Experimental Observations Concerning the Diffuse, Light Intensity Distribution Model

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Matsuura and Smith (1970) proposed a partially diffuse, light intensity distribution model for externally irradiated cylindrical photoreactors. The partially diffuse model is based on the postulation that the incident radiation arrives at the reactor walls as two-dimensional, parallel bands, perpendicular to the radial center line of the reactor. By varying the model parameter, the radiation band width, from zero up to a value corresponding to the reactor diameter, the model can be made to represent the intensity distribution extremes within the reactor corresponding to a radially incident model and a fully diffuse model, respectively. Matsuura and Smith applied their model to experimental data obtained by exposing an 0.001 M uranyl oxalate actinometer solution to a high pressure mercury lamp source. The average light intensity within the reactor was then determined from the observed decomposition rate of the oxalate ion. The band width of the model was varied between its limits, and at each setting, an intensity at the reactor wall, under conditions of no radiation absorption, was calculated from the model. Thus, the wall intensity was unique with respect to the band width and was consistent with the observed decomposition rate. These authors did not perform additional experiments which would permit a comparison of the calculated and observed wall intensities. Indeed, the experimental determination of the intensity at the wall under conditions of no radiation absorption would be a formidable task. Thus, no direct experimental evidence was presented concerning the ability of the partially diffuse model to accurately represent the true light intensity distribution within the reactor.

Roger and Villermaux (1975) have argued that the incident wall flux should be used in formulating the partially diffuse model instead of the intensity at the wall under conditions of no absorption as defined by Matsuura and Smith. They reasoned that the incident wall flux is determined solely by the radiation characteristics of the source and by the geometric arrangement of the reactor, source, and reflector. Under conditions where these elements are fixed, the incident wall flux possesses an inherent value which can not be adjusted so as to match observed actinometer decomposition rates and consequently is independent of the assumed band width. They derived new mathematical expressions for the partially diffuse model in which the incident wall flux was defined as the photon flux which passes, from the surroundings into the reactor, through a fixed unit area of the reactor wall.

Modification of the partially diffuse model by Roger and Villermaux is of particular interest since it permits direct experimental verification of the model. This is the case because the actinometer decomposition rates and the incident wall flux can be determined independently by use of different chemical actinometers.

The purpose of this note is to report experimental observations of the performance of a cylindrical photoreactor under conditions where the incident wall flux is accurately known and where the experimental decomposition rates of actinometer solutions can be critically compared with the decomposition rates calculated from the partially diffuse model as modified by Roger and Villermaux.

The experimental apparatus used in this work has been described previously by Williams and Yen (1973). In that work the incident wall flux was accurately determined by using an optically dense potassium ferrioxalate actinometer (0.15 M) to absorb essentially all incident radiation. The reactor was constructed so as to insure that the incident wall flux would remain constant whatever the optical density of the absorbing solution within the reactor. This was accomplished by utilizing 1.0 cm of the reactor, located at the axial center, for conducting the reactions, while the remaining 60 cm were optically transparent. A complete discussion of this point can be found in the subject paper.

After the incident wall flux was determined, two additional actinometer solutions were exposed in the reactor. The purpose here was to determine decomposition rates under conditions where total absorption of incident radiation could not be assumed. In the first case an 0.05 M uranyl oxalate solution, having an optical density of 1.64 at the principal wavelength of 253.7 nm, was used as a low optical density solution. In the second case an 0.005 M potassium ferrioxalate solution, having an optical density of 3.78 at the above wavelength, was used as a high optical density solution. The decomposition rates for each solution were determined experimentally. The analytic techniques for these determinations are described for the uranyl oxalate actinometer by Discher et al. (1963) and for the potassium ferrioxalate actinometer by Baxendale and Bridge (1955).

The spatially averaged theoretical decomposition rate for radiation of wavelength λ is $\bar{r}_\lambda$, where

$$\bar{r}_\lambda = \mu_\lambda \bar{I}_{Pd,\lambda} \Phi_\lambda \tag{1}$$

while the overall decomposition rate for all wavelengths is $\bar{r}$:

$$\bar{r} = \sum_\lambda f_\lambda \bar{r}_\lambda \tag{2}$$

The theoretical decomposition rate depends upon the intensity averaged over the cross section of the reactor and can be calculated from Equation (3):

$$\bar{I}_{Pd,\lambda} = \int_0^{R_1} 2\pi r I_{Pd,\lambda} dr / \pi R_1^2 \tag{3}$$

The general expression for the point intensity $I_{Pd,\lambda}$ is obtained from Roger and Villermaux, Equations (7), (13), and (14). Analytic solutions have been found for Equation (3) under certain restricted conditions. In particular, for the case of a nonabsorbing medium, the solution is represented by Equation (4):

Table 1. Radiation Characteristics of Source and Quantum Yields of Actinometers

Wavelength, nm λ	Fractional output, f_λ	Quantum yields: Uranyl oxalate Φ_λ	Quantum yields: Potassium ferrioxalate $\Phi\lambda$
253.7	0.92168	0.60	1.24
265.2	0.00141	0.58	1.23
280.4	0.00141	0.59	1.23
296.7	0.00349	0.57	1.24
302.2	0.00209	0.57	1.24
313.1	0.01395	0.57	1.17
334.1	0.00138	0.53	1.19
350.0	0.00136	0.51	1.22
365.4	0.01361	0.49	1.21
390.0	0.00064	0.57	1.05
453.8	0.03611	0.58	0.93
577.0	0.00287	0.58	0.01

Table 2. Experimental and Calculated Decomposition Rates

Actinometer solution	Experimental decomposition rate $\bar{r}$, kmole m^{-3} s^{-1}	Calculated decomposition rate $\bar{r}$, kmole m^{-3} s^{-1} (fully diffuse model)
0.05 M uranyl oxalate	1.91×10^{-5}	1.97×10^{-5}
0.005 M potassium ferrioxalate	4.60×10^{-5}	5.20×10^{-5}

Incident wall flux = 3.00×10^{-7} keinsteins m^{-2} s^{-1} (Williams and Yen, 1973).

$$\bar{I}_{Pd,\mu=0} = 4I_oY\left[\frac{1}{2Y^2}\sin^{-1}Y + \frac{1}{2}\sqrt{\frac{1}{Y^2}-1} - \frac{\pi}{4}\right] + \pi Y \quad (4)$$

This solution is obtained by completing the integration of Equation (20) in the Roger and Villermaux note. For a radially incident light distribution model ($R_2 \to 0$), the solution of Equation (3) is represented by Equation (5):

$$\bar{I}_{\text{rad},\lambda} = \frac{4I_0}{\sigma_\lambda}[1 - \exp(-\sigma_\lambda)] \quad (5)$$

When the model is fully diffuse ($R_2 = R_1$), the solution, as reported by Villermaux (1976), is given by Equation (6):

$$\bar{I}_{d,\lambda} = \frac{4I_0}{\sigma_\lambda}\left[1 - \int_0^1 \exp(-\sigma_\lambda\sqrt{1-x^2})\,dx\right] \quad (6)$$

The theoretical decomposition rates were calculated for the case of a fully diffuse model. The spectral energy distribution of the source and the quantum yields at each major wavelength are shown in Table 1. The experimental and calculated decomposition rates are compared in Table 2.

The calculated decomposition rates are 4.2 and 13.0% above the experimental rates for the low and high optical density cases, respectively. Since the fully diffuse model predicts the lowest possible decomposition rates obtainable from the partially diffuse model, there is no purpose to be achieved in exploring the effects of changing the band width.

These results indicate that the fully diffuse model can be relied upon for the a priori calculation of reaction rates once the incident flux is known. It is recognized that the results are limited to the specific elliptical reflector photoreactor used in these experiments. In particular, they were conducted by using an elliptical reflector of low eccentricity ($e = 0.402$). It is precisely under conditions of low eccentricity that Cerdá et al. (1973) have shown, through theoretical computations, that diffuse incident models are most likely to be applicable. Therefore, it is doubtful that equally good results could be achieved by the application of the fully diffuse model to experimental photoreactors involving elliptical reflectors of substantially greater eccentricities than those used in this work.

NOTATION

$2a$ = length of major axis of ellipse
$2b$ = length of minor axis of ellipse
e = $\sqrt{a^2 - b^2}/a$, ellipse eccentricity
f_λ = fractional output of source corresponding to wavelength λ, dimensionless
I_o = incident wall flux, keinsteins m^{-2}s^{-1}
$\bar{I}_{d,\lambda}$ = average intensity over reactor cross section calculated from diffuse model at wavelength λ, keinsteins m^{-2}s^{-1}
$\bar{I}_{Pd,\mu=0}$ = average intensity over reactor cross section under condition of no attenuation ($\mu = 0$) for the partially diffuse model, keinsteins m^{-2}s^{-1}
$I_{Pd,\lambda}$ = point intensity calculated from partially diffuse model at wavelength λ, keinsteins m^{-2}s^{-1}
$\bar{I}_{\text{rad},\lambda}$ = average intensity over reactor cross section for the radially incident model at wavelength λ, keinsteins m^{-2}s^{-1}
$\bar{r}_\lambda$ = spatially averaged reaction rate due to radiation of wavelength λ, kmole m^{-3}s^{-1}
$\bar{r}$ = spatially average reaction rate over all wavelengths, kmole m^{-3}s^{-1}
r = radial position coordinate, m
R_1 = radius of reactor, m
R_2 = half width of radiation band, m
Y = R_2/R_1, dimensionless
μ_λ = attenuation coefficient, m^{-1}
σ_λ = $2\mu_\lambda R_1$, optical density, dimensionless
Φ_λ = quantum yield at wavelength λ, kmole keinstein^{-1}

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Manuscript received February 20, 1976; revision received April 16, and accepted April 20, 1976.