Transfer of Photochemically-Produced Chlorine Atoms through a Grid

MICHEL RICHARD and
MICHEL LENZI

Centre de Gémè Photochimique
Ecole Nationale Supérieure de Chimie
Toulouse France

INTRODUCTION

In photochemical reactions, it can be useful to separate the purely photochemical step (radical producing step) from the thermal steps (radical reacting). So doing, only the relevant molecules are irradiated and side reactions will be impeded; the possibility of film deposits on the irradiation surface, as reported by many authors (Cassano and Smith, 1966; Ziolkowsky et al., 1973; Lucas, 1971), will be eliminated. No shutdowns will be needed for cleaning bulbs or transmitting surfaces.

Despite the numerous potential advantages of this technique, very few studies have been made in this field, partly due to lack of theoretical support. However, a mathematical approach of the concept of photochemical space intermittence has been employed by Noyes (1959) to measure diffusion coefficients of reactive free radicals. An application of Noyes's ideas has been proposed by Lucas (1971) as a two-chambered reactor, in which the photochemical reaction is divided into: a "bright" step where the absorbing material is irradiated; and a "dark" step where the activated species, transferred through a nearly opaque grid, are reacted.

Lucas presented the first experimental data for such a reactor in 1973. It was followed by the work of Dworkin (1978) and Mazich (1980) which deal with the use of a segregated reactor for the gas-phase photochlorination of chloroform.

Recently Lucas (1982) proposed a theory for the transfer of activated species, in which it appears that the transfer is governed mainly by two parameters: the volume of the irradiation chamber and the flow rate of the irradiated reactant.

This paper presents the results of an investigation carried out to confirm the effect of these parameters.

EXPERIMENTAL

The reaction chosen was the well-known chlorination of chloroform $CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$ (Huff and Walker, 1962; Chiltz et al., 1963; Dworkin and Dranoff, 1978) because of its simplicity and the ease of titration of the products. (Quantitative measurements were made by vapor-phase chromatography for CCl_4 and by volumetric analysis for HCl.)

All parts of the reactor in contact with the reagents were made of glass and teflon only. It used a section of an E.I.V.S.-Corning column, 80 mm internal diameter and 100 mm in length. The end pieces were fitted to the glass element with flanges, Figure 1. Teflon spacers of various thicknesses allowed the irradiation chamber to volume to be varied (length l). The lengths were 3, 13, and 33 mm. The chamber was sealed in several places with Viton "O" rings. The grid, one of the most important parts of the design, must be as thin as possible for a good transfer, and made in a totally opaque material. Ordinary teflon was thus discarded because of its translucency (Mazich, 1980), and a completely opaque material was used. The open areas of the grids varied from 0.82 to 2.3%, the hole diameter being 0.25 mm. The reaction temperature was maintained with heating tapes (65 or 90°C). The light source used was a Philips HPK 125 w Hg high-pressure lamp. A Milton-Roy controlled volume pump, feeding a 90°C thermostated vaporizer, supplied the reactor with chloroform. The vapor was directed into the reactor, near the grid, by means of a perforated membrane. The chlorine flow, monitored by a Brooks R-2-15-B rotameter, could be directed either to the reaction chamber (setup 1) or to the irradiation chamber (setup 2). Further details of experimental equipment and procedures may be found elsewhere (Richard, 1982).

RESULTS AND DISCUSSIONS

First of all, it was checked that the chlorine free radicals could survive passage through the grid (operating conditions given in Table 1).

When chlorine and chloroform are both introduced into the dark side of the reactor (setup 1), the rate of conversion of the chlorine, in the steady state, due only to the light passing through the grid (2.3% optical transparency) was 4.8%. However, when chlorine is introduced into the bright chamber (Area A) and chloroform into areas B (setup 2), the conversion rate of chlorine rose to 18%, all other operating conditions being the same. The high value measured in the case of setup 2 can only be explained by the transfer of activated species through the grid. The difference in conversion rate between setup 1 and setup 2 demonstrates that the CCl_4 production cannot be attributed to chloroform diffusing or flowing through the grid.

Again, working with the same conditions as before, when the grid was removed, the chlorine conversion rate was around 33% and decreased slightly with time.

The reaction rates measured for our reactor, whose dimensions are similar to that of Dworkin (1978), are about twice as high as those measured by Dworkin (1978). The reason is that the irradiation source is much more powerful in our case (17 W in the range 300–500 nm).

White film deposits have been observed by several authors (Ziolkowsky et al., 1967; Dworkin, 1978), but only a very faint, greasy, transparent film was observed inside our reactor after a long operating period (8 h) without separating grid. The formation of such deposits lowers the light intensity available for the reaction and hence the yield.

Obviously, the presence of the grid lowers the conversion rate, but this rate remains constant over very long periods due to the fact that the light source is no longer obscured. For an industrial purpose

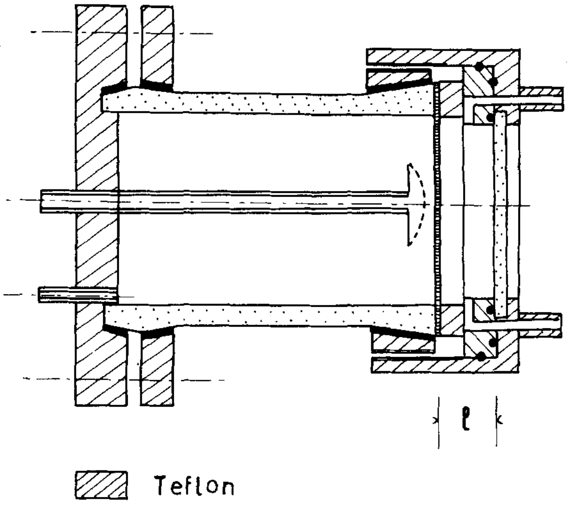

Figure 1. Cross section of the reactor.

TABLE 1. OPERATING CONDITIONS

	Preliminary Experiments	Series of 20 Runs
Grid Optical Transparency	2,30%	0,82%
Reactor Temperature	65°C	65°C
$Cl_2/CHCl_3$ Mole Ratio	1.5	1
Reactants Flow Rate (mole/min)	0.03	0.01-0.06
N_2 Flow Rate (mol/min)	0.03	0
Length of Irradiation Chamber (mm)	33	3, 13, 33

the transfer-reactor would be advantageous, being capable of running for long periods between overhauls.

Radical transport through the grid having been verified, a series of 20 experiments with various feed rates and irradiation chamber length was then carried out (Table 1). The transfer of radicals is determined by measuring the HCl and CCl_4 production, Table 2. As predicted by Lucas (1982), the behavior of the reactor depends on the value given to the length l. For the high values (33 and 13 mm) an optimum flow rate is about 0.03 mol/min.

However, no optimum flow rate was seen in the case where l = 3 mm within the limits studied, production rising steadily with input flow rate. It is also interesting to note that for small flow rates the reactor is more effective as the length is increased, and when high flow rates are used the optimum production is obtained with the smallest values of irradiation chamber length.

A simple equation describing our system was set up. The experimental data (HCl or CCl_4 production vs. flow rate for a given length l) was transformed, using new parameters as units.

Interestingly a linear relationship exists for a given value of l between the conversion rate and the space velocity of chlorine. The number of transfered radicals is inversly proportional to the chlorine space velocity.

Moreover high values of conversion rate obtained for l = 3 mm are below the ones measured in the case where l = 13 or 33 mm. This is due to the fact that for l = 3 mm chlorine does not absorb all the incident photons.

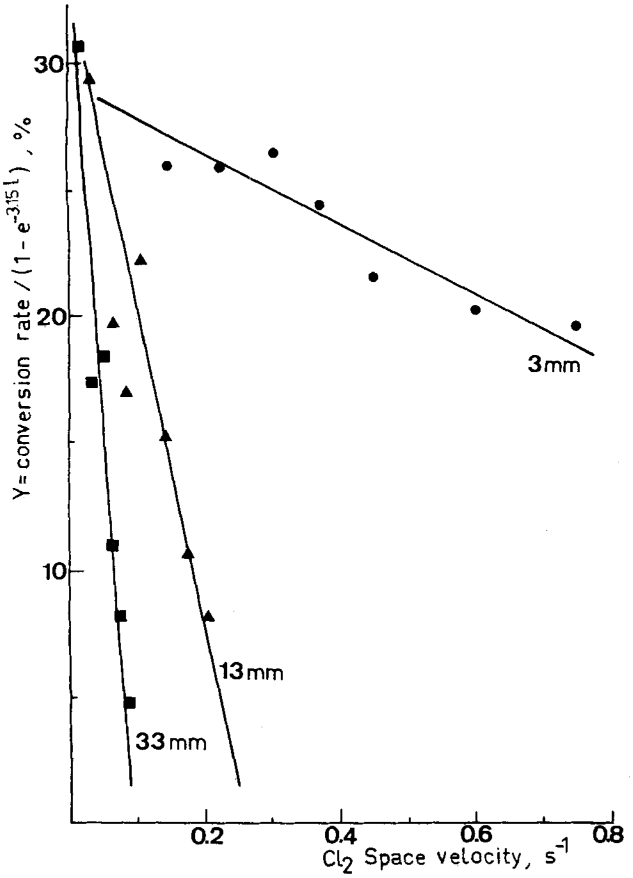

Figure 2. Parameter Y vs. Cl_2 space velocity in zone A.

TABLE 2. CCl_4 OR HCl PRODUCTION FOR DIFFERENT REACTANTS FLOW RATES AND VALUES OF l

CCl_4 Production mol/min $\times 10^{-3}$		Length of Chamber A (mm) 33	13	3
Reactants Flow Rate (mol/min)	0,01	1,53	1,44	0.78
	0,015	/	1,45	1,18
	0,02	1,74	1,66	1,62
	0,025	/	/	1,88
	0,03	2,80	3,29	1,95
	0,04	2,22	2,97	2,51
	0,05	2,06	2,60	3,07
	0,06	1,48	2,54	3,07

To take account of the influence of the length l on chlorine absorption, a parameter Y was defined as the conversion rate divided by the quantity $(1 - e^{-k.l})$ where k is the mean chlorine extinction coefficient ($k = 3.15\ cm^{-1}$).

The quantity Y, a relative indication of the number of transfered radicals for a given reactor configuration, is proportional to the overall quantum yield of our system. Figure 2 presents the variations of parameter Y vs. chlorine space velocity for each reactor configuration.

The set of curves shown in Figure 2 determines the highest conversion rate (29–30%) which may be obtained for small chlorine space velocities.

For a given value l of the irradiation chamber length, Y is linearly related to the chlorine space velocity V.

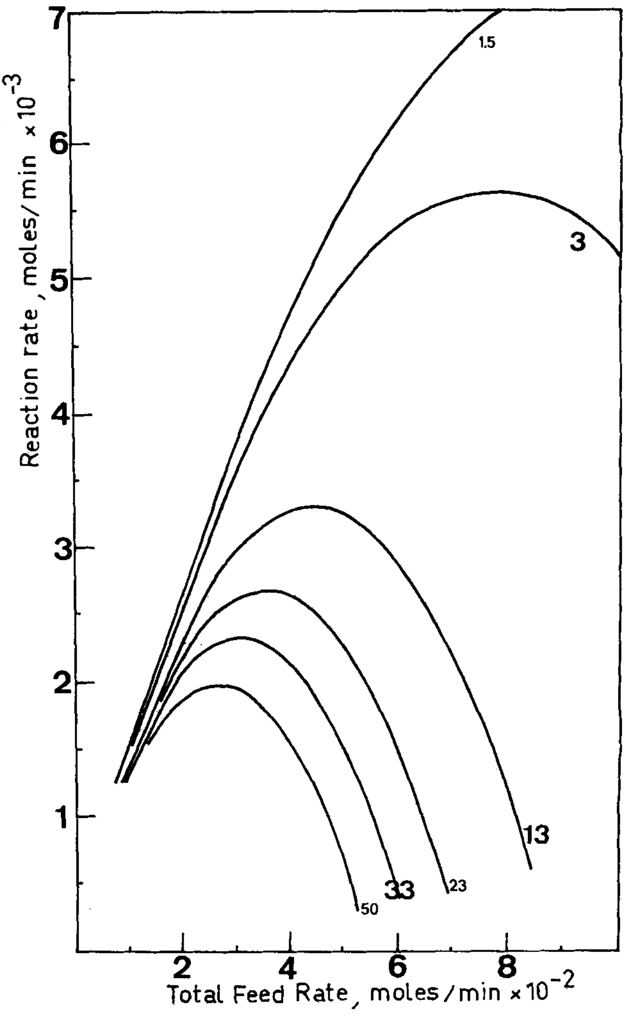

Figure 3. Reaction rate, computed with the hypothesis of total absorption of the incident photons.

$$Y = a\,V + b \tag{1}$$

A relationship between slope a and length l was found empirically, which, introduced into Eq. 1, gives:

$$Y\,(\%) = 29.5 - 1.48\,Q\,l^{0.37} \tag{2}$$

l : length of zone A (cm)

Q : Cl_2 flow rate (cm^3/s)

The chlorine conversion rate is then given by Eq. 3

$$\%\ \text{conversion} = (29.5 - 1.48\,Q\,l^{0.37})\,(1 - e^{-3.15l}) \tag{3}$$

Equation 3 allows the conversion rate and hence the production of our reactor to be predicted.

Curves were plotted using data obtained from Eq. 3. For example, in the case of Figure 3, reaction rate was computed for different length and flow rates, the amount of absorbed photons being constant. It is interesting to note that in this case, for each value taken for l, there is a particular flow rate for which reaction rate is optimized. The results presented in Figure 3 are consistent with the theory proposed by Lucas (1982).

These experiments demonstrated once more the possibility of transfer of radicals through a grid, and the potential advantages of segregated photoreactors.

The effect of the length of the irradiation chamber is underlined, and the data obtained are in good agreement with the work of Lucas (1973, 1982), which deals with the transfer of any kind of activated particle. It would, therefore, be interesting to investigate the transfer of activated species other than radicals.

LITERATURE CITED

Cassano, A. E., and J. M. Smith, "Photochlorination in a Tubular Reactor," *AIChE J.*, **12,** 1124 (1966).

Chiltz, G., et al., "Atomic Chlorination of Simple Hydrocarbon Derivatives in the Gas Phase," *Chem. Rev.*, **40,** 355 (1963).

Dworkin, D., "Free Radical Generation and Transfer in the Vapor Phase Chlorination of Chloroform," MS. Thesis, Northwestern Univ., Evanston, IL (1977).

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

Huff, J. E., and C. A. Walker, "The Photochlorination of Chloroform in Continuous Flow Systems," *AIChE J.*, **8,** 193 (1962).

Lucas, G., "A New Concept in Oximation by Nitrosyl Chloride Molecule," *Info. Chimie*, **99,** 77 (1971).

———, "Reactions par Transfert de Radicaux Libres," *ivid.*, **126,** 87 (1973).

———, "Transfer Theory for Trapped Electromagnetic Energy," *Technique et Documentation*, Lavoisier, Paris (1982).

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

Noyes, R. M., "Photochemical Space Intermittency. A Proposal for Measuring Diffusion Coefficients of Reactive Free Radicals," *J. Am. Chem. Soc.*, **81,** 566 (1959).

Richard, M., "Nouveaux Types de Réacteur Photochimique Industriel," Thèse de Docteur-Ingénieur, I.N.P.T., Toulouse, France (1982).

Ziolkowski, D., A. E. Cassano, and J. M. Smith, "Effect of Wall Deposit on Photochlorination Kinetics," *AiChE J.*, **13,** 1025 (1967).

Manuscript received November 1, 1982; revision received February 16, and accepted March 4, 1983.

Analytic Representation of Convective Boiling Functions

SERGIO EDELSTEIN,
A. J. PEREZ,
and J. C. CHEN

Department of Chemical Engineering
Lehigh University
Bethlehem, PA 18015

A widely used correlation (Collier, 1972; Hsu and Graham, 1976; Rohsenow, 1973) for prediction of convective boiling heat transfer coefficients was developed by Chen (1966). Although alternative approaches have been proposed by others (Borge et al., 1982), the Chen correlation remains widely used (Butterworth, 1982). Based on the concept that heat transfer is caused by two interacting, additive mechanisms (the ordinary macroconvective mechanism and a bubble-induced microconvective mechanism), the Chen correlation was first derived for the case of saturated boiling of single-component nonmetallic fluids and later extended to liquid metals (Chen, 1963) and subcooled boiling (Butterworth, 1972).

The Chen correlation includes two dimensionless empirical functions: an effective two-phase Reynolds number function, F, and a bubble-growth suppression function, S. In the original correlation, F and S were present as empirical graphical functions. Presently, most users utilize tables or piecewise fits to these graphical functions. Explicit expressions for these functions would be more useful for computer design and performance studies, especially when analyzing the parametric sensitivity of heat transfer rate to the various operating variables. As a minor, but useful contribution, this paper presents analytical representations for the F and S functions. Momentum transfer analogy is used to develop a physically meaningful explicit representation for the two-phase Reynolds number function, F. Additionally, an explicit equation is also developed (empirically) for the supression function, S.

As shown by Chen (1966), the F function can be related to the Lockhart-Martinelli pressure drop factor by means of the heat momentum transfer analogy,

$$f = (\phi_{Ltt})^{0.89} \tag{1}$$

where ϕ_{Ltt} is defined as the ratio of frictional pressure drop for two-phase flow to that for liquid-phase flow alone.

The Martinelli parameter (Lockhart and Martinelli, 1949) is defined as,

$$X_{tt}^2 \equiv \left(\frac{\phi_{vtt}}{\phi_{Ltt}}\right)^2 \tag{2}$$