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Photochlorination in a Tubular Reactor

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A method of describing the behavior of a single-phase, photochemical reaction in a tubular flow reactor is given. A simplified form of the equations is applied to experimental data for the chlorination of propane.

The results indicate that the reaction rate is second order in chlorine concentration and first order in light intensity at the wall. Independent experimental actinometer measurements permit the determination of absolute values of the kinetic constants. Such data are rarely available for photochemical reactions. Filter solutions flowing through a jacket around the reactor is shown to be a practical method for studying the effects of light intensity, as well as for cooling the reactor. The optical efficiency of the reactor lamp system was 11%.

The design of photochemical reactors presents a challenging problem because of the interaction of chemical and physical processes. Variations in light intensity and absorption with position can affect the rate of reaction, cause concentration gradients, and induce diffusion. Further, many photochemical reactions are best described by chain mechanisms. For these systems heterogeneous (wall) as well as homogeneous termination steps can occur. If the heterogeneous reaction is significant, diffusion to the reactor wall becomes important. Some of these complications may be eliminated in a stirred-tank (completely mixed) reactor, but this form is seldom plausible for gas phase reactions and may not be advantageous for liquid systems.

The first purpose of this paper is to develop equations for describing the behavior of tubular flow reactors for chain kinetics. The results are complicated, but it is shown that laboratory measurements can be made at conditions which simplify the equations. These latter results are then used to analyze data obtained in a laminar flow reactor for the chlorination of propane at 30°C. and at atmospheric pressure.

The literature includes descriptive reports (*1, 8, 13, 19*) on the scientific and commercial aspects of photoreactors and there are also a few papers on quantitative design. The first of these (*3*) considers the liquid phase reaction between hydrogen sulfide and *n*-octene–1. Backmixing in the flow reactor thwarted a complete analysis of the data. Gaertner and Kent (*11*) studied the photolysis of aqueous uranyl oxalate in an annular reactor. The reaction was of zero order in concentrations, so general conclusions about reactor performance were not possible. Nevertheless, the work confirmed the use of the uranyl sulfate reaction for measurement of light intensity. Schechter and Wissler (*24*) studied theoretically the performance of a laminar flow reactor. They included the effects of diffusion, convection, and light attenuation but used simple kinetics (nonchain reaction) and assumed a constant attenuation coefficient. A valuable contribution of their paper is the sound treatment of the boundary condition at the center of the tube.

Huff and Walker (*17*) reported on the photochlorination of chloroform in a tubular reactor. Their interpretation, while neglecting diffusion and flow effects, apparently represents the first contribution to reactor design for a chain reaction. There are two contributions of Dranoff and colleagues which attack the design problem for simple, nonchain kinetics. The first (*15*) includes equations for a completely mixed reactor with application to data on the photodecomposition of chloroplatinic acid. The second (*9*) considers the more important tubular flow reactor with the use of dimensional analysis. For simple reactions this approach can be useful for the scale-up of some parameters in the system. For chain reactions equations are obtained which are not practical for analysis and are probably not practical for scaling up as well. While these initial contributions are valuable, more work needs to be done both experimentally and theoretically in order to be able to analyze and to predict reactor behavior, particularly for chain reactions.

The chlorination of propane was chosen for the experimental measurements because the evidence (*21* to *23*, *25*,

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26) is compelling that a chain mechanism is involved, and operating conditions can be chosen so that the only significant product is monochloropropane. Kinetic analyses and data for photochlorination of hydrocarbons are summarized in a recent review (*7*) and information specifically for propane is also available (*2, 16, 28*).

TUBULAR FLOW REACTOR ANALYSIS

Consider the continuous flow of a homogeneous reacting fluid through a cylindrical tube with uniform radial light, without end effects, and at steady state. This situation is depicted in Figure 1, where the arrows indicate the rays of light. In general the behavior of the reactor is described by four conservation equations. momentum, mass, thermal energy, and radiation energy. The momentum and thermal energy equations establish the velocity and temperature profiles and are the same for photoreactors as for conventional reactors. Hence they need not be repeated here.

If longitudinal dispersion is neglected, the mass balance for species *i* may be written

$$-\frac{\partial(v_z C_i)}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}\left(D_{ei} r \frac{\partial C_i}{\partial r}\right) + \Omega_{i,\lambda} = 0 \qquad (1)$$

where D_{ei} is the effective diffusivity of the *i* species and Ω_i is its rate of production. Rigorously, there will be a separate equation for each wavelength λ as well as for each species, since the kinetic constants which establish Ω_i may be a function of λ. Photoreactions occur as a result of absorption of light, and this absorption reduces the intensity of rediation available to the subsequent element of fluid in the light path. Hence, to predict the reactor operation, it is necessary to know the distribution of the intensity throughout the system. According to Lambert's law, the absorption is equal to the product of the intensity and the attenuation coefficient μ of the fluid. From Figure 1 it is noted that at any point in the reactor there is direct radiation I_{dir} from the outside and opposite radiation I_{opp} from the center. By using Lambert's law for this cylindrical system with purely radial light, the radiation energy equation is

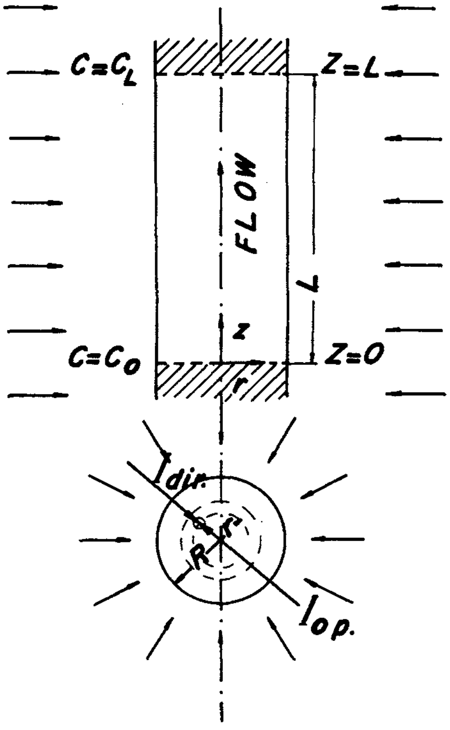

Fig. 1. Photoreactor geometry.

$$\frac{1}{r}\frac{\partial}{\partial r}(r I_{r,\lambda}) = \pm \mu_\lambda I_{r\lambda}, \qquad (2)$$

where I_r is the intensity of radiation at radial position *r*. Since μ and *I* are functions of wavelength, there is, in general, a separate equation for each λ.

The following assumptions are now made: (1) constant temperature and pressure; (2) constant physical properties; (3) no dark reaction; (4) effects of different wavelengths are additive; (5) mechanisms and kinetic constants are the same for different wavelengths; (6) no effects of light other than catalyzing the reaction; (7) laminar flow.

Some of these (4 and 5) might be evaluated experimentally by using monochromatic light sources or filter solutions. This point is discussed again in the treatment of the data. It is possible to apply corrections to satisfy assumption 3 and the importance of 5 can be reduced by avoiding large variations in spectral light distribution. Note that 5 eliminates the need for a separate Equation (1) for each wavelength. Many photochemical reactions have large heats of reaction so that significant temperature changes, both radially and axially, will exist in a tubular reactor. Assumption 1, then, would not be valid and scale-up of laboratory data will require evaluating these gradients by using the thermal energy conservation equation. A moderating factor is the low activation energy normally observed for photoreactions. The laminar flow restriction 7 means that the velocity is independent of *z*; it is given by the expression:

$$v_z = 2\,\bar{v}_z\left[1 - \left(\frac{r}{R}\right)^2\right] \qquad (3)$$

Also D_{ei} in Equation (1) becomes the molecular diffusivity for the species.

Suppose the concentration of each species at the reactor inlet is $(C_i)_o$. Consider, for the moment, that monochromatic light is used. Then the boundary conditions for Equations (1) and (2) are

at

$$z = 0, \quad C_i = C_{i_o} \qquad (4)$$

at

$$r = R, \quad I_r = I_w \qquad (5)$$

Also at $r = R$ there are two restrictions on the concentrations:

1. For species without wall reaction:

$$\frac{\partial C_i}{\partial r} = 0 \qquad (6)$$

2. For species with wall reaction:

$$\frac{\partial C_i}{\partial r} = -\frac{(\Omega_i)_w}{D_i} \qquad (7)$$

The boundary condition at $r = 0$ is obtained, following Schechter and Wissler (*24*), by making a mass balance on an element around the point $r = 0$, taking the limit as the radius of the element approaches zero. This gives

$$\left(\frac{\partial C_i}{\partial r}\right)_{r=0} = \lim_{r\to 0} \pm \frac{1}{rD_i}\int_0^r r'\,\Omega_i\,dr' \qquad (8)$$

Equations (1) to (8) in principle can be used to determine the concentrations of each species at the exit of the reactor and from these results the conversions can be obtained. To use the equations μ_λ and Ω_i must be established.

For most solutions the attenuation coefficient is an approximate linear function of the concentrations of the absorbing substance

$$\mu_\lambda = \alpha_\lambda C_i \tag{9}$$

where the molal absorptivity α_λ is a function only of wavelength. If more than one absorbing substance is present, the attenuation coefficient for the mixture is

$$\mu_{m,\lambda} = \sum_j \mu_{j,\lambda}\, x_j \tag{10}$$

Absorptivities are accurately known for some substances, for example chlorine.

The net rates Ω_i for each species depend upon the reaction mechanism. The steps involved in chain reactions may be illustrated with the chlorination of propane. Considering only a primary product, propyl chloride, the sequence believed to represent the process is

$$Cl_2 + h\nu \xrightarrow{k_1} 2\,Cl^* \quad \text{activation}$$

$$\left.\begin{array}{l} Cl^* + PrH \underset{k'_2}{\overset{k_2}{\rightleftarrows}} Pr^* + HCl \\[2ex] Pr^* + Cl_2 \underset{k'_3}{\overset{k_3}{\rightleftarrows}} Pr\,Cl + Cl^* \end{array}\right\}\text{propagation}$$

$$\left.\begin{array}{l} Pr^* \xrightarrow{k_4} \text{end} \\[2ex] Cl^* \xrightarrow{k_5} \tfrac{1}{2}\,Cl_2 \\[2ex] Cl^* + Pr^* \xrightarrow{k_6} PrCl \end{array}\right\}\begin{array}{l}\text{homogeneous}\\ \text{termination}\end{array}$$

$$\left.\begin{array}{l} Cl^* + W \xrightarrow{kw_1} \tfrac{1}{2}\,Cl_2 \\ Pr^* + W \xrightarrow{kw_2} \text{end} \end{array}\right\}\begin{array}{l}\text{heterogeneous (wall)}\\ \text{termination}\end{array}$$

The sum of these steps is the overall reaction

$$PrH + Cl_2 \rightarrow PrCl + HCl \tag{11}$$

To obtain practical expressions for Ω_i, it is necessary to consider various limiting cases. For example, it may be assumed that all reactions are irreversible and that the rate is controlled by one or more termination steps, either homogeneous or heterogeneous, or both. Application of the conservation of mass principle to each group of suppositions leads to a specific set of equations for Ω_i. The relative importance of any set can depend upon the reactant concentrations, presence of diluents, and characteristics of the wall surface.

The limitation of monochromatic light can be removed either: by using in Equation (2) an average value for μ and an average I from the polychromatic light source, or by summing Equation (2) over the wavelength intervals catalyzing the reaction.

SIMPLIFICATION OF EQUATIONS

The chief difficulties in utilizing Equations (1) to (8) for a chain reaction system are: (1) uncertainties in estimating D_i for the atomic and free radical species, (2) the complicated equations for Ω_i involving many kinetic constants, (3) variations in light intensity and kinetic equations due to wall deposits.

The second difficulty possibly could be lessened by applying stoichiometric relations between reactants and products to reduce the number of species. It should be noted that the conventional stationary state supposition, often applied in batch kinetic studies, is not generally applicable because of diffusion. Even the stoichiometric approach would require the additional assumption that the diffusion rates of the species were related by the stoichiometry of the reactions. The procedure in solving Equations (1) to (8) would be to develop a set of equations for Ω_i, as described in the previous section, and to verify them by comparing the solution with experimental data. However, the problems introduced by difficulties 1 and 3 are unresolved.

All three difficulties could be avoided in the laboratory for many reactions by operating with small conversions and small concentrations of absorbing species. This does not answer the design or scale-up problem directly but would provide a means of evaluating kinetic expressions for Ω_i. The rest of this section presents the simplifications in Equations (1) to (8) which are possible under these restraints; then the simplified equations are applied to the data for the chlorination of propane.

For small conversions the effect of the velocity profile on the conversion is slight (*7a*). Also in a cylindrical photoreactor the intensity increases toward the center of the tube. This tends to balance the effect of a longer residence time near the outer radius of the tube. Furthermore, diffusion will tend to flatten whatever concentration profile exists. Hence, for small conversions a uniform concentration profile and an average velocity may be assumed with little error.

In the wavelength region 2,500 to 5,000 Å. (the range of radiation for the lamp used), the only absorbing substance in the reaction system is chlorine. Hence, Equation (9) can be used to obtain μ for the mixture. However, for low concentrations of chlorine (the maximum value employed experimentally was 0.85 mole %), μ may be assumed zero without affecting significantly the radial distribution of radiation energy. Thus Equations (2) and (5) can be integrated, by assuming an average value of μ over the pertinent wavelength range, to give

$$\frac{I_{\lambda,r}}{I_{w,\lambda}} = \frac{R}{r} \lfloor \exp\left[-\mu_\lambda (R - r)\right] + \exp\left[-\mu_\lambda (R + r)\right] \tag{12}$$

Equation (12) was then used to evaluate $I_{\lambda,r}/I_{w,\lambda}$ as a function of r for two cases: (1) $\mu_\lambda = 0$ and (2) μ_λ evaluated from Equation (9) by taking the maximum value of α in the wavelength range and by using an average value of C_{Cl_2}. The two relationships differed by less than 0.3%. Hence the simplified form of Equation (12) with $\mu = 0$ can be used instead of Equation (2):

$$I_{\lambda,r} = I_{w,\lambda} \frac{2R}{r} \tag{13}$$

A flat concentration profile eliminates radial diffusion. Therefore the stationary state hypothesis for Pr* and Cl* should be applicable for evaluating the reaction rates. By referring to the reaction sequence, suppose that heterogeneous termination steps are negligible and that the homogeneous termination rate constants k_5 and k_6 are also small. Also assume that the propagation reactions are irreversible. Then the rate of production of propyl chloride (or disappearance of chlorine) is given by the relation

$$\Omega_{Pr\,Cl} = -\Omega_{Cl_2} = k_3\,(C_{Pr^*})\,(C_{Cl_2}) \tag{14}$$

Kinetic studies suggest that the rate of the activation step is first order with respect to the light *absorbed* (per unit volume) Ia_λ. Hence the stationary state hypothesis gives

$$\frac{d(C_{Cl^*})}{dz} = 0 = 2k_1\,Ia_\lambda - k_2\,(C_{Cl^*})\,(C_{PrH}) + k_3\,(C_{Pr^*})\,(C_{Cl_2}) \tag{15}$$

$$\frac{d(C_{Pr^*})}{dz} = 0 = k_2\,(C_{Cl^*})\,(C_{PrH}) - k_3\,(C_{Pr^*})\,(C_{Cl_2}) - k_4\,(C_{Pr^*}) \tag{16}$$

Equations (15) and (16) can be used to eliminate (C_{Pr^*}) from Equation (14), giving

$$-\Omega_{Cl_2} = \frac{2k_1k_3}{k_4}\, Ia_\lambda\, (C_{Cl_2}) \qquad (17)$$

The light absorbed is $I_{r,\lambda}\,\mu_\lambda$. Hence, from Equations (9) and (13)

$$Ia_{\lambda,r} = I_{\lambda,r}\mu_\lambda = \frac{2I_{w,\lambda}R}{r}\,\alpha_\lambda\,(C_{Cl_2}) \qquad (18)$$

Combination of Equations (17) and (18) gives the rate of disappearance of chlorine at any radius r:

$$-\Omega_{Cl_2} = \frac{2k_1k_3}{k_4}\,\frac{2I_{w,\lambda}R}{r}\,\alpha_\lambda\,(C_{Cl_2})^2 \qquad (19)$$

The rate varies with r only because Ia varies. Hence, the average rate can be obtained from Equation (19) by integrating radially with respect to area:

$$-\bar{\Omega}_{Cl_2} = \frac{2KI_{w,\lambda}R\,\alpha_\lambda\,(C_{Cl_2})^2 \int_o^R \frac{2\pi r}{r}\,dr}{\pi R^2}$$

$$-\bar{\Omega}_{Cl_2} = 4\,KI_{w,\lambda}\,\alpha_\lambda\,[Cl_2]^2 = k_{o,\lambda}\,(C_{Cl_2})^2 \qquad (20)$$

K is the composite rate constant ($2k_1k_3/k_4$) in units of cc./Einstein, which can be converted for a given wavelength to (cc.) (g.-mole)/erg. The constant $k_{o,\lambda} = 4KI_{w,\lambda}\,\alpha_\lambda$ is a conventional, second-order rate constant in cc./(g.-mole) (sec).

With these kinetic assumptions only one species is involved in the conservation equations. Hence, only one equation of the form of Equation (1) is needed. In view of the described restrictions this may be written as

$$-\bar{v}_z\,\frac{d\bar{C}_{Cl_2}}{d_z} + \bar{\Omega}_{Cl_2} = 0 \qquad (21)$$

Equations (1) to (8) are now replaced by (20) and (21) with boundary condition (4). Since α_λ and $I_{w,\lambda}$ are functions of λ, a summation must be made over the wavelength range which catalyzes the reaction. The validity of Equation (20), and hence the method of analysis, depend upon the degree to which the kinetic approximations represent the actual mechanism. The following sections show that the experimental data agree well with these equations. It may also be noted that empirical expressions of the form rate $= k_o(C_{Cl_2})^2$ are reported in the literature for correlating data on the chlorination of hydrocarbons.

To evaluate the rate constant K it is necessary to determine $I_{w,\lambda}$ and α_λ from independent data. Methods of doing this are described in the next section.

EVALUATION OF LIGHT ABSORPTION

The absorptivity α_λ of chlorine is available from the literature (*12, 14*). The intensity $I_{w,\lambda}$ at the inside wall of the reactor can be most accurately determined by measuring the extent of decomposition of oxalic acid in uranyl sulfate solution. The optical and kinetic features of this unique reaction have been established carefully (*5, 10, 11, 18*). The key points are that the reaction is zero order in concentrations and first order with respect to light intensity.

If it is assumed that the spectral distribution of the light at the inside of the reactor wall is the same as that leaving the lamp, $I_{w,\lambda}$ is related to the known total intensity by the ratio

$$I_{w,\lambda} = I_{w,tot}\,\frac{F_\lambda}{F_{tot}} \qquad (22)$$

The rate of the actinometer reaction [rate of production of $(COOH)_2$] is proportional to $I_{r,\lambda}$, which can be obtained from Equation (12). Then the rate is averaged across the radius of the reactor, $I_{w,\lambda}$ is replaced by Equation (22), and the result is summed over the pertinent wavelength range. This leads to the following expression for the rate in terms of $I_{w,tot}$:

$$-\bar{r}_t = \frac{2I_{w,tot}\,\sum_\lambda \Phi_\lambda\,\frac{F_\lambda}{F_{tot}}\,[1-\exp(-2\,R\mu_\lambda)]}{R} \qquad (23)$$

Equation (21) can be written for the actinometer reaction as

$$-\bar{v}_z\,\frac{dC_c}{dz} + \bar{r}_t = 0 \qquad (24)$$

where C_c represents the concentration of oxalic acid. By integrating and by expressing the result in terms of the conversion, volumetric flow rate Q, and reactor volume V_R, one obtains

$$\bar{x}_t = \frac{(C_c)_o - (C_c)_L}{(C_c)_o} = \frac{-\bar{r}_t}{(C_c)_o}\left(\frac{V_R}{Q}\right) \qquad (25).$$

All the quantities in Equation (25) are known except $I_{w,tot}$ and $\bar{r}_t$. Since the rate is available from experimental data $I_{w,tot}$ can be calculated by using Equation (25). Then from Equation (22) the intensity at the wall is known as a function of wavelength. This same procedure was used in a somewhat different way by Huff and Walker (*17*) to evaluate intensities. The pertinent feature about Equation (25) is that the conversion is directly proportional to V_R/Q.

APPARATUS

For Chlorination Data

To achieve near isothermal conditions, small conversions are generally necessary, and to avoid wall deposits and secondary chlorides, it was necessary to use a feed gas containing about 96 mole % nitrogen and a stoichiometric excess of propane. In the first part of the apparatus, shown in Figure 2, this feed gas was prepared by starting with cylinder gases and by including proper purification and metering equipment. The feed was then passed either to reactor system A or dark reactor (**9**). The latter tube duplicated in the dark the flow conditions in the quartz (light) reactor (**10**). After each run the same feed was passed through the dark reactor and on to the absorption and sampling system (**13, 14, 15, 16**). The analysis of the samples for the dark reactor run was used to establish the chlorine flow rate for the quartz reactor run and also the extent of the dark reaction.

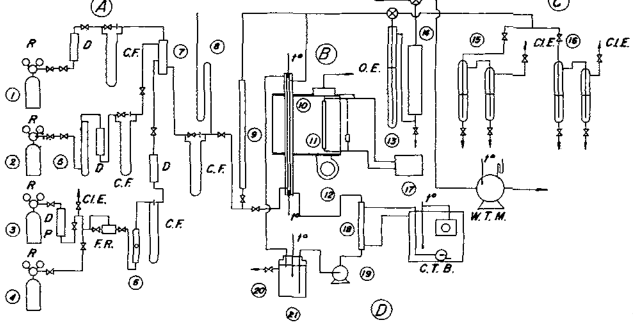

Fig. 2. Experimental equipment for chlorination.

The reactor system (Figure 3) was of the elliptical type, similar to those used by others (*3, 9, 11, 17*). The lamp and reactor were carefully mounted at the foci of an ellipse, which consisted of a highly polished, 0.032-in.-thick sheet of specularly finished aluminum. It is estimated that the surface reflected 80 to 90% of the total radiation in the range of λ between 2,500 to 4,500Å A 360-w. General Electric UA-3 Uviarc lamp was used. Its dimensions and spectral characteristics are available (*27*). The reactor (**10**) was a 2-mm. I.D. (4-mm. O.D.) tube of fused quartz whose other dimensions are shown in Figure 5. This gave a fairly uniform transmission of more than 90% up to 2,500Å. It was jacketed with a 16-mm. I.D., 18-mm. O.D. silica tube. Water, or filter solution, flowed through the annular space for cooling and to reduce the light intensity. To eliminate turbulence a 230-mm. length of straight tube was provided prior to the lighted portion of the reactor, and a 130-mm. section downstream. All the tubing except the desired reactor length was covered with black paper and masked with a 5-mm. layer of asbestos sheet. Temperatures were measured, as shown in Figure 3c, with ASTM thermometers to 0.1°C.

The product stream passed first through a bubbler tube (**13**) filled with water and then to an absorber (**14**) which contained calcium oxide, and finally to the chlorine exhaust system. Samples of either the light or dark reactor products were obtained by diverting the gas stream to a line of two absorbers (**15**) or (**16**) containing potassium iodide solution (3 wt. %). All the critical parts of the apparatus outside the reactor system were darkened with paint.

At least 1 hr. was allowed to reach steady state conditions, achieved when the entrance temperature at the reactor was constant at 28°C. and the exit temperature at 32°C. Blank tests with nitrogen flowing through the reactor showed the 4°C. difference to be due to the heat from the lamp. Because of the wall conditioning procedure (see next section), 90 min. were allowed after each change in feed composition before taking samples. Immediately afterward the dark reactor run was made.

The solutions from the absorber were analyzed for unreacted chlorine and for hydrogen chloride by titration with sodium thiosulfate and sodium hydroxide solutions, respectively.

For Actinometer Data

The intensity of the light was determined in the same reactor system as was used in the chlorination work. Degassed distilled water flowed through the jacket. The feed solution, 0.05 molal oxalic acid and 0.01 molal uranyl sulfate, passed through the reactor and after steady state, samples of the feed and product streams were taken for analysis. Flow rates and reactor length were controlled so that the conversion of $(COOH)_2$ was between 3 and 20%. Smaller conversions introduce errors in the analysis and larger values introduce uncertainties in the zero-order rate requirement, the possibility of bubble formation due to excessive formation of carbon monoxide and carbon dioxide, and the danger of reduction of UO_2^{++} (*20*). The samples were analyzed for oxalic acid by titrating with standard potassium manganate solution at 85°C.

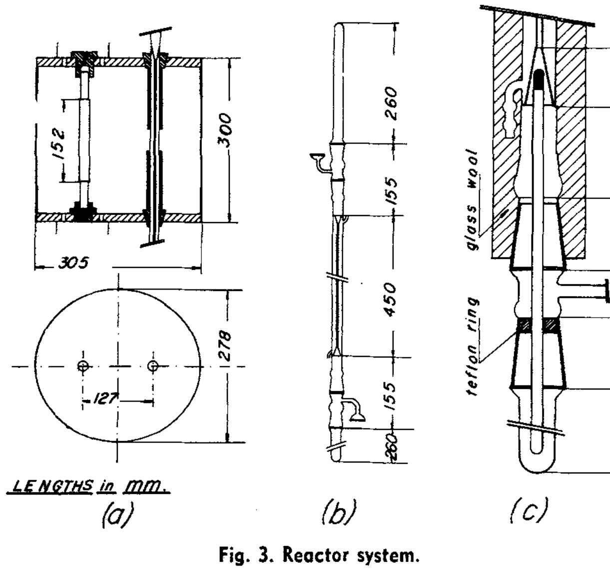

Fig. 3. Reactor system.

PRELIMINARY EXPERIMENTAL STUDIES

Before obtaining final data, preliminary chlorination runs were made to evaluate inhibition effects, wall deposits, the dark reaction, temperature variations, and the accuracy of the procedures. These runs extended over the initial 200 hr. of operation of the lamp—a period when the intensity may be less stable than later.

Purification—Inhibition

Photochlorination of propane appears to be inhibited primarily by iodine and oxygen. Iodine contamination was improbable, provided proper prtcautions were taken in connecting the sampling and reactor sections of the apparatus. There did exist the possibility of oxygen inhibition from the chlorine and nitrogen streams. This was checked by making runs with a tube of activated charcoal at 600°C. installed in the chlorine and nitrogen lines. The gases were cooled and then passed through a second tube of activated charcoal, maintained at 0°G. for chlorine and —78°C. in the nitrogen line. This procedure provided for the reaction of any oxygen at 600°C and adsorption of the carbon dioxide and carbon monoxide produced in the low-temperature beds of charcoal. The rate of chlorination was found to be the same in these runs as in the system described in Figure 2. Hence, use of prepurified grade feed gases along with the purification procedure shown in the figure was judged adequate to prevent inhibition of the chlorination.

Dark Reaction

Initial runs were made without light in the quartz reactor (**10**). With very precise analytical conditions, a small amount of dark reaction was detected (by the formation of small quantities of hydrogen chloride). The extent of the reaction was reproducible and sensitive to changes in concentration and flow rate. Because of this, the dark reactor was built and parallel runs made in it. It may be noted that Yuster and Reyerson (*28*) apparently did not observe a measurable amount of thermal reaction below 50°C.

The data obtained in the quartz reactor could be accurately corrected for dark reaction in our work simply by subtracting the rate of the dark reaction from that of the light reaction. This procedure would not be satisfactory if the dark reaction were a sizeable fraction of the total, because some of the steps in the reaction sequence probably are the same for both light and dark processes. In all the runs, the dark reaction was less than 10% of the light reaction.

Precision of Analyses

With conventional flow metering devices, it was not possible to measure the chlorine flow rate more accurately than about 5%. Hence, the analysis of samples for the dark reaction run was used to establish the chlorine rate. This was compared with the total chlorine rate calculated from the analysis of the samples from the light reaction. The chlorine mass balance obtained in this way was always accurate to better than 2%.

Precautions were necessary to determine accurately the hydrogen chloride produced at low conversions. Long adsorption times were required and also a precise *p*H meter was necessary to establish the endpoint.

Temperature Variations

The heat of monochlorination of propane is about 27,000 cal./g.-mole. With the feed compositions used and a conversion of 10%, the adiabatic temperature rise is about 2.5°C. This maximum ΔT was less than the 4°C. rise due to thermal energy from the lamp. The reaction temperature for each run was estimated by linear extrapolation between 28° and 32°C., according to the location of the lighted section along the reactor tube.

Wall Deposits

Data were not reproducible after several hours of operation when a very high light intensity was used or when the conversion exceeded 20%. Inspection of the reactor after these runs showed a yellow to brown deposit located at the illuminated section. Such wall deposits have been described previously by Yuster and Reyerson (28) and have been analyzed carefully by Chambers and Ubbelohde (6). In our case the deposit was insoluble in water and hydrogen chloride solution, only partially soluble in acetone or alcohol, and more soluble in carbon tetrachloride. It was readily removed by brushing after wetting the surface with carbon tetrachloride.

The deposit decreases the transmission of light, but the decrease in reaction rate seems to be greater than expected from this source. It appears reasonable that the deposit enhances the wall termination rate of the activated species. Some exploratory runs were made at extreme conditions. For example, at a Reynolds number of 1,000, a feed gas of 96 mole % nitrogen, 3% propane, and 1% chlorine, and a high intensity (no filter solution) illuminated length of 30 mm., the conversion decreased with time on stream from 40% after 1 hr. to about 20% after 5 hr. The concept that the deposit is a layer of adsorbed hydrocarbon compounds seems to be generally valid. At high chlorine concentrations the color could change to brown by chlorination reactions in the layer.

On the basis of this information the following procedure was adopted to ensure reproducible data:

1. After 8 hr., the reactor wall was cleaned with carbon tetrachloride and a brush, washed with carbon tetrachloride, acetone, alcohol, and then again with carbon tetrachloride. Finally, nitrogen was passed through the tube for 4 hr.
2. The reactor was operated at low light intensities (with filter solutions) with an excess of propane and at conversions less than 20%.
3. Ninety minutes was allowed, after changing conditions, before obtaining samples.

With these arrangements reproducibility of better than 2% was generally obtained between consecutive runs at the same conditions and also after runs for 6 to 8 hr. at different conditions.

Scope of Data

The described operating requirements could be satisfied over the ranges of variables given below, and chlorination data were obtained for these conditions. Flow rate: N_{Re} = 500 to 2,000. Feed gas composition: nitrogen = 94 to 99 mole %, propane = 1.5 to 3.5%, chlorine = 0.1 to 1.0%. Reactor length: 10, 20, and 40 mm. (nominal). Light intensity $\Sigma\ (I_{w,\lambda}\ \alpha_\lambda\ \theta)$: 0.38 to 1.63 $\times\ 10^{-2}$ Einsteins/(sec.)(g.-mole).

LIGHT INTENSITY VARIATIONS

One of the objectives of the experimental work was to study the effect of light intensity. To avoid the potential influence of variations in wavelength on the reaction rate, it is necessary to vary the intensity without changing the spectral distribution. Since this could not be accomplished by changing the lamp voltage, it was done by using a filter solution as the cooling medium flowing through the jacket around the reactor. It is not possible practically to develop a filter with a constant absorption coefficient for all wavelengths; the best approximation is to obtain a nearly constant absorption for those wavelength bands, of strong emission of the lamp, which are within the range of absorption by chlorine.

The problem of preparing filter solutions with specified wavelength-transmission characteristics is essentially an empirical one of combining inorganic salts. By using available information (*4, 21, 22*) four solutions consisting of different amounts of nickel chloride, ferric chloride and potassium chromate were prepared. The emission strength of the lamp used at various wavelengths is given in the first two columns of Table 1.† This information, along with the absorption data for chlorine, shows that the most important wavelength ranges are: 2,900 to 3,200 Å., 3,600 to 3,700 Å., and 4,000 to 4,100 Å. The percent transmission of the four aqueous solutions are shown as θ_{I}, θ_{II}, θ_{III}, and θ_{IV} in Table 1. It is seen from these data that the spectral distribution of the light reaching the reactor wall will be essentially the same for these four solutions, but the intensity will be increased progressively from solution I to IV. These four solutions were employed in the runs to investigate the effect of light intensity. A fifth solution was also used consisting of nickel chloride, potassium biphthalate, and potassium chromate. This filter gave a light distribution enriched in the 3,000 to 3,500 Å. interval. Its transmission characteristics are given in the column labeled θ_o in Table 1. This filter was used to study the effects of flow rate and chlorine composition at constant intensity. Comparison of rates of reaction with solution θ_o with the results by using the solutions $\theta_I - \theta_{IV}$ at the same intensity gave some indication of the effect of wavelength on the kinetics.

The absorption characteristics of the solutions were determined with a visible and ultraviolet spectrophotometer. The filter solutions were not stable for long periods, so frequent replacement was necessary. When filter solutions were used, it was necessary to multiply the right side of Equation (22) by θ_λ to obtain the wall intensity from actinometer runs with water in the reactor jacket. A similar correction was necessary in Equation (23).

RESULTS OF LIGHT INTENSITY MEASUREMENTS

Actinometer runs were first carried out after preliminary chlorination runs with high conversions (20 to 40%). For these data a wall deposit existed. Following this, low conversion chlorination data were obtained and then the actinometer runs were repeated. These latter runs were made at the three reactor lengths used in the chlorination measurements. In all cases the average reactor temperature was about 30°C. No difficulty was experienced in obtaining reproducible data as long as the flow rate was more than 2 cc./min.

The average rates of reaction as calculated from Equation (23) for each set of data are summarized in Table 2. The last three rows present the results obtained in the clean reactor. The rate values are constant within 3% for different reactor lengths. This indicates that the end effects (due to non-normal radiation) are negligible. However, the rates obtained with a wall deposit are about 6% lower. This is not likely due to changes in lamp characteristics. If these change, the intensity should decrease with time, yet the runs with deposit were carried out prior to the others. It seems clear that the rate and, hence, the light intensity are reduced by the wall deposit.

Table 2. Actinometer Results for Different Reactor Lengths

Run No.	Reactor length, mm.	Flow rate range, cc./min.	Exit conversion, %	Average rates of reaction, g.-mole/(cc.)(sec.)
A13-A25*	30.0	3.2 to 25.9	3.3 to 24.5	7.16×10^{-6}
A26-A31	10.5	2.4 to 16.9	1.0 to 14.5	7.74×10^{-6}
A33-A39	19.3	3.9 to 25.8	1.1 to 14.5	7.57×10^{-6}
A40-A51	40.5	6.9 to 83.6	1.4 to 17.3	7.54×10^{-6}

* With wall deposit.

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† Tabular material has been deposited as document 9057 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

For purposes of evaluating the light intensity, an average rate $\bar{r}_t = 7.62 \times 10^{-6}$ g.-mole/(cc.) (sec.) was used in Equation (23). In the first two columns of Table 3† are the emission spectra of the lamp as supplied by the manufacturer (27). From this information and the absorptivity and quantum efficiency (*5, 10, 18*) it was possible to carry out the summation in Equation (23). By using this result and the value of $\bar{r}_t$, the total intensity as determined from Equation (23) was 147.3×10^{-8} Einsteins/(sq. cm.) (sec.). Finally, this value and the flux ratio for the lamp were used in Equation (22) to evaluate the wall intensity $I_{w,\lambda}$ for any wavelength. All of these results are given in the last column of Table 3. They are the intensities which, when multiplied by the proper transmission coefficient (Table 1), give $I_{w,\lambda}$ needed to interpret the chlorination data.

Optical Efficiency

A specific characteristic of a reactor lamp system is its optical efficiency ξ. This may be defined as the amount of light reaching the inside wall of the reactor divided by the amount of light emitted by the lamp, both per unit length. In equation form

$$\xi = \frac{2\pi R (I_{w,\mathrm{tot}})}{F_{\mathrm{tot}} \left(\dfrac{1}{L_L}\right)} = \left[\frac{2\pi L_L}{F_{\mathrm{tot}}}\right] R I_{w,\mathrm{tot}} \qquad (26)$$

The quantity in brackets is a characteristic of the lamp alone, while $RI_{w,\mathrm{tot}}$. is a measure of what might be termed the ideality of the lamp reactor system. The efficiency will be less than unity for several reasons: (1) the radiation is not entirely radial, (2) the lamp and reactor will not be exactly centered at the foci of an ellipse, and (3) the transmission of the silica reactor wall and the reflectance of the aluminum surface are not 100%.

The data in Table 3 give values of F_{tot} and $I_{w,\mathrm{tot}}$, so that the efficiency is $\xi = \dfrac{2\pi(15.2)(0.1)\,147.3 \times 10^{-8}}{132.6 \times 10^{-6}} =$ 0.11, or 11%, where 15.2 cm. is the length of the lamp. Since no significant differences in r_t were observed for different reactor lengths, the efficiency does not vary with L over the range studied. It may be noted that the illuminated length of the reactor was a small part of the total length of the lamp reactor system.

RESULTS OF CHLORINATION RUNS

Kinetics at Constant Light Intensity

For differential reactor operation, Equation (21) can be integrated to give

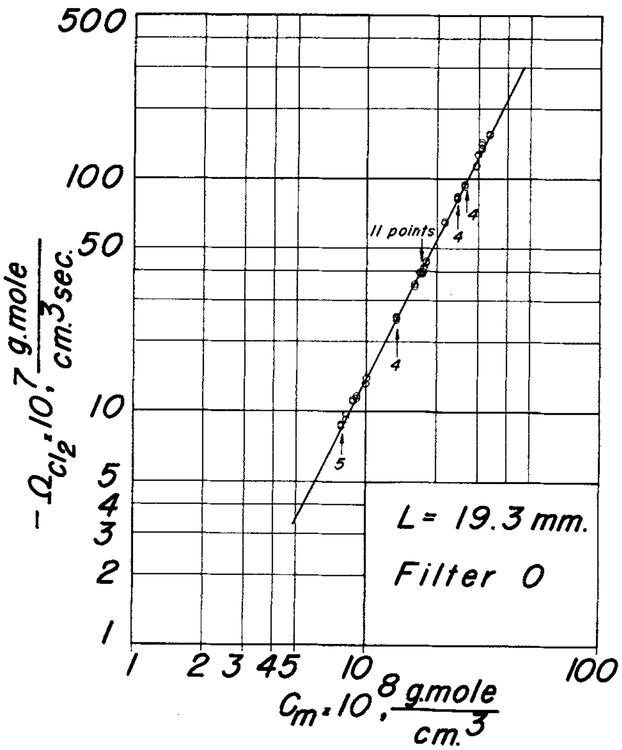

Fig. 4. Effect of chlorine concentration.

$$-\bar{\Omega}_{Cl_2} = \frac{Q[(C_{Cl_2})_o - (C_{Cl_2})_L]}{V_R} \qquad (27)$$

Rates of reaction were calculated from the experimental data with this expression. Plotting the rate vs. the arithmetic average concentrations should establish the order of the reaction with respect to each component. About fifty runs were carried out at various flow rates and concentrations of chlorine and propane for this purpose. The reactor length was fixed at 19.3 mm. and the spectral distribution of the light was constant and corresponded to that obtained with filter solution 0 (Table 1). The results are plotted in Figure 4 and a least square evaluation of the slope of the line gives 1.98. This indicates that the rate is second order in chlorine concentration for our operating conditions. For these data two runs were made at each condition. The agreement of the points in the figure indicates the degree of reproducibility.

The data in Table 4 show that there is no effect of propane concentration, between 1.5 and 3.5 mole %, on

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† See footnote on page 1129.

TABLE 4. EFFECT OF PROPANE CONCENTRATION

Run No.	Flow rate × 10^4 g.-mole/sec.	Nitrogen, mole %	Chlorine, mole %	Propane, mole %	$(C_{Cl_2})_o \times 10^7$ g.-mole/ml.	x_{Cl_2}, %	$C_m \times 10^7$ g.-mole/cc.	$-\Omega_{Cl_2} \times 10^7$ g.-mole/ (sec.)(cc.)	$k_o \times 10^{-8}$ g.-mole/ (sec.)(cc.)	Error %, in mass balance
D-9	8.80	96.0	0.43	3.50	1.779	6.3	1.723	40.38	1.360	0.25
D-10	8.80	96.0	0.43	3.50	1.779	6.2	1.720	39.59	1.334	0.10
D-11	8.79	97.0	0.44	2.53	1.781	6.1	1.726	39.40	1.323	0.67
D-12	8.79	97.0	0.44	2.53	1.781	6.1	1.726	39.40	1.323	0.11
D-13	8.74	97.6	0.44	1.92	1.820	6.4	1.762	41.69	1.345	0.86
D-14	8.74	97.6	0.44	1.92	1.820	6.5	1.760	42.59	1.374	0.75
D-15	8.82	98.1	0.44	1.49	1.804	6.2	1.748	40.68	1.335	0.60

Reaction temperature = 30.5°C.; Reynolds number = 1,010 (approx.). Reactor length = 19.3 mm. Filter solution 0, $\Sigma(I_{w,\lambda}\,\theta_\lambda\,\alpha_\lambda) = 1.628 \times 10^{-2}$ Einsteins/(sec.)(g.-mole).

TABLE 5. EFFECT OF FLOW RATE ON RATE CONSTANT k_o

Run No.	Flow rate × 10^4 g.-mole/sec.	Reynolds No.	Nitrogen, mole %	Chlorine, mole %	Propane, mole %	$(C_{Cl_2})_o$ × 10^7 g.-mole/cc.	x_{Cl_2}, %	C_m × 10^7 g.-mole/cc.	$-\overline{\Omega}_{Cl_2}$ × 10^7 g.-mole/(sec.)(cc.)	k_o × 10^{-8} cc./(g.-mole)(sec.)	Error in mass balance, %
D-31	4.390	505	96.3	0.20	3.46	0.812	6.0	0.787	8.894	1.433	1.50
D-25	4.400	506	96.2	0.36	3.46	1.414	10.0	1.343	25.721	1.429	0.40
D-33	6.511	750	96.3	0.23	3.47	0.908	4.7	0.887	11.515	1.466	0.67
D-35	6.520	751	96.2	0.35	3.47	1.389	6.8	1.341	25.488	1.417	0.30
D-3	8.791	1012	96.1	0.41	3.47	1.662	6.0	1.612	35.826	1.378	0.70
D-5	8.815	1015	95.9	0.68	3.46	2.743	9.5	2.613	93.710	1.375	0.66
D-21	13.216	1521	95.9	0.62	3.44	2.530	6.3	2.450	85.693	1.428	0.67
D-23	13.239	1524	95.8	0.79	3.43	3.228	7.8	3.102	135.619	1.411	0.11
D-49	17.392	2002	95.9	0.65	3.47	2.683	5.0	2.615	95.005	1.391	0.37
D-51	17.426	2006	95.7	0.85	3.46	3.465	6.6	3.351	160.746	1.432	0.40

Reaction temperature = 30.5°C. Reactor length = 19.3 mm. Filter solution 0, $\Sigma(I_{w,\lambda}\,\theta_\lambda\,\alpha_\lambda) = 1.628 \times 10^{-2}$ Einsteins/(sec.)(g.-mole).

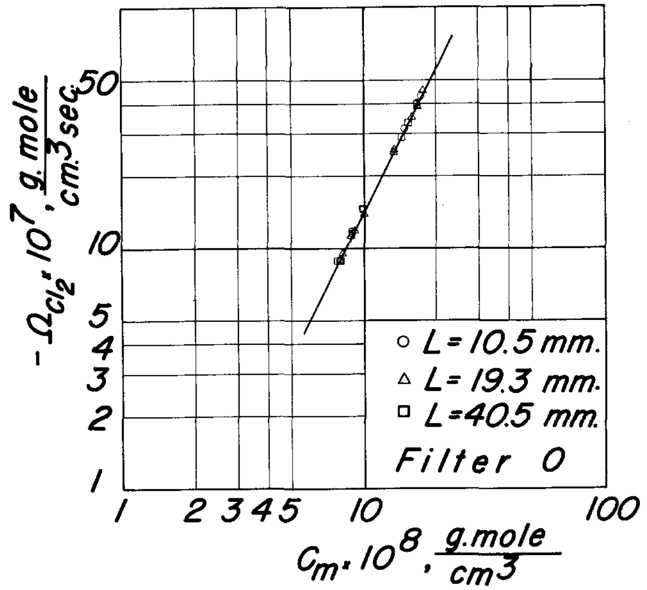

Fig. 5. Effect of reactor length.

the rate $-\overline{\Omega}_{Cl_2}$. These results are for constant chlorine concentration and constant flow rate.

Thus Equation (20), which is developed on the basis that the rate is directly proportional to the light *absorbed* and the chlorine concentration, satisfactorily explains the data. If this expression for $\overline{\Omega}_{Cl_2}$ is substituted in Equation (21) and integrated over the length of the reactor, the result expressed in terms of the conversion of chlorine is

$$x_{Cl_2} = \frac{(C_{Cl_2})_o - (C_{Cl_2})_L}{(C_{Cl_2})_o}$$

$$= \frac{K}{K + \dfrac{Q}{V_R (C_{Cl_2})_o}\left[\dfrac{1}{4\Sigma\alpha_\lambda\, I_{w,\lambda}\theta_{o,\lambda}}\right]}$$

or

$$K = \frac{Q}{V_R (C_{Cl_2})_o}\left[\frac{1}{4\Sigma\alpha_\lambda\, I_{w,\lambda}\,\theta_{o,\lambda}}\right]\frac{x_{Cl_2}}{1 - x_{Cl_2}} \quad (28)$$

where α_λ for the summation term is obtained from (*12, 14*), $I_{w,\lambda}$ in Table 3, and $\theta_{\lambda,o}$ in Table 1. For this filter $\Sigma\alpha_\lambda\, I_{w,\lambda}\,\theta_o = 1.628 \times 10^{-2}$ *Einsteins/(sec.) (g.-mole)*. The kinetic constant K was calculated with Equation (28) and from it the conventional second-order constant k_o

$$k_o = 4K\Sigma(\alpha_\lambda\, I_{w,\lambda}\,\theta_o) = \frac{Q}{V_R (C_{Cl_2})_o}\frac{x_{Cl_2}}{1 - x_{Cl_2}} \quad (29)$$

This latter constant is also tabulated in Table 4. Table 5 shows a series of runs with different flow rates within the range 11 to 43 cc./sec. (at reactor conditions). The nonvariance of the k_o values shows that flow rate had no effect on the kinetics. Note that all the data were in the laminar flow region.

Some runs were made at longer (40.5 mm.) and shorter (10.5 mm.) reactor lengths, all other conditions being the same as before. Figure 5 is a plot of $\overline{\Omega}_{Cl_2}$ vs. the arithmetic average concentration of chlorine for these data. Again the line is straight and the slope essentially 2.0. For comparison, some of the data for L = 19.3 mm. are also shown in the figure.

Table 6 gives the average values of K and k_o for the three reactor lengths. As with the actinometer data no end effects are apparent.

Effect of Light Intensity

According to Equations (20) and (29) the rate of reaction, or the rate constant k_o, should be directly proportional to $\Sigma\alpha_\lambda\, I_{w,\lambda}\,\theta_o$, which is a measure of the light intensity at the wall. Chlorination runs were made by using the four filter solutions I-IV (Table 1) in the reactor jacket. From the measured conversion k_o was calculated from Equation (29). The absorptivity information from (*12, 14*), and the θ_λ and $I_{w,\lambda}$ data from Tables 1 and 3 were used to establish $\Sigma(\alpha_\lambda\, I_{w,\lambda}\,\theta_\lambda)$ for each of the solutions. Figure 6 shows these results. The linear nature of the data provides evidence that the rate is proportional to the first power of the light intensity. This can be shown in an alternate way by noting if K is constant. The averages of the K values obtained from Equation (28) for

TABLE 6. KINETIC CONSTANTS FOR DIFFERENT REACTOR LENGTHS

No. of runs averaged	Reactor length, mm.	Flow rate range, cc./sec.	Initial (C_{Cl_2}) range, mole %	$\overline{k}_o$ × 10^{-8} (cc.)(sec.)/g.-mole	$\overline{K}$ × 10^{-15} cc./Einsteins
48	19.3	11 to 43	0.1 to 1.0	1.403	2.154
6	10.5	11 to 22	0.2 to 0.5	1.429	2.194
6	40.5	22 to 43	0.2 to 0.5	1.388	2.131

Reaction temperature = 30.5°C. Filter solution 0, $\Sigma(I_{w,\lambda}\,\theta_\lambda\,\alpha_\lambda) = 1.628 \times 10^{-2}$ Einsteins/(sec.)(g.-mole). Propane concentration = 3.5 mole % (approx.). Flow rate measured at reactor conditions.

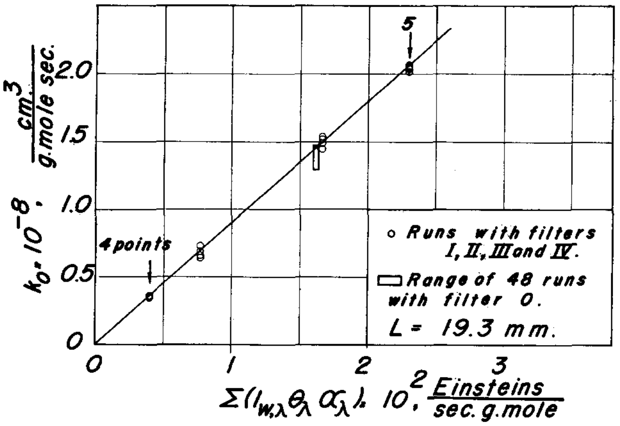

Fig. 6. Influence of light intensity.

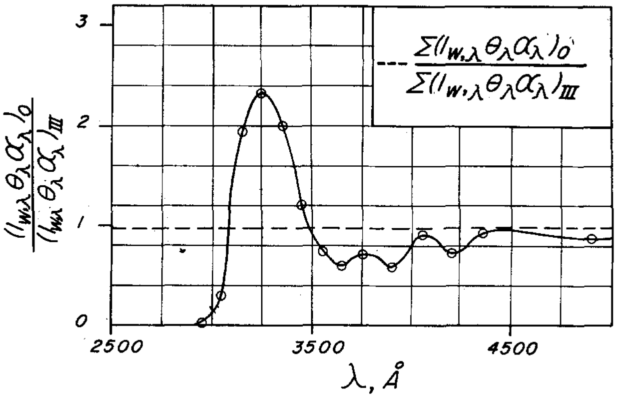

Fig. 7. Ratio of $(I_{w,\lambda}\theta_\lambda\alpha_\lambda)$ for filters 0 and III vs. λ.

each run are summarized in Table 7 for the four filter solutions. For a sixfold change in intensity, the change in K is but 2.5%.

Effect of Spectral Distribution

There were insufficient data to investigate this variable carefully. However, filter solutions 0 and III provide approximately the same total light intensity (Table 7) but a different distribution of energy with wavelength. Filter solution 0 is enriched in the lower wavelength range as indicated in Figure 7 where the ratio of $(\alpha_{w,\lambda}\ I_{w,\lambda}\ \theta_\lambda)$ for the two solutions is plotted vs. λ. The kinetic constant K for filter solution 0, as evaluated from the data of Figure 4, is shown in the last row of Table 7. It is about 5% less than K for filter solution III. This difference could be due to errors in summing the light intensity or to experimental errors. There is also a possible theoretical explanation based upon spectral distribution. For nonchain reactions the quantum efficiency is a function of wavelength. If the quantum efficiency of the primary process in the chlorination reaction was also dependent upon λ, then k_1 and K would also depend upon the wavelength. A qualitative proposal of the same nature has been given by Anderson (*1*). More data are needed to determine if the primary kinetic constant is truly a function of λ.

DISCUSSION

A second-order rate expression can also be obtained from other hypotheses for the reaction mechanism. One would be to assume that the propyl radical is terminated by the heterogeneous wall process rather than homogeneously, and that the diffusivity of Pr* is very large. This leads to an equation that includes the radius R, but otherwise is the same as Equation (19). Measurements on reactors of different radii would be required to distinguish between the two hypotheses. However, the absence of wall deposit at the experimental conditions is evidence in favor of the homogeneous termination step.

Writing the homogeneous termination step as first order in Equation (16) is an assumption. It supposes that the propyl radical is terminated by collision with molecules, other than Pr*, present at constant composition, for example nitrogen. No evidence was found in the literature suggesting the formation of polymerization products of the propyl-propyl type which would be expected from a second-order termination process.

The difficulty in centering a 2-mm. I.D. reactor at the focus of the elliptical reflector, the fact that the lamp is a tube of finite diameter, and the imperfections in the elliptical surface all prevent exactly radial light. Hence the diffusely lighted zone in the neighborhood of the focus may give a nearly constant light intensity across the reactor. For constant intensity, Equation (18) becomes

$$Ia_\lambda = 2\ I_{w,\lambda}\ \alpha_\lambda\ (C_{Cl_2}) \tag{30}$$

and Ia_λ is independent of r. By using Equation (32), the average rate becomes

$$-\overline{\Omega}_{Cl_2} = 2\ K\ I_{w,\lambda}\ \alpha_\lambda\ (C_{Cl_2})^2 \tag{31}$$

This result differs from Equation (20) only by a factor of 2. Hence, if constant light intensity were assumed, the K values reported in the tables would change by this factor, while k_o would be the same.

CONCLUSIONS

Equations were developed for describing the behavior of a chain type of photoreaction in a tubular reactor. The application of these equations in a very simple form to the chlorination of propane showed that:

1. The rate was directly proportional to the light absorbed and to the chlorine concentration, according to Equation (17). This is equivalent to a rate expression [Equation (20)], which is first order in light intensity at the wall and second order in chlorine concentration.

Table 7. Kinetic Constants for Different Light Intensities

No. of runs averaged	Filter solution	Flow rate range, cc./sec.	Initial (C_{Cl_2}) range, mole %	$\overline{k}_o \times 10^{-8}$ cc./(sec.) (g.-mole)	$\Sigma(I_{w,\lambda}\ \alpha_\lambda\ \theta_\lambda)10^2$ Einsteins/ (sec.)(g.-mole)	$\overline{K} \times 10^{-9}$ cc./Einsteins
4	I	11 to 22	0.2 to 0.5	0.353	0.4000	2.206
4	II	11 to 22	0.2 to 0.5	0.676	0.7670	2.204
4	III	11 to 22	0.2 to 0.5	1.507	1.6655	2.261
5	IV	11 to 43	0.2 to 0.4	2.045	2.2779	2.242
48	0	11 to 43	0.1 to 1.0	1.403	1.6280	2.154

Reaction temperature = 30.5°C. Reactor length = 19.3 mm. Propane concentration = 3.5 mole % (approx.). Flow rate at reactor conditions.

2. The rate was independent of propane concentration. Caution should be used in extrapolating these results because of the small conversions, chlorine concentrations, and small reactor diameter. The small chlorine concentrations resulted in small absorptions and simplified the intensity-radial position relationship. With higher conversions and concentrations, wall deposits could become important, and heterogeneous terminations might be significant. In this case the rate equation could depend upon reactor diameter and flow rate. It appears to us that high chlorine concentrations and larger reactor diameters would require thorough understanding of the effects of wall deposits and, for quantitative analysis, a numerical solution of the complicated mass balance and intensity equations [Equations (1) and (2)] and postulated rate expressions for Ω_i.

3. The use of filter solutions is a convenient way to study experimentally the effect of light intensity on the kinetics of a photoreaction. Similarly, it appears that the same procedure would be applicable to studying the effect of spectral distribution of the light.

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NOTATION

C = concentration, g.-mole/cc.
D_e = effective diffusivity, sq. cm./sec.
D_i = molecular diffusivity of species i, sq. cm./sec.
F_λ = flux of the light source (lamp) at wavelength λ, Einsteins/sec. or ergs/(sec.)(g.-mole)
F_{tot} = total flux of the lamp, Einsteins/sec.
h = Planck's constant, (ergs)(sec.)/molecule
I = light intensity, Einsteins/(sq. cm.)(sec.)
Ia = light absorbed (per unit volume), Einsteins/(sec.)(cc.)
k_1, k_2,etc. = kinetic constants corresponding to individual of steps in the chlorination of propane
k_w = kinetic constant of wall reaction
k_o = second-order rate constant, (sec.)(cc.)/(g.-mole)
K = overall kinetic constant for chlorination, (cc.)/Einstein
L_L = length of light source (lamp), cm.
L = length of illuminated section of tube, or reactor length, cm.
Q = volumetric flow rate, cc./sec.
R = radius of reactor tube, cm.
r = radial distance, cm.
r_t = rate of actinometer reaction, g.-mole/(sec.)(cc.)
v_z = velocity in axial direction of reactor tube, cm./sec.; $\overline{v}$ = average velocity across tube
x = conversion; x_t refers to actinometer reaction
z = axial distance in reactor tube, cm.

Greek Letters

α = molal absorptivity, sq. cm./(g.-mole)
λ = wavelength of light, cm. or Å.
μ = attenuation coefficient, cm.$^{-1}$
ν = frequency of light, sec.$^{-1}$
θ = transmission coefficient
Ω_i = rate of formation of i species, g.-moles/(sec.)(cc.)
Φ = quantum efficiency, moles/Einstein
ξ = optical efficiency

Subscripts and Superscripts

$*$ = activated species or free radical
i = individual chemical species
o = reactor entrance
L = reactor exit (length L)
w = wall of reactor
r = at radial distance r
z = axial direction
— = average

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