The Incident Wall Intensity in Elliptical Reflector-Photoreactors

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The elliptical-reflector photoreactor is frequently used in the study of photochemical reaction kinetics. The incident light intensity at the reactor wall must be determined in such studies so that the light intensity in the reactor cross section can be computed by application of an appropriate light distribution model.

The incident wall intensity can be directly determined by use of a strongly absorbing chemical actinometer solution which absorbs nearly all light energy as it passes through the reactor. Alternately, the use of a moderately absorbing actinometer solution will yield a value for the average light intensity within the cross section from which the incident wall intensity can be computed by means of an assumed light intensity distribution model. The former approach, utilizing a potassium ferrioxalate actinometer, has been applied by Ragonese and Williams (1971) while the latter approach, using the uranyl oxalate actinometer, has been discussed by Matsuura and Smith (1970). The resulting incident wall intensity is then used, in conjunction with a light intensity distribution model, to compute the intensity distribution which prevails in the reactor cross section when the reaction system of interest is studied.

The incident wall intensity, as determined by the above methods, can be erroneous if the optical density of the actinometer solution differs from that of the reaction system under study. This possibility has been referred to by Cassano, Matsuura, and Smith (1968) although no quantitative information was given to determine the magnitude of the possible error. This error arises when the optical density of the reaction system is small compared to that of the actinometer because a light ray can pass through the reaction fluid and reflect off the surrounding elliptical surface onto the reactor walls, thus increasing the incident wall intensity relative to that determined with the actinometer. The use of a high optical density actinometer in conjunction with a low optical density reaction system would lead to a low estimation of the true incident wall intensity which exists when studying the reaction system while the opposite result prevails in the inverse case. Since quantitative information on the magnitude of this error is not available, those working in this field are unable to assess whether or not this error is likely to be of importance in their study.

It is, of course, preferable that the investigator match the optical densities of the actinometer and reaction system, thus eliminating the possibility of error. Unfortunately this can not always be done, especially when a polychromatic source is used and the two systems exhibit different absorption characteristics in the output spectrum of the source.

The purpose of this note is to present an experimental method by which the maximum possible error in the incident wall intensity, due to unmatched optical densities, can be approximated and to apply this method to a particular elliptical reflector-photoreactor.

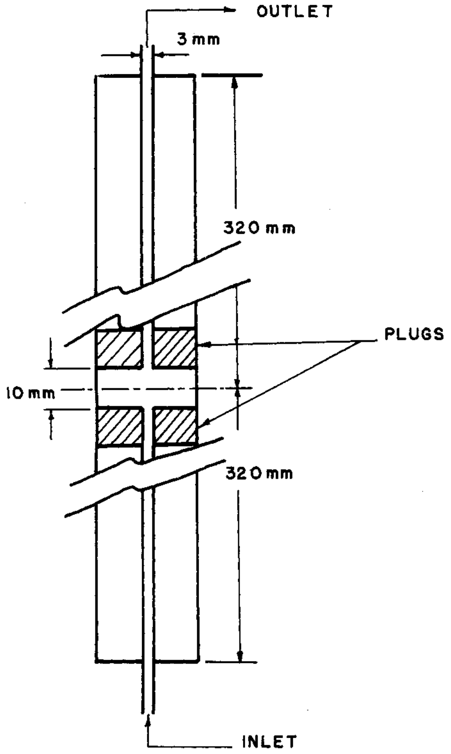

Fig. 1. Schematic diagram of reaction cell.

EXPERIMENTAL METHOD

An elliptical reflector-photoreactor and a potassium ferrioxalate actinometer were used in this work. The photoreactor is described by Zolner and Williams (1972) while the actinometer and associated method of analysis are discussed by Ragonese and Williams (1971). The potassium ferrioxalate actinometer concentration was 0.15 molar in a 1.0 normal sulfuric acid solution. The light source was a 19.1 mm O.D. General Electric low-pressure mercury vapor lamp which provided 92.17% of its energy output at a wave length of 253.7 nm. The actinometer absorbed over 99% of the light at this wave length passing through a 25 mm path length which is equivalent to the diameter of the reactor described below. Thus, the results of the actinometer experiments can be used to directly determine the incident wall intensity.

The wall intensity at the longitudinal center of a 25 mm I.D. quartz tube was determined using the reaction cell shown schematically in Figure 1.

A 10 mm length of the quartz tube was isolated for study by means of two Plexiglas plugs which were fitted with O-rings and machined to fit inside the quartz tube. These plugs were positioned symmetrically with respect to the longitudinal midpoint of the tube such as to provide a 10 mm path length between them. This section of the quartz tube is referred to as the reaction cell which is small compared to the total tube length of 640 mm. The centers of the plugs were drilled to provide for the insertion of 3 mm O.D. quartz tubes which extend beyond the length of the 25 mm quartz tube in both directions. These 3 mm tubes were used for the continuous introduction and removal of actinometer solution from the reaction cell. The 3 mm tubes were painted black to prevent the exposure of actinometer solution while being transported to and from the reaction cell. The apparatus used to continuously circulate a batch of actinometer fluid through the reaction cell is shown schematically by Ragonese and Williams (1971). This arrangement allows light to pass through the 25 mm quartz tube, except for the small reaction cell, and be reflected off the surrounding elliptical-reflector surface. The incident intensity measured at the reaction cell wall approximates the intensity which would prevail under the limiting case of a transparent reaction system.

The 25 mm quartz tube was then wrapped with black paper, except for the reaction cell surface, and the incident wall intensity was redetermined. This case corresponds to the use of an extremely high optical density (opaque) reaction system since light can not penetrate the 25 mm quartz reactor tube.

RESULTS AND CONCLUSIONS

The wall intensity was 3.00×10^{-7} keinsteins $m^{-2}s^{-1}$ in the case of the transparent reactor and 2.58×10^{-7} keinsteins $m^{-2}s^{-1}$ in the case of the opaque reactor. These numbers are the averaged values for duplicate determinations in which the conversion of the actinometer was held to less than 1% for any given determination of the incident wall intensity. This result approximates the maximum attainable difference in incident wall intensity for this particular elliptical-reflector reactor and might be approached in practice if a high optical density liquid actinometer were used in conjunction with a low optical density gas phase reaction system.

This difference in incident wall intensity is solely attributable to that portion of the lamp output which passed through the transparent section of the 25 mm tube and was reflected onto the reaction cell wall. This difference will diminish as the optical density of the reaction system approaches that of the actinometer. For example, if the optical density of the reaction system was only 1.0 then approximately 63% of the light would be absorbed in passing through the reactor diameter according to the Beer-Lambert absorption equation. Therefore, as an approximation, the difference in incident wall intensity would be reduced 63% from the difference reported here. While the results obtained are limited to the specific elliptical reflector-reactor geometry used, they are of some value in estimating the expected effect in other reactors. For example, if the reactor tube diameter were decreased with respect to the lamp diameter in a geometrically similar reflector, the maximum difference in wall intensity would also be expected to decrease relative to the result reported here since a smaller fraction of the source output would be intercepted by the reactor.

This result should serve to alert workers in this field to the magnitude of the potential error possible in determining the incident wall intensity when the optical density of the actinometer and reaction system are different and to provide an experimental method by which the error can be determined.

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The Possible Role of Diffusion in Metabolism

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When considering most chemical reactions, it is the usual chemical engineering practice to examine the overall process of diffusion of reactants to the zone where the chemical reaction occurs in order to determine if the diffusion step or the reaction step is the rate-controlling one. However, in the biological sciences it is more common to look at only the reaction step when considering metabolic reactions, thus overlooking the possibility that diffusion might be the rate-limiting factor. In addition, people involved in studying the metabolic conversion of various reactants to products also very frequently assume that the reactions are first order and calculate their data using this assumption, which may be quite valid. However, since first-order kinetics and diffusion-controlled reactions result in mathematical equations having the same concentration dependency, it is possible that mass transfer control of the metabolic reactions could also be read into their results.

In order to determine if diffusion is the controlling mechanism in a chemical reaction it is usual to do one of three types of experiments: (1) vary the temperature and examine the magnitude of the activation energy, (2) vary the distance for mass transport and see if that affects the reaction rate, and (3) vary the diffusivity and look at that effect on the reaction rate, or combinations of these three experiments. However, when the reactions to be studied occur in a living animal, it is not possible to do experiments (1) and (2). The usual mammalian temperature is 37°C and is relatively constant, and the distances of reaction obviously cannot be varied. Thus, it would appear that variations in the diffusivity provide the best experiment for this purpose.

Let us now examine a simplified reaction scheme for glucose metabolism in the body shown in Figure 1. Various intermediates of the reaction sequence are left out of this diagram, and the complete mechanism can be found in any standard biochemistry test; however, the more important features are shown. Pyruvate and lactate intermediates are frequently measured as an indication of metabolism. For example, if there is an oxygen

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