H^{E*} = heat of solution at saturation conditions and 298 K (J/mol)
MW = average molecular weight of liquid phase at saturation conditions (kg/kmol)
$t_{\max}$ = time at which maximum temperature difference occurs (min)
$(-\Delta T)_{\max}$ = maximum experimental temperature difference at the interface (K)

Greek Letters

$\theta_{\max}$ = maximum theoretical temperature change defined by Eq. 1 (K)
ρ = density (kg/m^3)

Subscripts

i = top or lighter liquid phase
j = bottom or heavier liquid phase
ij = physical property for component i in phase rich in component j

LITERATURE CITED

Aguirre, F. J., "Mass and Heat Transfer in Partially Miscible Liquid-Liquid Systems," Ph.D. Thesis, Univ. of Pittsburgh (1982a).

Aguirre, F. J., G. E. Klinzing, S. H. Chiang, and W. K. Jing, "Temperature Measurements During Mass Transfer in Partially Miscible Liquid-Liquid Systems," *Chem. Eng. Commun.*, 17, 117 (1982b).

Austin, L. J., W. E. Ying, and H. Sawistowski, "Interfacial Phenomena in Binary Liquid-Liquid Systems," *Chem. Eng. Sci.*, **21**, 1109 (1966).

Davies, G. A., and J. D. Thornton, "Coupling of Heat and Mass Transfer Fluxes in Interfacial Mass Transfer in Liquid-Liquid Systems," *Letters in Heat and Mass Transfer*, **4**, 287 (1977).

Thornton, J. D., and T. J. Anderson, "Surface Renewal Phenomena in Liquid-Liquid Droplet Systems with and without Mass Transfer," *Int. J. of Heat and Mass Transfer*, **24**, No. 11, 1847 (1981).

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Photochlorination of Methane in a Two-Zone Photoreactor

DIPAK CHAKRAVARTY and
J. S. DRANOFF

Chemical Engineering Department
Northwestern University
Evanston, IL 60201

In recent studies (Dworkin and Dranoff, 1978; Mazich, 1980; Richard, 1982), the two-zone photoreactor concept was evaluated via the gas-phase photochlorination of chloroform. Lucas (1971, 1973) originally proposed that by-product formation and deposition of opaque films on reactor windows could be eliminated by using a perforated teflon diaphragm or grid to divide the flow reactor into two zones. He suggested that reactive species formed in the photoinitiation zone would flow through the grid into the thermal reaction zone where reaction would be completed.

The previous studies verified that chlorine-free radicals will behave in this way and explored the influence of grid thickness and open area, photoinitiation chamber length and reactant gas flow rates on reactor performance. They showed that increased open area favors higher reaction rates, while increased total gas flow rate or photoinitiation chamber length may increase or decrease reaction rates. The purpose of this study was to investigate the use of the two-zone reactor for the more complex photochlorination of methane.

EXPERIMENTAL

The photochlorinations of methane and its first three chlorine derivatives proceed as:

$$CH_{4-n}Cl_n + Cl_2 \xrightarrow{h\nu} CH_{3-n}Cl_{n+1} + HCl, \quad n = 0, 1, 2, 3 \tag{1}$$

These reactions have been carried out commercially (Hirschkind, 1949; Sconce, 1962), both thermally and photochemically. While thermal chlorination usually requires temperatures in excess of 250°C, photochlorination at 300 to 500 nm will proceed at 25°C. In either case, all four reaction products (CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4) are produced, even at low conversions which should favor the production of CH_3Cl, unless the feed composition is specifically regulated. (For example, a high methane:chlorine ratio favors the production of CH_3Cl.) Furthermore, methane and chlorine form explosive mixtures between approximately 40 and 90 mol % chlorine (Seya, 1970)—another factor in determining reactor feed conditions.

Methane photochlorination was studied most extensively by Ritchie and Winning (1950), who showed that dark reaction was negligible at 25°C and that the reaction proceeded by a radical chain mechanism.

For the production of CH_3Cl:

$$\text{Initiation: } Cl_2 \xrightarrow{h\nu} 2\,Cl\cdot \tag{2a}$$

$$\text{Propagation: } Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl \tag{2b}$$

$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot \tag{2c}$$

$$\text{Termination: } Cl\cdot + Cl\cdot \xrightarrow{\text{wall}} Cl_2 \tag{2d}$$

$$CH_3\cdot + Cl\cdot \xrightarrow{\text{wall}} CH_3Cl \tag{2e}$$

$$CH_3\cdot + CH_3\cdot \xrightarrow{\text{wall}} C_2H_6 \tag{2f}$$

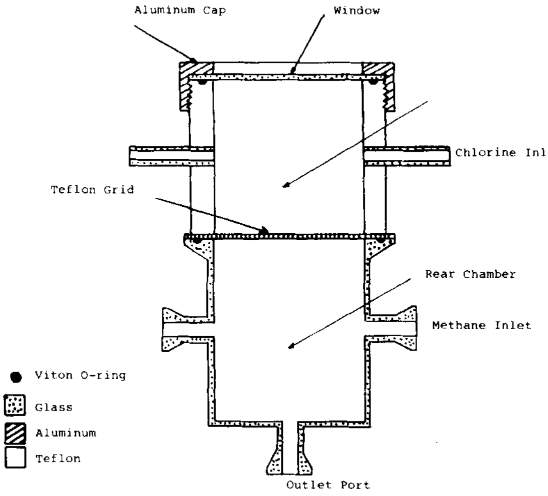

Figure 1. Sectional view of assembled reactor.

The subsequent reactions follow in the same fashion, beginning with Step 2b, but with CH_4 replaced by the appropriate chlorinated derivative.

The cylindrical reactor designed for this study is illustrated in Figure 1. It consisted of a forechamber machined from glass-filled teflon and the same glass rear chamber used previously by Mazich (1980; Mazich and Dranoff, 1984). Forechamber units were constructed with a 5.0 cm inner diameter and lengths of 1.91, 3.81, and 5.08 cm. Two diametrically opposed gas inlet ports were located at the midpoint of each cylinder, Figure 1. The upper end of the cylinder was sealed by a pyrex window and a Viton O-ring held in place by a threaded aluminum cap.

Four teflon grids were used in this work; their characteristics are indicated in Table 1. Additional experimental details are presented elsewhere (Chakravarty, 1981).

The fore and rear chambers were clamped together with the cylindrical axis horizontal, and the reactor was supported within an electrically heated air bath maintained at 30 ± 1°C. The bath had a pyrex window through which the reactor was illuminated by two Westinghouse F8T5/BLB fluorescent lamps. All feed and product lines were glass tubing connected by heat shrinkable teflon and O-ring joints.

Reactor effluent gas to be analyzed was first bubbled through a scrubber filled with supersaturated NaOH solution to remove Cl_2 and HCl and then injected via a sampling valve into a gas chromatograph. Of the components remaining after scrubbing, only methyl chloride (CH_3Cl) is very slightly soluble in the concentrated alkaline solution, so that the latter is quickly saturated making the exit gas representative of the reactor effluent. Preliminary testing with pure component gases (Cl_2, CH_4, CH_3Cl) and liquids (CH_2Cl_2, $CHCl_3$, CCl_4) verified the accuracy of the sampling system and permitted calibration of the gas chromatograph.

RESULTS AND DISCUSSION

After initial tests verified that thermal reaction was negligible, several preliminary experiments were made without a grid but with the feed gases delivered separately, chlorine to the forechamber and methane to the rear chamber (standard feed arrangement). Flow rates of chlorine and methane were maintained at a 10:1 ratio (2.1×10^{-4} gmol/s and 0.21×10^{-4} gmol/s, respectively) to avoid concentrations in the explosive range and to minimize the backflow of methane to the forechamber. One to two hours were required to achieve steady state. (Chromatographic analysis alone required approximately 20 min per sample.) For the preliminary experiments, Table 2, the reported reaction rate is the overall rate of methane disappearance.

TABLE 1. TEFLON GRID CHARACTERISTICS

Grid	Thickness (cm)	No. of Holes	Hole Dia. (cm)	Open Area (cm²)	Open Area %
1	0.0254	88	0.0762	0.401	1.98
2	0.635	88	0.0762	0.401	1.98
3	0.0254	361	0.0508	0.732	3.61
4	0.0254	741	0.0381	0.845	4.17

These results, which serve mainly as a point of reference for the subsequent two-zone reactor data, revealed two interesting facts. First, while the rate of reaction was essentially unchanged as the forechamber length was reduced from 5.08 to 3.81 cm, it increased markedly when the distance was reduced further to 1.91 cm. Second, the product distribution shows the expected pattern—all four chlorinated products present in substantial amounts, but with CH_2Cl_2 predominating.

Since the flow patterns in this reactor are not known, it is not possible to subject the rate data to further kinetic analysis. While there must be mixing of the chlorine and methane streams induced by the inlet jets of chlorine, complete mixing is unlikely. In the previous work on photochlorination of chloroform without a grid (Mazich and Dranoff, 1984), overall rates were comparable to those found here but showed the opposite trend with increasing forechamber distance. Different flow patterns resulting from the different chlorine inlet arrangements in these two studies may be responsible for the observed trends. However, no further mechanistic explanation is apparent at present.

It should be noted that there was no problem with film deposition in any of these experiments.

Subsequent experiments were conducted in the two-zone reactor configuration using the teflon grids described in Table 1. In all such experiments, the reactor effluent stream contained only CH_4 and CH_3Cl, with trace amounts of CH_2Cl_2 in marked contrast to the results shown in Table 2 and by others (Ritchie and Winning, 1950).

Table 3 presents results of experiments with thin and thick grids and standard and reversed flow. The effect of grid thickness is indicated in Table 3a. Although the thin grid is known to transmit ultraviolet radiation in the range used here (Mazich and Dranoff, 1984), when the large forechamber is filled with chlorine the radiation should be almost completely absorbed before the grid. Hence, the decrease in rate with the thick grid reflects the loss of chlorine radicals due to recombination during passage through the grid. It is otherwise encouraging to note that the observed reaction rates are not severely diminished compared to the no-grid data of Table 2.

For the reversed flow experiments reported in Table 3b, there should be no attenuation of the radiation in the forechamber since it is filled with nonabsorbing methane. Therefore, the reaction rate for reversed flow results from transmission of radiation through the grid to the rear chamber with initiation of chlorine radicals there. Experiments 4a and 4b suggest that 7 to 8 times as much radiation is transmitted through the solid portion of the thin grid itself as through the grid openings. Furthermore, for the thick grid (Experiments 7 and 4b), the ratio of rate in the reversed and standard flow cases is very close to the open area fraction which is the

TABLE 2. SEGREGATED FEED: NO GRID EXPERIMENTS

Expt.	Forechamber Length (cm)	CH_4 Reaction Rate (gmol/s) × 10^7	Fractional Conversion	Product Distribution Mole Fractions CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
5	5.08	41.4	0.197	0.158	0.366	0.251	0.225
10	3.81	39.1	0.186	0.127	0.411	0.277	0.185
13	1.91	61.1	0.291	0.157	0.295	0.279	0.269

TABLE 3a. TWO-ZONE REACTOR: STANDARD FEED FLOW ARRANGEMENT

Experiment	Forechamber Length (cm)	Grid	Reaction Rate (gmol/s) × 10^7	Fractional Conversion
6	5.08	1	33.6	0.160
7	5.08	2	23.8	0.113

TABLE 3b. TWO-ZONE REACTOR: REVERSED FEED FLOW ARRANGEMENT*

Experiment	Forechamber Length (cm)	Grid	Reaction Rate (gmol/s) × 10^7	Fractional Conversion
4	5.08	None	57.0	0.015
4a	5.08	1	4.20	0.0011
4b	5.08	2	0.51	0.00013

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* For these 3 experiments only, flow rates of methane and chlorine were 3.9 and 0.33 × 10^{-4} gmol/s, respectively.

TABLE 4. TWO-ZONE REACTOR: STANDARD FEED ARRANGEMENT

Experiment	Forechamber Length (cm)	Grid	Reaction Rate (gmol/s) × 10^7	Fractional Conversion
6	5.08	1	33.6	0.160
8	5.08	3	39.5	0.188
9	5.08	4	47.3	0.225

same as the ratio of radiation incident on the chlorine molecules in the reactor in those two cases.

The effect of grid open area is explored further in Table 4 which shows clearly that rate increases strongly with increasing open area. Since radiation transmission through the thin grids is not important in these experiments because of the long, chlorine-filled forechamber, this increase probably results from changes in flow pattern and corresponding changes in wall termination phenomena.

The effect of forechamber length is illustrated in Tables 5a and 5b. For both thick and thin grids, the rate of reaction is essentially constant for forechamber lengths of 1.91 and 3.81 cm, being slightly higher on average for the thin grid. However, when the forechamber length is increased to 5.08 cm, the rate increases in both cases. This result is not in accord with the previous experience of Mazich and Dranoff (1983), who reported the opposite trend. However, Richard (1982) and Lucas (1973) have both reported similar effects. Indeed, Richard's data for the photochlorination of chloroform show that the effect reverses as reactant flow rates increase.

Neglecting the termination of chlorine radicals in the forechamber, a reasonable assumption in the absence of an inert gas species, an increase in forechamber length at low flow rates should increase the absorption of radiation and result in production of more Cl radicals to react with methane. As the gas flow rate increases, however, mixing and turbulence in the forechamber may become intensified, increasing radical recombination at the walls and causing the reaction rates to fall. Increasing the forechamber length in this regime would merely add additional surface for the recombination reactions. Clearly, more experimental observations are needed to elucidate the importance of these mechanisms.

TABLE 5a. THIN GRID TWO-ZONE REACTOR: STANDARD FEED ARRANGEMENT

Experiment	Forechamber Length (cm)	Grid	Reaction Rate (gmol/s) × 10^7	Fractional Conversion
6	5.08	1	33.6	0.160
11	3.81	1	14.0	0.067
14	1.91	1	16.0	0.076

TABLE 5b. THICK GRID TWO-ZONE REACTOR: STANDARD FEED ARRANGEMENT

Experiment	Forechamber Length (cm)	Grid	Reaction Rate (gmol/s) × 10^7	Fractional Conversion
7	5.08	2	23.8	0.113
12	3.81	2	14.0	0.067
15	1.91	2	14.0	0.067

The present investigation confirms the feasibility of the two-zone photoreactor concept and unexpectedly demonstrates that reaction selectivity may be strongly affected by operation in this mode. The implications of this result may be significant if it can be shown to be of more general validity. This work also confirms the strong influence of forechamber length and flow rate on reactor performance. All of these factors merit further study if the mechanistic details of the two-zone photoreactor are to be properly understood.

Literature Cited

Chakravarty, D., "Photochlorination of Methane in the Two-Zone Photoreactor," M.S. Thesis, Northwestern Univ., Evanston, IL (1981).

Dworkin, D., and J. S. Dranoff, "Free Radical Transport in a Photochemical Reactor," *AIChE J.*, **24**, 1134 (1978).

Hirschkind, W., "Chlorination of Saturated Hydrocarbons," *Ind. Eng. Chem.*, **41**, 2749 (1949).

Lucas, G., "A New Concept in Oximation by the Nitrosyl Chloride Molecule," *Inf. Chimie*, **16**, 33 (1971).

Lucas, G., "Reactions par Transfert de Radicaux Libres," *ibid.*, No. 126, 87 (Dec., 1973).

Mazich, K. A., "Free Radical Transport and Light Transmission in the Two-Chambered Photochemical Reactor," M.S. Thesis, Northwestern Univ., Evanston, IL (1980).

Mazich, K. A., and J. S. Dranoff, "Free Radical Transport in a Two-Zone Photoreactor," *AIChE J.*, (Nov., 1984).

Richard, M., "Noveaux Types de Reacteur Photochimique Industriel," Thesis, L'Institut National Polytechnique de Toulouse, Toulouse, France (1982).

Sconce, J. S., Ed., "Chlorine, Its Manufacture, Uses and Properties," Reinhold Publishing, New York (1962).

Seya, H., "ACM Process-Methane Chlorination Process," *Chem. Economy and Eng. Rev.*, **2**, 34 (1970.

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