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A Study of Perfectly Mixed Photochemical Reactors

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The performance of a perfectly mixed photochemical reactor has been analyzed for systems having low light absorption coefficients. The analysis has been tested by an experimental study of the decomposition of hexachloroplatinic acid in dilute aqueous solution. Results tend to verify the analysis, but indicate the need for additional experimental work.

Although photochemistry continues to develop as an important branch of theoretical chemistry, industrial applications of photochemical processes have been notably few. Since photochemical reactions sometimes offer distinct advantages over thermal reactions, this situation is perhaps surprising. One of the contributing factors may be the lack of quantitative procedures for the design and scale-up of suitable reactors. This is a complex problem, more difficult than the usual chemical reactor problem, which represents a challenging area for chemical engineering research and development. Unfortunately, the problems of design and analysis of photochemical reactors have received only sporadic attention in the chemical engineering literature during the last fifteen to twenty years. In view of this situation, it was decided to initiate a research program into photochemical reactor design and scale-up. The present paper presents the results of one such investigation into the behavior of perfectly mixed reactors.

PREVIOUS WORK

Previously reported studies of photochemical reactor design have all dealt essentially with continuous flow reactors of the tubular type. The first investigation in recent years was reported by Baginski in 1951 (*1*). He studied the reaction of hydrogen sulfide and n-1 octene in the liquid phase, using a tubular reactor irradiated from the

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outside. The reactor and a tubular ultraviolet light source were located at the foci of an ellipsoidal cylindrical reflector. Although no broad generalizations were obtained in this work, it is noteworthy since the type of reactor configuration used has served as a model for several subsequent investigations. Sometime later, Gaertner and Kent (*2*) studied the ultraviolet photolysis of aqueous uranyl oxylate solution in a similar reactor in which the reactor cross section was a circular annulus. Because of the low conversions achieved and the fact that this reaction is zero order with respect to light intensity, their results cannot be safely generalized. In 1962 Huff and Walker (*3*) studied the gas phase photochlorination of chloroform in an apparatus essentially the same as that used by Baginski. Their analysis was primarily concerned with the chemical kinetics of the reaction rather than the reactor engineering problems. About the same time Schechter and Wissler (*4*) analyzed the differential equations that describe a tubular, laminar flow photochemical reactor, assuming reaction rate to be first order with respect to concentration and light intensity. Foraboschi (*5*) also analyzed such a system by dimensional analysis. Both of these treatments are of limited value because of the very specific type of behavior considered. Recently, Dimon (*6*) attempted a more general analysis and paved the way for a subsequent experimental study by Dolan (*7*) aimed at the determination of important parameters in photochemical flow reactors. Using a reactor of the Baginski type, Dolan studied the hydrolysis of chloroplatinic acid and was able to achieve a good correlation of data obtained over a limited range of conditions. In addition to these research publications, two interesting survey articles have appeared in the recent past. The first by Doede and Walker (*8*) in 1955 covers most of the work done to that time. The second article by Marcus, Kent, and Schenck (*9*) summarizes later results.

These papers constitute the main literature pertinent to the design of photochemical reactors. None of these studies deals with the relatively simple case of perfectly mixed photochemical reactors. Since these are apt to be of some industrial significance and are readily amenable to analysis, it was felt worthwhile to begin such an investigation. Therefore, the present work was undertaken. The results to be shown below are applicable to systems involving well-mixed fluids having low absorption coefficients, such as gaseous or very dilute liquid systems.

THEORETICAL DEVELOPMENT

The analysis of a photochemical reactor involves two important aspects that must be combined with the usual material balance considerations for the particular reactor type of interest. These are:

1. The specification of the light intensity profile throughout the reactor. This may be considered essentially as the result of a balance on the electromagnetic radiation, which is used to initiate and promote the chemical reaction.

2. The description of the kinetics of the reaction in question. Typical relationships are different from the type one would encounter in "normal" chemical reactor analysis.

Let us now consider these features in somewhat more detail. The intensity of the electromagnetic radiation will be diminished as the light passes through the reacting medium. It is this light absorption which is responsible for the chemical reaction that follows; no photochemical reaction can occur without some light absorption. Thus, an intensity profile will always exist. The light intensity may be treated as a vector having the direction of the light rays. Considering monochromatic light at this stage, the conservation equation for the light is given by the vector form of Lambert's law.

$$\operatorname{div} \vec{I} = -\mu\,|\vec{I}| \tag{1}$$

The equation states that the rate of absorption of light energy per unit volume of absorbing medium is proportional to the magnitude of the rate at which energy impinges on the volume element. When applied to any specific geometry, this equation will yield the appropriate light intensity profile. As defined here, the intensity vector has the dimensions of a flux; that is, it represents the rate at which light energy falls on a unit area.

If light of several wavelengths is involved, a similar balance may be written for each wavelength. In general, the coefficient μ will be different for each wavelength. Rather than introduce this complexity here, the following analysis will be restricted to the case of monochromatic light.

The reactor of interest in this work consists of the annular space between two concentric circular cylinders, as shown in Figure 1. The reacting fluid is contained in this space and is irradiated by a light source mounted along the axis of the cylinders. It is assumed that the fluid is well mixed by some means; hence, all properties which depend upon concentration will be constant throughout the reactor vessel. This applies in particular to the absorption coefficient μ. This assumption of perfect mixing leads to a considerable simplification in the analysis of the light intensity profile not permissible for other reactor types.

It will be further assumed that the light source emits rays which are purely radial. For this case, the differential equation for light intensity becomes

$$\frac{1}{r}\frac{d}{dr}(r\,I_r) = -\mu\,I_r \tag{2}$$

This equation may be integrated from the inner radius of the annulus r_o where the light intensity is I_{r_o}, to any point within the reactor. Thus

$$I_r = \frac{r_o I_{r_o}}{r}\,e^{-\mu(r-r_o)} \tag{3}$$

Equation (3) represents the light intensity profile for such a reactor.

Let us now consider the second facet of the reactor analysis. Although there are alternate ways to express the

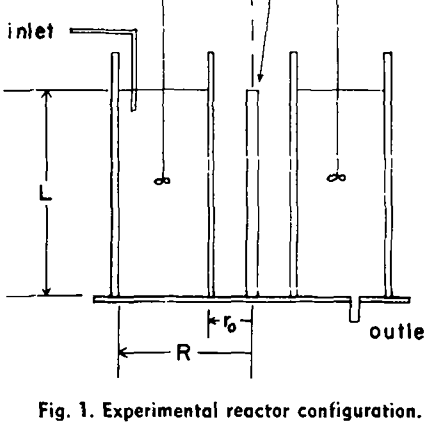

Fig. 1. Experimental reactor configuration.

rate of a photochemical reaction, one very general form is shown in Equation (4):

$$dP = \mu \, |\vec{I}| \, \varphi \, dV \tag{4}$$

In this expression, μ and φ are normally functions of the wavelength of the incident light. Furthermore, they normally depend strongly on concentration. Usually μ is taken to be a linear function of concentration, although this simplification is not always justified. The quantum efficiency φ is apt to be a somewhat more involved function of concentration, not suitably expressed by any simple form. It may also depend on the actual light intensity. Although one might seek to identify these functions in order to give the rate expression an explicit concentration dependency, nothing is gained by this procedure. Rather, it is just as appropriate to keep μ and φ in the expression as implicit (nonlinear) functions of concentration.

The above is not intended to infer that expressions based on a mechanistic approach to the reaction rate process have no place in photochemical reactor analysis. As always, a valid mechanism will frequently lead to very useful results not discernible from an empirically based rate equation. However, in view of the complex dependencies that may exist in photochemical reactions, the search for accurate mechanisms is likely to be a significant research task in itself. This should not delay reactor analysis, which may be equally well made using empirical rate data.

Using the above relationship for the rate of reaction per unit volume, one can find an equation for the overall rate of reaction occurring within the stirred reactor at any given instant by integrating Equation (4) over the entire reactor volume. Thus, assuming a light source of strength $2\pi \, r_o \, I_{r_o}$ (units of energy per unit time per unit length) located at the inner radius, the total rate of reaction within the vessel is given as in Equation (5):

$$P = \int_o^L \int_{r_o}^R \mu \, \varphi \, I_r \, 2\pi \, r dr \, dz$$

or

$$P = \varphi \, [2\pi \, L \, r_o \, I_{r_o}] \, \{1 - e^{-\mu(R-r_o)}\} \tag{5}$$

In Equation (5) and in subsequent discussion, it will be assumed that φ is independent of I.

This equation has three terms representing the quantum efficiency, the total incident energy, and a nondimensional term for energy absorption. The second term consists of two items: the intensity of the light source and the area upon which this light is incident. The absorption term is of the form $\{1 - e^{-\mu l}\}$. Application of the same approach to stirred reactors of different configurations will lead to equations of the same type, with appropriate modifications of the area and pathlength terms in each case (*10*). Because of its exponential nature, the absorption term may be quite sensitive to changes in μ and l. Thus, for a medium which absorbs light strongly, the effective pathlength and associated reactor volume may be quite small, whereas a weakly absorbing medium may have rather long effective pathlengths and large reactor volumes. Analyses of the behavior of this absorption term for any specific system will quickly indicate the appropriate reactor dimensions for that case.

In the derivation of Equation (5), no specific mention has been made of whether the reactor is a batch-stirred reactor or a continuous flow reactor. In general, the result will apply equally well to either case. The reaction rate for the vessel depends only on a given light intensity profile and quantum efficiency resulting from a given concentration in the vessel. Whether this concentration is a steady state value, as would be achieved in a continuous flow-stirred tank reactor, or an instantaneous value that might be achieved at some point during the operation of a batch reactor, makes no difference in the analysis that has been presented thus far.

Although this analysis has been based on the use of a monochromatic light source, it may be easily extended to cover problems involving polychromatic sources by linear combination of the contribution due to each wavelength band. Alternatively, one might hope to apply the monochromatic analysis directly by proper selection of average wavelength-dependent parameters. Although less rigorous, such an approach would be most useful if found to be satisfactory. This has been the emphasis in the present study. With this in mind, Equation (5) could be used for the prediction of reactor performance and reactor design if all the parameters were known. Alternatively, it could be used in the correlation of experimental data and calculation of scale-up factors for such data. It was felt that an experimental verification of this result would be in order, and the work described below was therefore undertaken.

EXPERIMENTAL

In order to carry out a significant test of Equation (5), it is necessary to have an appropriate reactor and reacting system. The reaction chosen was the decomposition of chloroplatinic acid in dilute aqueous solution. This reaction is promoted by ultraviolet light over a wide range of UV wavelengths and takes place at room temperatures. Furthermore, the reaction results in the formation of hydrochloric acid, making possible analysis by electrical conductivity. The pioneering work on this reaction was done by Boll (*11*) during the early part of this century. He determined that in the presence of ultraviolet light, 10^{-4} molar chloroplatinic acid will decompose as follows

$$\begin{aligned} 2\,H_2PtCl_6 + 11\,H_2O \xrightarrow{UV} {} & 11\,HCl + \\ & H_2Pt(OH)_6 \cdot H_2Pt(OH)_5Cl \end{aligned} \tag{6}$$

with a slower secondary reaction

$$\begin{aligned} H_2Pt(OH)_6 \cdot H_2Pt(OH)_5Cl + H_2O \xrightarrow{UV} {} & HCl \\ & + 2\,H_2Pt(OH)_6 \downarrow \end{aligned} \tag{7}$$

The overall stoichiometry to complete reaction is given by Equation (8):

$$H_2PtCl_6 + 6\,H_2O \xrightarrow{UV} 6\,HCl + H_2Pt(OH)_6 \downarrow \tag{8}$$

There are several intermediate steps in this reaction resulting in a stagewise elimination of chlorine from the original reactant to a final chlorine-free precipitate. Boll studied the kinetics of the reaction and found that the local rate depended on reactant concentration to the second power and light intensity to the first power. In addition, he reported extinction coefficients and quantum efficiencies that depended on solution concentration and light wavelength.

This reaction system was ideal for the present study because of these features. It is convenient experimentally because of the very dilute solutions that may be used and the ease with which reaction may be followed. It is sufficiently complex and dependent on reaction conditions to provide a thorough test of the previous analysis for reactor scale-up.

From the results of previous experiments with hexachloroplatinic acid, it is known that the absorption coefficient is rather low at wavelengths in the near ultraviolet range. This is a desirable feature for experimental studies in that it permits the use of reasonably sized reactors with no danger of complete light absorption. Therefore, it was decided to study this reaction with an ultraviolet lamp having its peak radiation in the near ultraviolet range, approximately 3,600 Å. An additional advantage of operating in this wavelength range is that absorption of the ultraviolet radiation by the transparent reactor walls is minimized.

The reactor used was of the configuration presented in Figure 1. As shown, this consists of a circular annular reaction zone having a slender light source located at the center line. The reactor itself was constructed of acrylic plastic. The inner and outer walls were made of tubing that was cemented to a circular base plate. Inlet and outlet lines were provided in order to permit continuous flow as well as a batch operation. The light source used was a General Electric Model F8T5/BL, a nominal 8-w. black light bulb having an output of 890 mw. in the near ultraviolet region. More complete data on this lamp are available from the manufacturer.

Two such reactor vessels were constructed and used in these experiments. Both had the same internal cylinder diameter, but differed in the diameter of the outer vessel. Pertinent dimensions are shown in Table 1.

The remaining equipment consisted of flow- and dip-type conductivity cells for solution analysis and a feed flow control and measuring system for continuous operation. Further details of the apparatus are presented elsewhere (*10*).

The reactor was provided with two polyethylene stirring rods to assure food mixing. It was decided not to locate any baffles within the reaction vessel in order to minimize obstructions in the light path. Since this raised questions about the adequacy of mixing within the reactor, a series of mixing tests was carried out. The vessel was initially filled with a dilute solution of potassium chloride (KCl), and washed out with a continuous stream of distilled water at a constant flow rate. Assuming perfect mixing, the outlet concentration (and concentration within the reactor) should decrease exponentially with time. Solution conductivity measurements were made as a function of time and the results clearly indicated exponential decay of vessel concentration. Such tests were performed at two different flow rates for the large reactor vessel and one high flow rate for the smaller vessel, all within the range of interest for this work. In all cases the results indicated perfect mixing, with average contact times within 2% of values calculated from vessel volume and the input flow rate.

Feed solution used in these experiments was 10^{-4} molar chloroplatinic acid in deionized water. Such solutions were made by accurate dilution of 10^{-2} molar stock solution of reagent grade chloroplatinic acid and water. The stock solution was prepared and allowed to age for approximately one week before use. This was found to be necessary in order to standardize the initial conductivity of the reacting solution. It was found that freshly prepared 10^{-2} molar solution tended to increase in conductivity for a period of perhaps a day, after which constant conductivity would be obtained. This behavior has been noted previously (*6, 7*) and, based on conductivity measurements, is thought to be due to an initial dark reaction in which two atoms of chlorine are split from the hexachloroplatinic acid to produce a tetrachloroplatinic acid molecule. This, in fact, is probably the actual molecule undergoing photolysis in the experiments. It should be noted that the reaction could be started or stopped at will by turning the lamp on or off. Thus, no significant dark reaction is involved. No precipitation was apparent in experiments not carried to complete reaction.

Batch reactions were carried out with this equipment as follows. The outlet tube was closed by a pinch clamp and the vessel filled with reactant. The stirring motors were then started and the dip cell was positioned in the vessel to record solution conductivity. After initial conductivity was measured, the lamp and a timer were started simultaneously. Thereafter, the time was noted as the conductivity changed by predetermined increments. Temperature in the vessel was noted periodically and appropriate adjustments were made on the temperature compensator of the conductivity bridge. Flow runs were made in this equipment by first filling the vessel and reacting to some desired conductivity, as in the batch reactions. The inlet and outlet flows were then started, and carefully adjusted to be equal. The conductivity of the solution in the vessel was measured either by using the dip cell or a flow cell in the outlet stream. This conductivity was checked at various time intervals until steady state values were achieved. All experiments were carried out in the absence of room lighting in order to avoid reaction from this source. Only sufficient light was used to illuminate the conductivity bridge and timer. Some problems were encountered with this equipment because of the large volume of the reactor. This requires a considerable throughput volume before steady state conditions may in general be achieved, and hence the equipment was not very flexible for the continuous flow runs. However, it was possible to obtain several interesting experimental observations which will be discussed below.

Table 1. Reactor Dimensions

Dimension	Small reactor	Large reactor
Inner cylinder, i.d.	2 in.	2 in.
Inner cylinder, o.d.	2½ in.	2½ in.
Outer cylinder, i.d.	6¼ in.	9¾ in.
Effective pathlength ($R - r_o$)	1⅞ in.	3⅝ in.
Operating liquid level, L	10½ in.	10½ in.
Operating volume	4.43 l.	11.98 l.

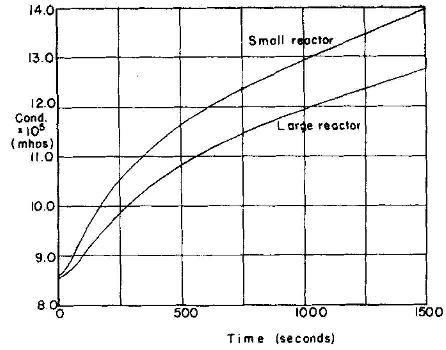

Fig. 2. Typical batch reaction data.

RESULTS

Several batch and flow runs were made with this equipment. The objective of the batch runs was to compare the ratio of the reaction rates observed in the large and small reactors to that predicted by Equation (5). Figure 2 shows typical batch experimental data for the two reactors. These data show the solution conductivity as a function of time. The conductivity of the starting solutions was approximately 8.6 × 10^{-5} mhos. This compares very favorably with the conductivity of 2 × 10^{-4} molar hydrochloric acid, which is 8.49 × 10^{-5} mhos. (*12*), and it verifies the previously mentioned assumption that the initial reactant was tetrachloroplatinic acid rather than the hexachloroplatinic acid from which the reactant solutions were prepared. Although Figure 2 shows reaction times up to 1,500 seconds, actual experiments were continued to 4,000 or 5,000 seconds. However, the data do not indicate any unusual trends at these longer times. Reproducibility in these experiments was excellent, as shown in Figure 3. Complete data are presented elsewhere (*10*).

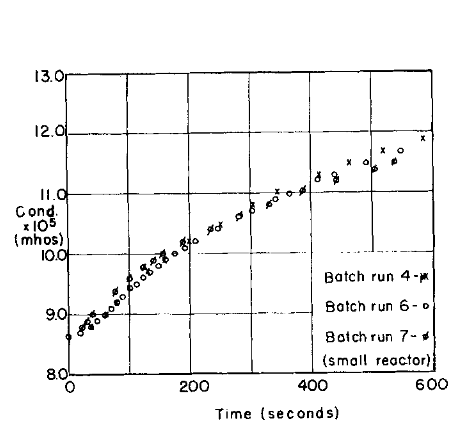

Fig. 3. Reproducibility of batch data.

In several batch experiments the reaction was allowed to continue to completion. In one such run it was determined that the final conductivity was 25.3×10^{-5} mhos. For comparison, the conductivity of 6×10^{-4} molar hydrochloric acid is 25.4×10^{-5} mhos. This indicates that the final reaction was the complete elimination of all six chlorine atoms from the original molecule to produce 6×10^{-4} molar hydrochloric acid, as in Equation (8). Furthermore, in this experiment a small precipitate was observed, which is apparently the platinum hydroxide mentioned earlier.

An interesting feature of the batch curves is the initial portion, which exhibits a low rate and an inflection point very near the beginning of the experiment. It is not known definitely whether this is characteristic of the reaction or the equipment, although the latter is suspected. It is quite likely that the lamp output does not reach its steady state value until some time after the current is turned on and a steady operating temperature is reached. (The lamp operating temperature was found to be approximately 50°C. Therefore, no particular cooling requirements were necessary, and there was no difficulty in maintaining the temperature of the reacting liquid within the reactor constant during the experiments, subject only to small fluctuations in room temperature.)

The batch curves were used to test the previously discussed scale-up equation. In order to do this it was necessary to calculate the reaction rate at various times in both vessels. Since the reaction rate is directly proportional to the slope of the conductivity-time curve, rates were determined at various conductivities (conversions) by approximating the local derivatives by difference quotients.

Reaction rates for both vessels were thus determined for conductivities ranging from 9.0×10^{-5} to 16.0×10^{-5} mhos. in increments of 0.5. The resulting ratios of production of hydrochloric acid are compared in Figure 4. High points on this figure correspond to low conversions. As shown, these data are well fit by a straight line through the origin with a slope of 1.8. Thus, the reaction rate in the larger reactor is 1.8 times that in the smaller vessel over this range.

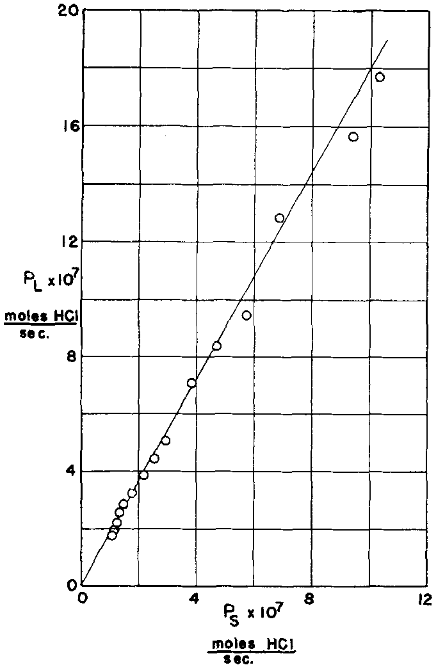

Fig. 4. Batch rates.

The predicted value of this ratio may be found by applying Equation (5) to both vessels. Values of the pathlengths in both cases and the extinction coefficient are required for this purpose. Since the ratios are calculated at the same conversion (composition) and the analysis assumes monochromatic radiation, the extinction coefficient and the quantum efficiency would be expected to be the same in both cases. (More general treatments involving polychromatic radiation would have to account for changes in these parameters with spectral distribution changes produced by light absorption within the reactors.) Thus, prediction of the relative rates reduces to the calculation shown below

$$\frac{P_L}{P_S} = \frac{1 - e^{-\mu(R_L - r_o)}}{1 - e^{-\mu(R_S - r_o)}} \tag{9}$$

The pathlengths are known exactly from the dimensions of the two reactors. Estimation of the absorption coefficient is a more complicated problem. For a monochromatic light source the coefficient could be evaluated for the appropriate concentration in the vessel. However, the light source used operates over a range of wavelengths, with a prominent peak at approximately 3,600 to 3,700 Å, as noted earlier. Hence, it is necessary to determine a representative average absorption coefficient. Following previous workers (*2*, *6*), μ is averaged over wavelength with light intensity as a weighting factor. For this purpose it is first necessary to find the light intensity within the reactor. The light emitted by the lamp must first pass through the inner wall of the reactor, which does absorb a small fraction of the ultraviolet light being used. This was measured by examining the UV absorption of the acrylic tubing in a spectrophotometer. Over the range of interest it was found that the tubing transmits approximately 75% of the incident radiation. It is also necessary to determine the absorption coefficient of the solution as a function of concentration. Several measurements were therefore made with the spectrophotometer and solutions of various concentrations. These data (*10*) show that there is a significant change in transmission as a function of concentration and wavelength. Over the near ultraviolet range the reactant solution transmits more light than the products. At lower wavelengths the reverse is true. In particular, the absorption coefficient of the reactant is approximately 0.1 cm.$^{-1}$ or less in the wavelength range of the light source.

With the above data, an average μ value can be calculated in the following manner. Manufacturer's data for the light source are examined to find the lamp output as a function of wavelength. Actual radiation incident in the solution is determined from the lamp output corrected for the transmission of the inner reactor cylinder. Values of μ for the solution at a particular concentration and as a function of the wavelength are then averaged over wavelength with the calculated incident light intensity as a weighting factor. This average is performed as a summation over a number of narrow wavelength bands (rather than as an integral average) for convenience.

The result of this calculation at a conductivity of 12×10^{-5} mhos. was a value of μ_{avg} equal to 0.224 in.$^{-1}$. When this value is inserted into Equation (9), the predicted ratio of the reactant rates is found to be 1.62. This calculation of μ_{avg} is subject to some error because of imperfect information about the lamp output. The data used represent average values which may differ significantly from the particular lamp used in this investigation. Furthermore, ageing of the lamp is likely to produce some variation in output. Fortunately, however, large changes in the value of μ do not affect this reaction rate ratio strongly over the present range of conditions. For example, a value of μ equal to one-half the previous value, that is, 0.112 in.$^{-1}$, leads to a ratio of rates equal to 1.76. Thus, the calculation is relatively insensitive to small changes in μ.

The predicted ratio of 1.62 is approximately 10% lower than the average experimental value of 1.8 found in this work. It is felt that a 10% agreement at this stage is quite acceptable and that these results tend to verify the use of Equation (5) for scale-up of such reactors. Closer agreement would certainly be desirable and further study to that end should be undertaken.

Another fact that bears on this agreement is the assumption of radial radiation on which the predictive equations were based. No precautions to insure this effect were actually taken in setting up the experimental apparatus other than the use of a slender light source (large L/D). It is likely that some nonradial or skew radiation emanates from the light source and passes through the reacting vessels. This can be accounted for by a more detailed analysis, which, however, was not felt appropriate at the present stage of this work. In view of the neglect of this fact, it is all the more startling that the data agree with the predictive equation as well as they do.

In addition to the batch runs, some flow experiments were also carried out with this equipment as a further test of the analysis. Although both reactors were used for this purpose, the only reliable data were obtained with the smaller one. Steady state operation was achieved at several conversions and the corresponding reaction rates throughout the entire vessel were calculated, using material balance relationships for the continuous stirred tank reactor. These values are compared with batch reaction rates at the same concentrations in Table 2.

The data show that as extent of conversion (conductivity) of the solution increases, the ratio of reaction rate in the flow reactor to reaction rate in the batch reactor increases from about 1 to 1.3. Presumably, this ratio would continue to increase as concentration and conversion increase. This might be interpreted to disagree with the usual expectation that reaction rate in a continuous stirred tank reactor should be equal to the instantaneous reaction rate in a batch reactor operating at the same concentration. However, such behavior is strictly true only for the case of single reactions. As indicated previously, the reaction being studied here probably takes place by a number of sequential steps, each of which involves the removal of another atom of chlorine from the chloroplatinic acid molecule. Thus, starting with the tetrachloroplatinic acid, there are four such series reactions that may occur. The rates of these reactions are apt to be somewhat different, and this fact is no doubt responsible for the difference observed in Table 2. (This type of behavior can be easily demonstrated by considering, for example, a series of two first-order reactions.) The same trend was observed in the large reactor. However, since these data were relatively imprecise, they are not presented here.

Table 2. Steady State and Batch Production Rates in the Small Reactor

Feed flow rate, $\frac{\text{liters}}{\text{sec.}} \times 10^8$	Conductivity, mhos $\times 10^5$	Hydrochloric acid production rate, $\frac{\text{moles hydrochloric acid}}{\text{sec.}} \times 10^7$ Flow	Batch
13.53	10.22	5.46	5.43
7.42	10.99	4.29	3.97
5.39	11.78	3.97	3.22
1.73	13.90	2.19	2.00
1.17	15.2	1.67	1.27

In summary, it is felt that the experimental data presented here tend to verify the simple descriptive equation for the type of reactor being considered, at least for the purposes of radial scale-up. No attempt has been made to predict the actual reaction rate in a particular vessel. This would have required calculation of the quantum efficiency, a more complicated function of concentration and radiation wavelength. Although this type of calculation would certainly be desirable to give a thorough test to the theory, the comparative test made here does indicate the utility of the analysis for scale-up consideration. Since any development program is certain to involve some experimental measurements, scale-up is perhaps a more immediate and important problem to the design engineer than the a priori calculation of reaction rate would be. The same type of approach used here should also be useful in the design and scale-up of reactors of other geometrical configurations.

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NOTATION

$\vec{I}$ = light intensity $\frac{\text{energy}}{(\text{area})\,(\text{time})}$
l = pathlength, length
L = reactor height, length
P = production (reaction) rate, moles/(time)
r = radial coordinates, length
r_o = inner radius of reactor, length
R = outer radius of reactor, length
V = reactor volume, (length)^3
μ = extinction coefficient, length^{-1}
φ = quantum efficiency, moles reactor per mole of quanta absorbed

Subscripts

L = refers to large reactor
S = refers to small reactor

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