Free Radical Transport in a Two-Zone Photoreactor

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Dworkin and Dranoff (1978) reported a study of the gas-phase photochlorination of chloroform in a novel photoreactor which was divided into two different functional zones by a perforated teflon diaphragm or grid. The idea of physically distinguishing the photoinitiation zone and the subsequent thermal reaction zone for free radical photoreactions originated with Lucas (1971), who later (1973) presented some experimental results obtained for a gas-liquid reaction, the photooximation of cyclohexane.

Our subsequent study (Dworkin and Dranoff, 1978) proved that this type of reactor could be utilized effectively in a gas-phase system. Furthermore, it demonstrated that segregation of the reactor into two zones essentially eliminated the problem of opaque wall deposit formation and verified that chlorine-free radicals formed at 1 atm pressure would indeed survive the passage from the irradiated zone through small diameter holes in a thin teflon diaphragm and bring about reaction in the dark or nonirradiated zone. That study was, however, limited to a reactor with a fixed irradiated zone length, a parameter found by Lucas to be a very important determinant of reactor performance.

This study was aimed at development of a more flexible laboratory reactor with which more definitive data could be obtained for this system. This paper presents the design of the photoreactor and the results of the experiments conducted with it.

EXPERIMENTAL

The reaction used in this work was once again the photochlorination of chloroform:

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

As noted previously, this is a free radical chain reaction which may be initiated by exposure of chlorine gas to light over a broad wavelength range. The initiating radiation used in this work was in the near ultraviolet range (peak intensity around 360 nm) and was furnished by two Westinghouse F8T5/BLB black light fluorescent lamps mounted in a suitable reflector.

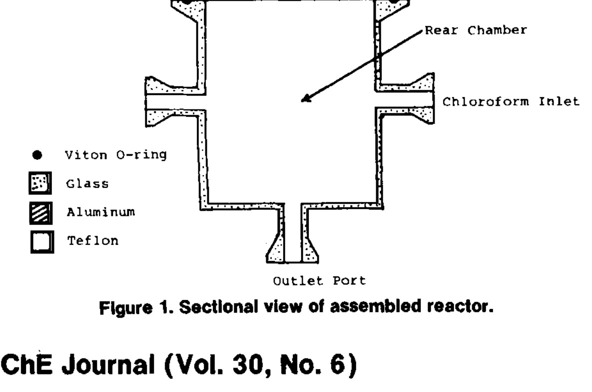

Figure 1. Sectional view of assembled reactor.

The cylindrical reactor, as well as all other parts of the equipment which came into contact with reactant chlorine or the product gases, was made of teflon and glass sections sealed with Viton o-rings. As shown in the assembled section view of Figure 1, the irradiated zone of the reactor was fabricated from glass-filled teflon sections with gas-tight seals provided by Viton o-rings at various locations. The thermal reaction zone was made of glass. The essential feature of this design was that it permitted easy variation of the length of the irradiated zone or forechamber. This length could be changed by replacement of the inner concentric teflon cylinder and matching metal spacer. The former along with the teflon base piece constituted the cylindrical wall of the forechamber. One end of the chamber was sealed by the pyrex glass window while the teflon grid formed the other end. The thermal reaction zone or rear chamber was made from a section of 5 cm i.d. tubing with an o-ring joint. Chlorine gas was supplied to the forechamber through two holes machined in the outer cylinder and either two or six holes located in the lateral surface of the teflon base piece. Feed gas entered the rear chamber through two diametrically opposed inlet ports. That chamber was also fitted with a thermal well and a drain line containing a glass and teflon stopcock.

The entire reactor assembly was held together by an external metal clamping arrangement. The outer teflon cylinder, base piece, teflon grid, and glass section were clamped together first in the reactor support frame and then the inner cylinder, window, and metal spacer were fixed and held in place by a second set of pressure screws. The entire assembly was wrapped with electrical heating tape, and thermocouples were placed in the thermal well and on the exterior surfaces to permit monitoring and control of the reactor temperature. Relevant dimensions of the reactor are indicated in Table 1.

As noted above, the glass window of the reactor was made of pyrex, which is essentially transparent to the radiation used in this work. Most of the experiments were made with a thin teflon grid which was 0.0254 cm (10 mil) thick. This grid contained 88 holes having a diameter of 0.0397 cm ($^1/_{64}$ in.), yielding 0.867% open area. A second grid having a thickness of 0.635 cm ($^1/_4$ in.) and also containing 88 holes of the same diameter was also used for several experiments.

Following initial testing of this reactor, a small teflon-covered metal ring was added at the teflon base piece of the forechamber, Figure 1. This was found to be necessary to offset problems of deflection and creep of the teflon base piece itself, particularly under clamped, high-temperature conditions (77 to 155°C). Slow distortion of the base piece made it difficult to maintain adequate seals in the reactor for periods of more than a few hours. The metal ring was useful in overcoming this problem and extending the operational times.

The remaining apparatus consisted of a feed supply and monitoring system and a product recovery and analysis section. Liquid chloroform was pumped into the system by a positive displacement pump and vaporized in a coil submerged in a heated bath. High-purity chlorine and nitrogen (for purging) were supplied from pressurized cylinders. All of the feed and product lines were covered with electrical heating tape and maintained at approximately 100°C to avoid condensation. Product samples were obtained by diversion of the reactor effluent gases to a small glass sampling loop chilled in a dry ice-ethanol bath. Cold, condensed samples were added slowly to aqueous KI solutions to remove the chlorine, and the liberated iodine was then reduced by titration with aqueous sodium thiosulfate. Following centrifugation, the organic phase was separated and analyzed

TABLE 1. REACTOR DIMENSIONS

Forechamber	Rear Chamber
Outer Cylinder Dia., 7.1 cm	Outer Dia., 7.0 cm
Irradiated (Window) Dia., 4.0 cm	Inside Dia., 5.0 cm
Outer Cylinder Length, 5.5 cm	Length, 6.0 cm
Irradiated Zone Length, 0.95, 3.33 or 4.45 cm	Volume, 117.8 cm^3

for chloroform and carbon tetrachloride by gas chromatography. Preliminary tests of the entire system with premixed liquid feeds containing $CHCl_3$ and CCl_4 and flowing chlorine (but no radiation) proved that samples could be recovered and analyzed quantitatively by this method. Further details concerning the equipment and its operation may be found elsewhere (Mazich, 1980).

RESULTS AND DISCUSSION

Preliminary experiments were carried out with this reactor but without teflon grid, thus corresponding to more conventional photoreactor operation with the exception that the two gas feed streams entered the reactor separately (chlorine in the forechamber and chloroform in the rear). These experiments, run at 77°C, showed that the reactor would reach steady state in well under 30 minutes with no significant change in reaction rate over two hours. Observed rates of reaction (CCl_4 production rates) for a forechamber length of 0.95 cm and a combined feed rate of 3.34×10^{-4} mol/s (Cl_2 to $CHCl_3$ molar ratio of 0.92) were approximately 4.0×10^{-6} mol/s. Although the reactor flow pattern in these experiments was not known, it was certainly too complex to permit a ready analysis of the rate data or a meaningful quantitative comparison with previous results. However, an important qualitative observation was made. Although in the previous study by Dworkin (1977), experiments run under comparable conditions with no grid yielded a white deposit on the reactor window and a rapid drop-off in measured reaction rate, only a faint deposit was formed with this reactor, and no diminution of the reaction rate was observed. Similar results have recently been reported by Richard (1982) in a comparable experiment done elsewhere.

The lack of heavy film formation is probably due to the flow pattern which arises in the present reactor. As pointed out above, Cl_2 gas enters the forechamber radially through two small holes located in the teflon base piece. These two jets produce a strong gas flow parallel to the reactor window, thus effectively "scouring" that surface while also preventing significant inflow of $CHCl_3$ from the rear chamber. As a test of this hypothesis, another experiment was made using a second base piece containing six equally spaced radial inlet holes but with all other conditions the same. A heavier film formed in this case, but still without significant variation in the observed rate of reaction over a 90-min period. The formation of a heavier deposit under slower inlet velocity conditions is supportive of the proposed flow pattern effects. One final preliminary experiment was carried out with the two inlet hole base but a forechamber length of 4.45 cm. In this case the film formed was again very light, while the observed rate of reaction increased almost twofold. Scouring of the window is unlikely in this situation because of the increased distance between the chlorine inlet holes and the window. However, the flow pattern may still be such as to prevent significant penetration of $CHCl_3$ molecules into the forechamber. The increased rate may simply reflect enhanced utilization of the incident radiation because of the increased effective reactor volume.

The remaining experiments were made using a teflon grid. For most of these it was found necessary to make the flow rate of gas in the forechamber higher than that in the rear chamber in order to minimize back flow through the grid and subsequent mixing of the feed gases in the irradiated zone. There were no problems with deposit formation in any of these experiments.

Results of some of these experiments are indicated in Table 2. Rates reported there are average values for the indicated time intervals. Early replicated experiments showed that measured rates were reproducible to within 5%.

Initial experiments were made using the thin grid and some of the results are listed in Table 2. Experiment 8 confirmed that the reactor does function effectively in this configuration although the rate with a grid in place was only about ¼ that measured with no grid. However, reversed flow experiments, numbers 11 and 13, showed that the grid was essentially transparent to the radiation used. In these reversed flow experiments, chloroform, which does not absorb radiation in the 360 nm range, was fed to the forechamber while chlorine was delivered to the rear zone. Flow rates of the two gases were interchanged to maintain the fixed 3:1 forechamber to rear chamber flow ratio used in this work. Because this increased significantly the mole fraction of $CHCl_3$ in the reactor, it was necessary to raise the temperature of the reactor in order to avoid condensation of this reactant. Thus, the reversed flow experiments were made between 153 and 155°C. Note that the measured rates in Experiments 11 and 13 were very close as expected, since forechamber length should play no role with a non-absorbing gas present, and about twice that found in Experiment 12 in which the standard feed arrangement was used at 155°C. Experiment 12a was run without illumination to check the dark reaction at this temperature and showed that the latter contributed less than 10% to the measured rate.

The conclusion drawn from the foregoing experiment was that with a forechamber length of 0.95 cm, significant radiation reached the grid surface unabsorbed and was transmitted through the teflon to initiate additional reaction in the rear chamber. In order to check further on this phenomenon, experiments were run with the thick grid. The latter had been separately tested using a photometer and found to transmit negligible radiation. Table 2 presents the results of these experiments. These show that the rate at 77°C is reduced to approximately ½ that of the thin grid experiments. This reduction is due to two factors: (1) the elimination of light transmission through the grid itself, and (2) the deactivation of more chlorine radicals during their passage through the longer grid holes. Incidentally, estimates of the transit times for the chlorine gas through the grid openings under these experimental conditions are 2.6×10^{-4} s for the thin grid, and 25 times that or 6.4×10^{-3} for the thick grid.

TABLE 2. GRID EXPERIMENTS

Experiment	Feed Flow Arrangement	Temp. (°C)	Forechamber Length (cm)	Reaction Rate (gmol/s) $\times 10^7$	Time (min)
Thin Grid (0.0254 cm)					
8	Standard	77	0.95	10.3	30–75
11	Reversed	153	0.95	39.0	30–80
13	Reversed	155	4.45	42.4	15–30
12	Standard	155	0.95	23.2	21
12a	Standard	153	0.95	2.4	(No lamp)
16	Standard	77	3.33	8.7	45–60
17	Standard	77	4.45	4.8	30–60
Thick Grid (0.635 cm)					
14	Standard	153	0.95	7.1	10–25
15	Standard	77	0.95	4.9	2–15
18	Standard	77	3.33	3.3	15
19	Standard	77	4.45	3.4	15

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* Feed flow rates were: Cl_2—3.75×10^{-4} gmol/s and $CHCl_3$—1.25×10^{-4} gmol/s in all experiments except 11 and 13 in which they were interchanged.

Comparison of Experiments 14 and 15 show that the reaction rate at 153°C is higher by 2.2×10^{-7} mol/s, very close to the rate of the thermal reaction at this temperature as measured in Experiment 12a.

Additional data were obtained at longer forechamber distances as shown for Experiments 16, 17, 18 and 19 in Table 2. In these cases, it is expected that transmission of radiation through the grid would not be significant since the increased path lengths insure that only negligible amounts of radiation should penetrate through the chlorine gas to reach the grid surface. Nonetheless, the thin grid data do show that the rate is larger than that for the thick grid, as expected because of radical deactivation effects, but still decreasing with forechamber length. It may be that the flow pattern in the rear chamber differs somewhat due to grid thickness and this factor contributes to the observed rate. Some experiments were also made to check the effect of total flow rate and molar ratio of the feed gases on the rate of reaction, but these did not indicate any significant trends.

It should be noted that Richard (1982) has recently reported studies made with a reactor of comparable design but illuminated with a high-pressure mercury lamp. His results indicate rates similar to those reported by Dworkin (1977) and also show that there is an optimum flow rate for each forechamber length at which the rate goes through a maximum.

Comparison of the reaction rates found in this work with those observed previously by Dworkin indicate that his rates were approximately 10 times higher, despite an incident intensity which was only ¼ of that in this work. His reactor diameter was twice that used here and his grid contained 2.5 times as many openings per unit area. The difference in rate suggests that an increased reactor surface to volume ratio in the present smaller diameter case has a pronounced influence on radical termination rates. The effect of hole distribution in the grid similarly may reflect a change in radical termination rates as the number of holes per unit area is changed. However, such conclusions must remain speculative at present in the absence of additional data.

This study has demonstrated clearly that chlorine radicals can indeed be transported through small-diameter holes in a relatively thick piece of teflon in sufficient number to initiate measurable reactions in a dark reactor zone. The measurements have shown that thin, apparently opaque, teflon diaphragms can transmit significant amounts of near UV radiation and this fact should be considered in the design and analysis of future two-zone reactors. The potential of the two-zone reactor concept for photoreactions which are subject to deposit and by-product formation remains considerable. However, its benefits may also be achieved by appropriate control of the reactor flow pattern.

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Simplest Equation of State for Vapor-Liquid Equilibrium Calculation: a Modification of the van der Waals Equation

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There is evidence in the literature (Döring and Knapp, 1980; Lira et al., 1981; Adachi et al., 1983a) that practically identical results in vapor-liquid equilibrium (VLE) calculations can be obtained from various cubic equations of state, in spite of their differences in representing pure-component properties, and these results are frequently comparable to those obtained from more complex equations of state. In applying these cubic equations to VLE calculations, the general practice is to treat the cohesion parameter a temperature-dependent in addition to the inclusion of an adjustable binary interaction coefficient k_{ij}.

It is less costly to use a simpler equation, especially when the required number of iterative calculations is large, as in the VLE calculations for multicomponent systems. The objective of this work is, therefore, to obtain a suitable but simplest possible equation for VLE calculations.

We attempted to develop and compare three generalized temperature functions for representing Ω_a, which is related to the parameter a by $a = \Omega_a R^2 T_c^{\,2}/P_c$. The performance of several selected cubic equations has been evaluated. The VLE values used as the basis for the evaluation are limited to binary mixtures of normal fluids, which are important to petroleum and cryogenic industries.

SELECTION OF EQUATIONS FOR EVALUATION

The Redlich-Kwong (RK) (1949) equation as modified by Soave (SRK) (1972) and the Peng-Robinson (PR) equation (1976) are two of the currently popular equations.