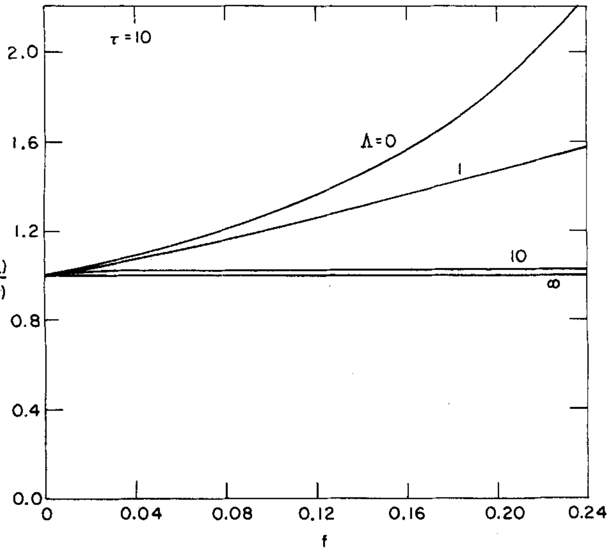

Fig. 6. Errors in measurement of radiation using the photosensitized reaction in the batch slab reactor.

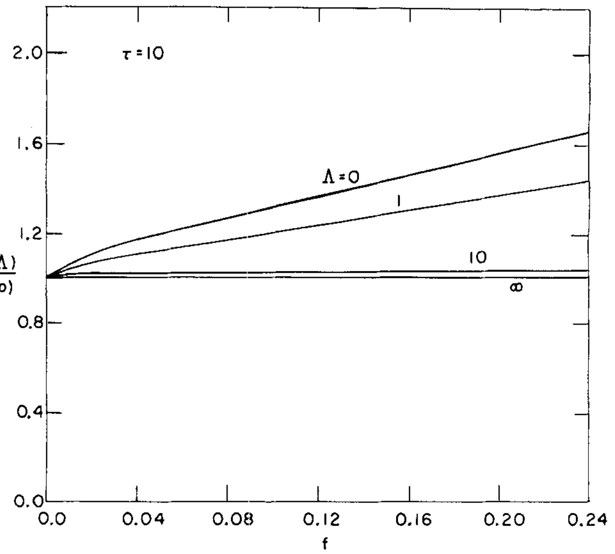

Fig. 7. Errors in measurement of radiation using the photosensitized reaction in the laminar flow tubular reactor.

For the present we indicate by illustration the magnitude of the errors which might be encountered in chemical measurements of radiation using a photosensitized reaction if the presence of nonuniform initiation is not properly accounted for. For this purpose in Figure 5 we have drawn line *AB* corresponding to some conversion, f. In an actinometric or dosimetric measurement one exposes the chemical system to radiation for a known interval of time and measures the resulting conversion in the system. It is often tacitly assumed in such measurements that diffusion in the direction of radiation attenuation is very rapid. With this assumption, the value of $\theta = k\mu I_0 t$ corresponding to the conversion, f, is that corresponding to the intersection of *AB* with the curve for $\Lambda \to \infty$. Let us denote this value by $\theta(\infty)$. If in fact during the measurement the actual value is Λ, then the true value of θ is $\theta(\Lambda)$ corresponding to the abscissa of the intersection of *AB* with the curve for the correct value of Λ. If one deduces the value of the incident intensity assuming $\Lambda \to \infty$ when it is not, then the factor by which it must be multiplied to obtain the true incident intensity is $\theta(\Lambda)/\theta(\infty)$. Values of this ratio, derived from Figure 5 for the batch reactor as indicated above, are plotted in Figure 6 against f for $\tau = 10$ with Λ as a parameter. Figure 7 presents similar information for the tubular reactor derived from the solution of Equation (15). The range of f considered is that of small conversions within which actinometers and dosimeters are usually used. It may be seen that for systems of optical thickness, $\tau = 10$, even at 10% conversion the true intensity is as much as 30% greater than the one corresponding to $\Lambda \to \infty$.

It should be pointed out that the introduction of stirring, and not necessarily vigorous stirring, in the batch reactor would increase Λ effectively to infinity, thereby

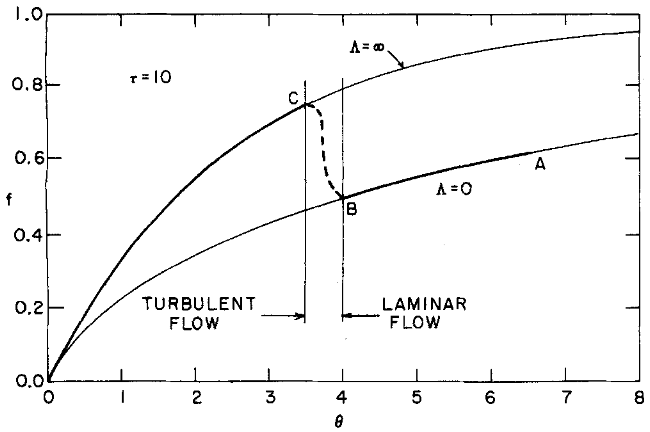

Fig. 8. Laminar-turbulent flow transition in the tubular reactor with the photosensitized reaction.

eliminating the error. Except in the case of unusually intense radiation sources, the mean lifetime of the reactant is of the order of minutes to hours whereas with not very vigorous stirring the effective diffusion lifetime may be reduced to the order of seconds.

Dosimetry and actinometry errors might be more likely to occur in the continuous tubular reactor. This reactor would very likely be used in the laminar flow region, as was conceived in the derivation of Equation (15), because actinometric reactions are of low quantum yield and, with available light sources, large residence times are usually required to realize conveniently measurable conversions. Stirring or mixing would thus be absent and radial reactant movement would occur via the slow process of molecular diffusion.

Laminar-Turbulent Flow Transition

The nature of the change in conversion arising upon a transition from the laminar to the turbulent flow regime in the presence of nonuniform initiation may be described with reference to Figure 8. In this figure the conversion histories from Figure 2 for the tubular reactor with $\tau = 10$ have been replotted. The abscissa is θ rather than $\theta/\overline{R}$. We imagine a reactor to be operating in the laminar flow region at point A. In the laminar flow regime, the diffusion which occurs is molecular diffusion for which we assume Λ is effectively zero. We now imagine the velocity to be increased progressively so that the operating point moves along the curve for $\Lambda = 0$ until the laminar-turbulent flow transition region is encountered at point B. When the flow has become fully turbulent, further increases in velocity cause the operating point to move from point C along the curve for $\Lambda \rightarrow \infty$. This is the curve appropriate for plug flow. Instead of a smooth steady decrease in f as the velocity is increased,† an increase in f is encountered as the flow becomes turbulent.

Whether a change of the type described will occur depends on the actual values of Λ in the two flow regions and on the location of the transition region on the θ-scale. If the flow transition occurs at very small values of θ where very little variation in f is possible, then of course the change in f will be imperceptible.

ACKNOWLEDGMENT

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NOTATION

c = concentration of reactant A, mole/cc.
c_0 = initial concentration of reactant A, mole/cc.
C = c/c_0, dimensionless
$C(\theta)$ = average dimensionless concentration in batch reactor at time θ or mixed average dimensionless tubular reactor effluent concentration
D = diffusion coefficient of reactant A, sq.cm./sec.
f = average fraction conversion of A in batch reactor at time t; mixed average fraction conversion in tubular reactor effluent, dimensionless
I = radiation intensity, einstein/sq.cm.-sec.
I_a = absorbed radiation intensity, einstein/cc.-sec.
I_0 = incident intensity, einstein/sq.cm.-sec.
k = proportionality constant in Equation (13), cc./einstein
r = radial position, cm.
r_0 = tubular reactor radius, cm.
R = reaction rate, mole/cc.-sec.
$\overline{R}$ = average dimensionless radius: $\overline{R} = 1$ for slab reactor; $\overline{R} = 1/4$ for tubular reactor
t = time, sec.; $z/\overline{u}$ for tubular reactor
t_1 = mean lifetime of reactant A at incident radiation intensity, sec. See Tables 1 and 2
$\overline{u}$ = mean velocity in tubular reactor, cm./sec.
x = position coordinate in slab reactor normal to slab surfaces, cm.
x_1 = slab reactor thickness, cm.
X = x/x_1, dimensionless
z = distance along tubular reactor axis from start of illuminated length, cm.

Greek Letters

α = molar absorptivity, base e, sq.cm./mole.
θ = t/t_1, dimensionless
Λ = mean free path ratio, dimensionless. See Tables 1 and 2
μ = linear absorption coefficient, cm.$^{-1}$
ρ = r/r_0, dimensionless
τ = optical thickness, dimensionless. See Tables 1 and 2
quantum yield, mole/einstein
ψ = ratio of characteristic diffusion time to mean reactant lifetime at incident intensity, dimensionless. See Tables 1 and 2

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† Actually even with uniform initiation a change in conversion peculiar to the laminar-turbulent transition would be expected, as the result of the change in residence time distribution. This change would be small compared to that observable in an optically dense but otherwise identical system.