NOTATION

$A_{i,k}$ = submatrix of partial derivatives of linearized equations on stage i with respect to variables on stage k (if i, k is omitted, $i = i$, and $k = i - 1$)
B = submatrix of partial derivatives of linearized equations on stage i with respect to variables on stage i
$C_{i,k}$ = submatrix of partial derivatives of linearized equations on stage i with respect to variables on stage k (if i, k is omitted, $i = i$, and $k = i + 1$)
F_i = function vector for stage i
f_{ij} = flow rate of component j in feed to stage i
I = identity submatrix
L_{ij} = flow rate of component j in liquid leaving stage i that enters next stage in the system
M_{ij} = material balance equation for component j on stage i
$p_{i,k}$ = replacement submatrix for linearized equations on stage i with respect to variables on stage k (if i, k is omitted, $i = i$, $k = i + 1$)
q_i = replacement for function vector for stage i
S_i = ratio of vapor sidestream flow rate from stage i to vapor flow rate leaving stage i that enters next stage in the system
s_i = ratio of liquid sidestream flow rate from stage i to liquid flow rate leaving stage i that enters next stage in the system
V_j = flow rate of component j in vapor leaving stage i that enters next stage in the system
$\overline{\Delta X_i}$ = vector of Newton-Raphson corrections to variables for stage i
β = dummy submatrix
$\leftarrow$ = is replaced by

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Free Radical Transport in a Photochemical Reactor

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Although the field of photochemistry has expanded enormously in recent years, industrial exploitation of photochemical processes has been slow to develop. Photochlorination and photosulfoxidation processes have received industrial attention from time to time. However, the only large scale process apparently now in operation is the photooximation of cyclohexane to produce caprolactam, the monomer of Nylon 6, which is carried out by Toray Industries of Japan (Mellor et al., 1974; Pape, 1975). In view of the potential selectivity offered by the photochemical route, it is somewhat surprising that more widespread application has not occurred. Undoubtedly, operational difficulties inherent in photoprocesses have played a role in slowing such development. In particular, photodegradation of products and side reactions promoted by the high intensity sources used commercially as well as the ever present problem of opaque wall deposit formation frequently combine to make the photochemical route undesirable on a practical scale. Formation of wall deposits and tarry masses have been reported by many workers as common experimental problems to be overcome in practice (Chiltz et al., 1963; Cassano and Smith, 1966; Ziolkowski et al., 1967; Shah, 1968; Isaacson and Ting, 1970; Lucas, 1971).

Lucas (1971) suggested that these problems might be eliminated entirely if the photoreaction process was separated into the two distinct operations of photoinitiation and subsequent thermal reaction and if these operations were carried out in different zones of the photoreactor. This would eliminate the direct irradiation of reaction products that frequently leads to undesired side reactions and would also prevent tar and deposit forming constituents from interacting at the radiation transmitting surfaces of the reactor. Such operation demands, of course, that the reactive species produced by photoinitiation be successfully transported to the point where the subsequent reactions may occur.

Lucas (1973) later enlarged on this idea and presented some experimental data for the gas-liquid photooximation of cyclohexane. The reaction was carried out in a segregated reactor divided into two zones by a teflon grid of low optical transparency and irradiated at one end by a mercury lamp. Gaseous NOCl and hydrochloric acid carrier gas were injected continuously into the zone closest to the lamp as well as into the liquid cyclohexane in the other zone of the reactor. The data reported by Lucas indicate that free radicals produced by the photodecomposition of NOCl were indeed transported intact through the grid and initiated reaction with the liquid cyclohexane on the other side. Furthermore, there was little or no evidence of wall deposit or tar formation found in this operation.

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Lucas' approach appears to have great promise and the potential to change completely the design of photoreactors, as well as opening interesting questions concerning the lifetimes and propagation of radical species. If successfully developed, it might permit the commercialization of photochemical processes which have previously been discarded owing to the effects mentioned above. In view of this potential and the apparent lack of other independent evidence of the validity of this approach, it was decided to carry out an investigation to confirm the concept and to extend its generality further if possible. This paper presents the initial results of this investigation.

EXPERIMENTAL

The reaction selected for study was the gas phase photochlorination of chloroform:

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl \qquad (1)$$

This reaction appears to follow a free radical chain mechanism initiated by the exposure of chlorine gas to light (Huff and Walker, 1962; Chiltz et al., 1963; Shah, 1968; Oshen, 1972; Sugawara et al., 1973). It was selected because it is both typical of free radical photoprocesses and known to produce light blocking wall deposits as reaction proceeds (Chiltz et al., 1963; Shah, 1968). Previous gas phase studies suggest that the wall deposit results from the chain terminating formation of C_2Cl_6 during reaction. The deposit is visible as a white film which may be removed by brushing the wall with a suitable solvent.

The reactor used for this work was a two piece cylindrical Pyrex glass vessel with an inside diameter of 10.2 cm and an overall length of 7.6 cm. As shown in Figure 1, the two chambers of the reactor were held together with an external clamp and sealed using fluorocarbon-silicone gasket material. A teflon grid was inserted between the chambers to separate the vessel into zones A and B which were 2.54 and 5.08 cm long, respectively. Because of the circular clamp used, the irradiated surface of the reactor was a circle 7.62 cm in diameter. The vessel was fabricated with a number of connections for the introduction of and removal of various streams. Also present, but not shown in the figure, was a thermowell which penetrated to the center of zone B. This permitted continuous monitoring of reactor temperature during experiments.

The reactor was supported externally and connected to feed and product recovery systems by means of glass tubing joined by heat shrinkable teflon. All lines as well as the reactor itself were wrapped with electrical heating tapes which could be controlled to maintain the piping at approximately 100°C and the reactor at either 62° or 74°C, the temperatures used in this study.

Chlorine and nitrogen gases were delivered to the reactor from cylinders. Nitrogen was also used to displace liquid chloroform from a feed tank into a vaporizing coil located in a 100°C constant temperature bath. By means of the feed system piping and valving, it was possible to supply nitrogen, chlorine, or mixtures of both gases to zones A and/or B during experiments. Likewise, chloroform vapor could be introduced into either zone of the reactor.

Product gases were removed from the vessel at the outlet port and passed into the product recovery system. The latter consisted of a cold water condenser to remove the liquid products, a gas separator, and an off-gas treating train of bubblers containing sodium hydroxide and KI solutions. Reactor product samples were obtained by diverting the effluent into a removable separatory funnel submerged in an ice-water bath. Pressure in the reactor was slightly above atmospheric owing primarily to the depth of liquid in the gas bubblers.

The light source used in these experiments was a General Electric F8T5/BLB black light bulb. This fluorescent source emits approximately 0.9 W in the ultraviolet range, mainly around 360 mμ, and is well suited for initiation of chlorine radicals. The lamp was mounted 12.7 cm from the reactor vessel window. Prior to the experiment, the lamp was aged by continuous operation for 100 hr.

Two teflon grids were used in these experiments. Both were prepared by making holes in a sheet of teflon which was 10 mils (0.025 cm) thick. The holes were arranged in a square pattern with the dimensions shown in Table 1. As indicated there, the total open area of both grids was quite small.

The progress of the reaction was monitored by analysis of the condensed liquid samples. Dissolved chlorine was first removed by contacting the sample with an aqueous solution of KI and subsequent titration of the liberated iodine with sodium thiosulfate. When all of the dissolved chlorine and iodine were thus removed, the organic phase (consisting of $CHCl_3$ and CCl_4) was analyzed by index of refraction measurement. Previous tests showed this technique to be quick and accurate and in agreement with gas chromatographic analysis which was used initially. The latter was discarded because of the corrosive nature of the untreated condensed samples.

This apparatus was used for a series of experiments involving both of the teflon grids as well as with no grid at all. It was found that the reactor reached steady state conditions within approximately 10 min of the introduction of reactants, following an initial warm-up period for the light source and the heating elements. Samples were therefore taken 10 min after reaction was initiated. In several experiments, the reaction was continued for up to 2 hr, with samples taken at 10 min intervals, to determine the stability of reactor performance.

Further details of the experimental equipment and procedures may be found elsewhere (Dworkin, 1977).

RESULTS AND DISCUSSIONS

Preliminary experiments were first carried out with this equipment to verify that there was no dark or thermal reaction between chlorine and chloroform at

TABLE 1. TEFLON GRID CHARACTERISTICS

Grid	Number of holes	Hole diameter	Open area
1	91	0.158 cm	1.78 cm^2 or 2.2%
2	800	0.0397 cm	0.99 cm^2 or 1.2%

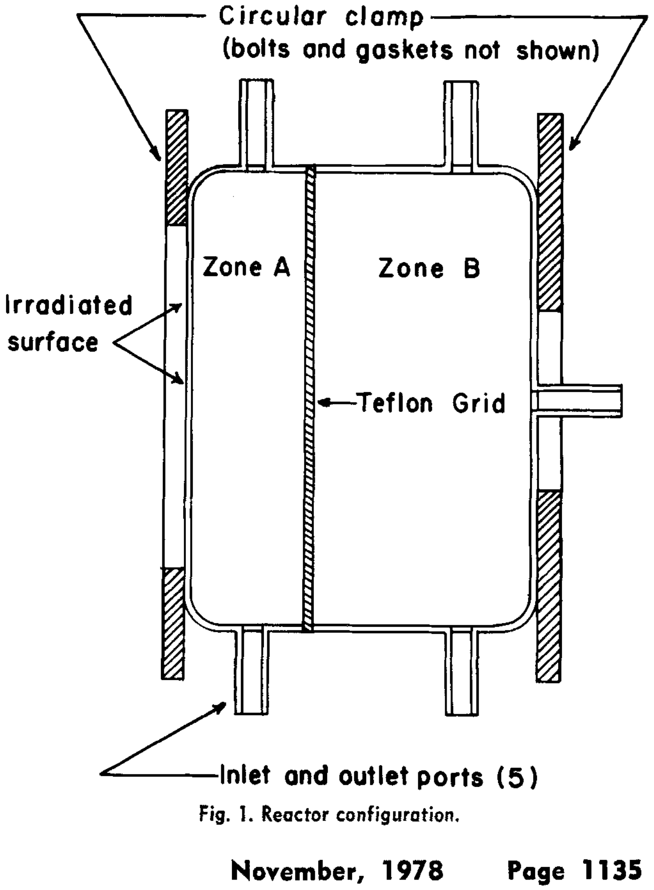

Fig. 1. Reactor configuration.

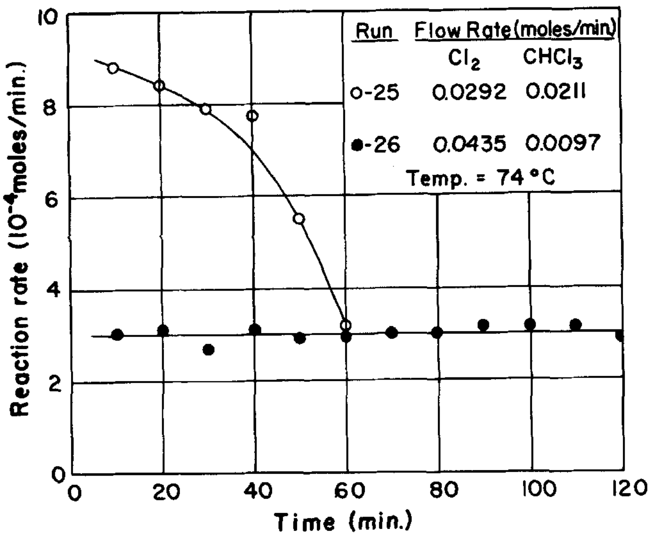

Fig. 2. Reaction rate vs., time, grid 1.

temperatures up to 74°C. Tests were then made with the two reactants fed to zone B and nitrogen fed to zone A to determine the extent of reaction due to radiation penetrating the teflon grids. With grid 1 in place, no measurable reaction was detected, thus indicating that no significant light was transmitted into zone B. Since grid 2 had a smaller open area than grid 1, the same conclusion will apply when it is used. Furthermore, calculations of the light absorption to be expected when zone A contains chlorine gas at 1 atm indicated that more than 90% of the radiation entering zone A would be absorbed by the gas before reaching the grid in any case. Thus, it was concluded that reaction in zone B could not be initiated by radiation passing through the teflon grid.

A series of experiments with various feed rates and compositions was then carried out. In all of these tests, chlorine gas was admitted only to zone A of the reactor, while chloroform vapor entered the reactor only in zone B.

Experiments with grid 1 demonstrated that reaction to produce carbon tetrachloride did occur in this segregated reactor. It was found, however, that wall deposits would form on the radiation transmitting surface of the reactor unless the chlorine flow rate was approximately five times that of chloroform. Figure 2 presents data for two runs made at 74°C. In run 25, the growth of a whitish wall deposit was observed as the reaction rate decreased strongly during the 1 hr run. Under the conditions of run 26, the reaction rate was only one third that at the beginning of run 25, but it remained essentially constant during the 2 hr duration of the experiment. Furthermore, no film deposit formation was evident during this experiment. Since film deposit growth is normally associated with side reactions which follow the photoinitiation step of the chlorination, some chloroform must have been present in zone A under the lower chlorine flow rate conditions. Apparently, chloroform was able to diffuse or flow through the grid because of the pressure and overall flow distribution in the reactor. However, the increased chlorine flow rate in run 26 was apparently sufficient to prevent significant chloroform flow through the grid.

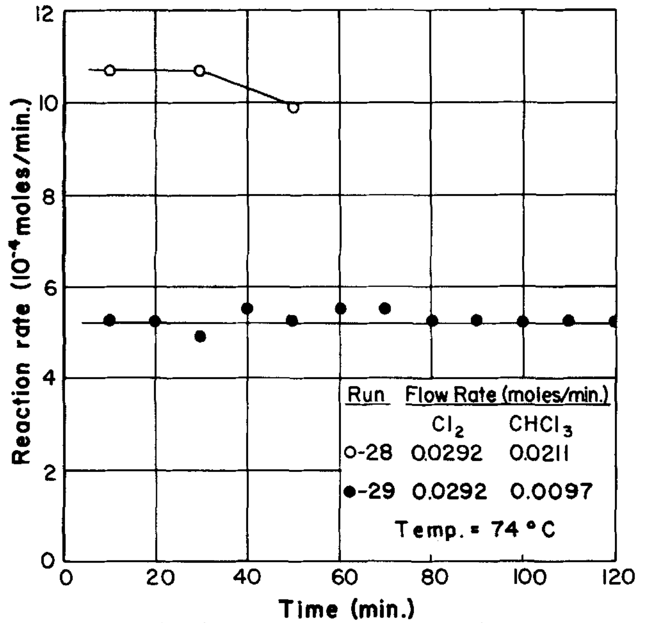

Fig. 3. Reaction rate vs., time, grid 2.

These results suggested that use of a grid with smaller openings would make it easier to maintain a slightly higher pressure in zone A and thereby eliminate backflow of chloroform into that chamber. Experiments with grid 2 immediately verified this conclusion, as shown by the curve for run 28 in Figure 3. Although this run was made at the same conditions as run 25, the data show little or no indication of a falling rate. It should also be noted that the rate of reaction for this run was unexpectedly higher than that for grid 1 under the same conditions, despite the smaller diameter of the grid holes. Also shown on Figure 3 are data for a 2 hr steady run (run 29) with grid 2 under slightly different flow conditions. The latter demonstrates quite clearly the attainment of a constant rate of reaction with no evidence of a decrease with time. Furthermore, no film deposit was observed during this experiment.

This experimental evidence supports the conclusion that chlorine free radicals formed in zone A were indeed transported through the teflon grid and subsequently reacted with chloroform in zone B to produce the desired product. The precise mechanism by which this transport occurs, however, can not be determined from these experiments.

The efficiency of the process was investigated by a number of other tests. As shown in Figure 4, dilution of the chlorine gas with nitrogen has a drastic effect on the rate of reaction, as might be expected. Nitrogen molecules undoubtedly furnish the third bodies needed to deactivate chlorine free radicals. The significance of

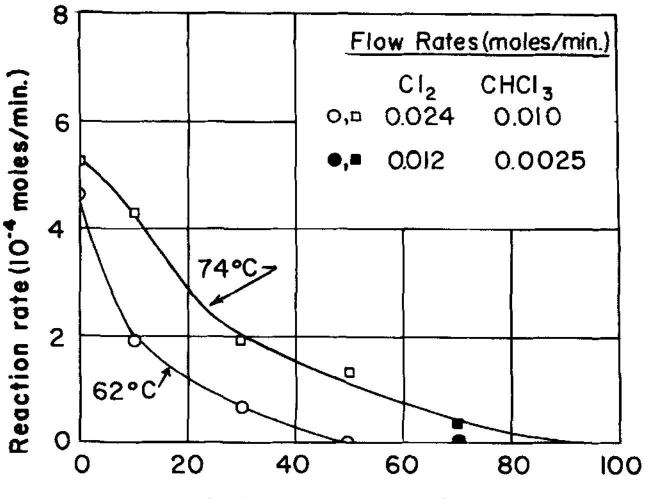

Fig. 4. Effect of inert gas on rate grid 2.

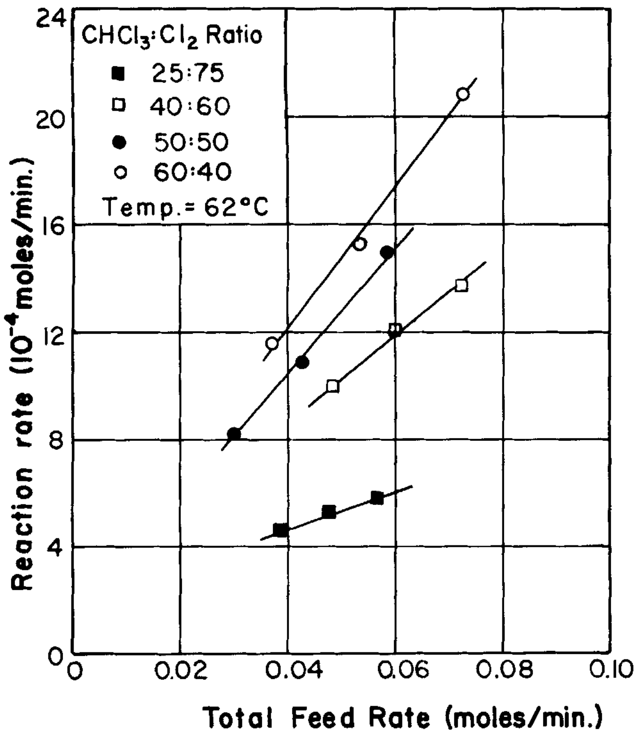

Fig. 5. Effect of feed rate on reaction rate, grid 2.

the particular shape of these curves is not obvious at present. Figure 5 presents data of twelve other runs made with grid 2 in which the relative flow rates of chlorine and chloroform as well as the total feed rate to the reactor were varied and the initial rates of reaction determined. Interestingly, the rate of reaction increases significantly with total feed rate but decreases as the ratio of chlorine to chloroform increases. Lucas (1973) previously found that the rate of reaction in his gas-liquid system depended upon the feed rate of the gaseous NOCl, increasing with feed rate under some conditions and decreasing under others. This suggests that an optimum feed rate will exist for a particular reacting system and geometry.

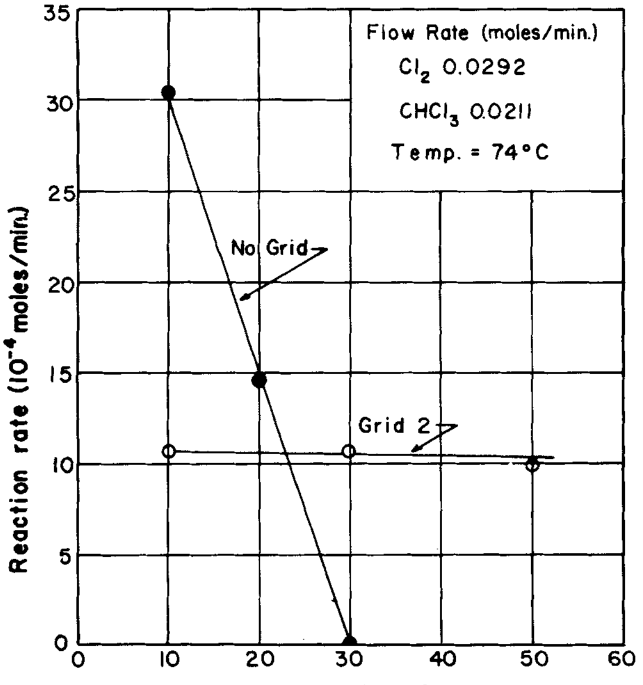

Fig. 6. Reaction rate vs., time with and without grid 2.

Finally, reaction data were taken without any grid at all. For these experiments, the reacting gases occupied the entire volume of the vessel. The results are plotted in Figure 6 along with corresponding data obtained with grid 2. This figure illustrates the inherent advantage of the segregated, two zone reactor concept. Although the rate with the nonsegregated reactor was initially some three times that found with grid 2, it very rapidly fell to zero as wall deposits formed, while the segregated reactor continued to react effectively. Clearly, operation with the latter would quickly prove to be preferable and ultimately more efficient.

These experiments have demonstrated that the gas phase chlorination of chloroform can be carried out successfully in a two zone segregated reactor. The results confirm the previous work of Lucas done with a gas-liquid reaction and suggest that the technique may have wider applicability than originally suspected.

From the point of view of photoreactor design, this type of reactor has the very significant advantage of eliminating wall deposit formation and could lead to much more efficient photoprocesses than those in current or recent use.

Furthermore, it appears that the concept rests on the rather unexpected successful transport of free radicals through a grid with very low open area. Much remains to be determined concerning such radical transport, including the effects of grid type and geometry, the length of zone A, the intensity of incident radiation, chlorine gas density, various inert gases, and the possible extension of this approach to liquid-liquid systems. Successful investigations of these factors may permit the application of this radical transport technique in a wide range of industrial processes.

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