

Chemical Kinetics of the Reactions of SiCl_4 , SiBr_4 , GeCl_4 , POCl_3 , and BCl_3 with Oxygen

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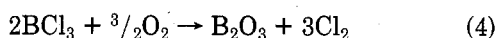
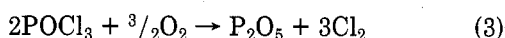
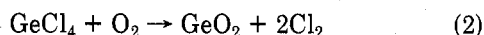
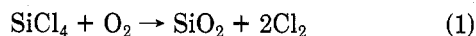
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The chemical kinetics of the reactions which contribute to the modified chemical vapor deposition process of fiber waveguide fabrication have been studied by following the steady state reactant concentrations under a variety of experimental conditions. It was found that the reaction of SiCl_4 , GeCl_4 , POCl_3 , and SiBr_4 with a large excess of O_2 follows reaction kinetics which are first order. The kinetics of the reaction of BCl_3 with oxygen are more complex.

Introduction

The manufacture of highly transparent glass fibers for optical communications most commonly involves modified chemical vapor deposition technique for the formation of the pure glassy material.¹ This process relies on the oxidation of silicon tetrachloride and certain other metal halides to their respective oxides. There is very little available information on the chemical kinetics of the reactions involved:



The reaction mechanism are not known, but probably involve oxychloride intermediates.² As part of a study directed toward increasing the efficiency of optical fiber manufacture, we have studied the rates of these reactions. In the present study, we have limited our observations to the rates of disappearance of the initial halide reagent in the presence of large excesses of oxygen. Among the questions we attempted to address were the following: Does each of the reactions proceed to completion under the conditions normally used for fiber fabrication? Are there differences in reaction rates during simultaneous deposition which could lead to segregation of components during deposition of the glass?

We made some simplifying initial assumptions about these reactions. The most important assumption is that, in spite of the apparent complexity of the reactions, the kinetics will be first order with respect to the halide reagent when oxygen is in large excess. The assumption implies that there is a slow step in the reaction and that this step involves only one halide reagent molecule. This might be the case, for example, if the reaction is initiated by thermal dissociation of a metal-halide bond. This first assumption can be simply written

$$-dc/dt = kc \quad (5)$$

where c is the reagent concentration.

The second assumption is that k in eq 5 follows an Arrhenius law

$$k = k_0 \exp(-E_a/RT) \quad (6)$$

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These two assumptions can be combined into one equation to yield

$$\ln \left[-t^{-1} \ln \left(\frac{c}{c_0} \right) \right] = -\frac{E_a}{RT} + \ln k_0 \quad (7)$$

Thus, our assumptions can be tested by testing the validity of this equation with respect to the three independent parameters: reaction time, t ; initial concentration, c_0 ; and temperature, T .

Experimental Section

The reactions were followed in a flow system using IR spectroscopy. Oxygen was bubbled through the SiCl_4 , SiBr_4 , POCl_3 , or GeCl_4 liquids and the resulting vapor mixture was added to an additional stream of O_2 gas. When BCl_3 was used, its flow was regulated directly by a mass flow controller. The combined gases were passed through a fused quartz reaction cell, which was heated by a tube furnace. The exhaust gas from the heated cell passed into a 4.7-cm long spectrometer cell with AgCl windows, and the absorbance of the gas was read on an IR spectrophotometer at a wavelength corresponding to the strongest absorption peak for each reactant. For SiCl_4 , the peak read was 620 cm^{-1} . For GeCl_4 , the peak read was 460 cm^{-1} . The wavelengths used for SiBr_4 , POCl_3 , and BCl_3 were 500, 590, and 955 cm^{-1} , respectively.

The temperature inside the furnace was measured with a Pt-Pt-10% Rh thermocouple at a point between the cell and the muffle. In order to better define the reaction time, we employed a reaction cell which was constructed from a 5.5 cm long piece of 10-mm i.d. fused quartz tubing. The tubing was fused at each end to 4-mm i.d. fused quartz tubing. The flow velocity through the 4-mm tubing was so high that almost no reaction occurred outside of the 5.5-cm hot zone. The flow rates through the hot zone ranged from 208 to $724 \text{ cm}^3/\text{min}$, so that the reaction time varied from 0.36 to 1.25 s.

Results

SiCl_4 . Our results indicate that the kinetics of the reaction of SiCl_4 with oxygen fit eq 7 very well. Figure 1 shows the Arrhenius plot (eq 7) for the data taken for a series of experiments in which the initial concentration of SiCl_4 was varied from a partial pressure of 0.9×10^{-2} to 3.8×10^{-2} atm. These data are a good fit to the equation with $E_a \approx 100 \text{ kcal/mol}$. Figure 2 shows the Arrhenius plot for a series of experiments in which the reaction time was varied from 0.35 to 1.25 by varying the gas flow rate.

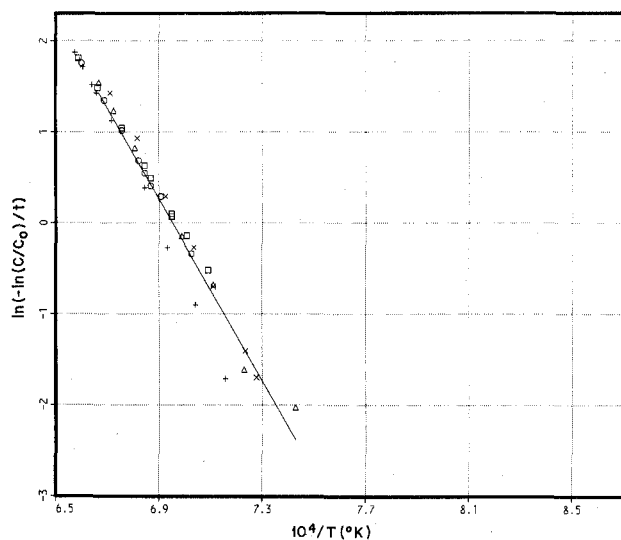


Figure 1. Arrhenius plots for SiCl_4 from five experiments in which the initial concentration, C_0 , of SiCl_4 was varied as follows: Δ , 0.0038 atm; \square , 0.0022 atm; $+$, 0.0017 atm; \circ , 0.0015 atm; \times , 0.0009 atm.

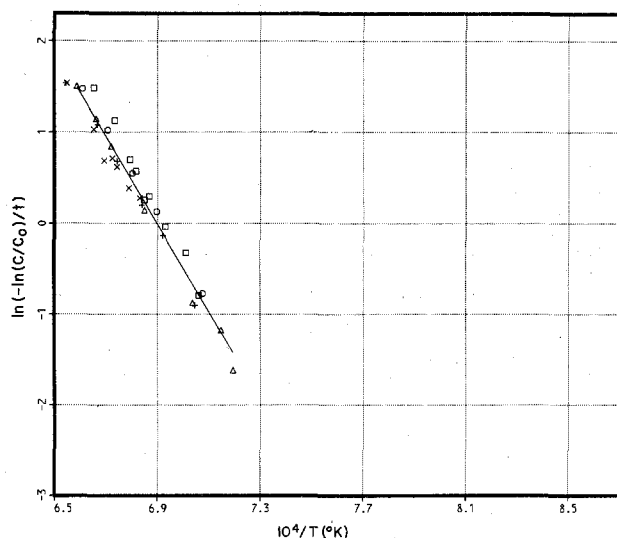


Figure 2. Arrhenius plots for SiCl_4 from five experiments in which the reaction time was varied as follows: \square , 1.25 s; \circ , 0.77 s; Δ , 0.60 s; $+$, 0.43 s; \times , 0.35 s.

In each of these experiments the data are good fits to eq 7.

On the basis of these data, we can conclude that our assumptions that the reaction is first order in the presence of excess O_2 and that it obeys an Arrhenius law are justified. This information may be used to extrapolate the reaction rate to the conditions used in a glass fiber fabrication experiment. Typical conditions for such an experiment are an initial concentration of SiCl_4 of 0.13 atm, a maximum temperature greater than 1400 °C, and a reaction time of at least 0.10 s. The extrapolation of our data using eq 7 indicates that only about 0.01% of the SiCl_4 remains unreacted.

SiBr₄. The reaction of SiBr_4 with oxygen appears to be similar to SiCl_4 , but the activation energy is only about 67 kcal/mol. The Arrhenius plot of our data for SiBr_4 with $t = 0.5$ s is shown in Figure 3b. As in the case of SiCl_4 , our assumption of a first-order reaction appears satisfactory.

GeCl₄. GeCl_4 reacts with oxygen at lower temperatures than SiCl_4 . Typical experimental results are shown in Figure 3a. The Arrhenius plot of data taken for several reaction times is a good fit to eq 7 with an activation energy of about 60 kcal/mol. Data taken in experiments with

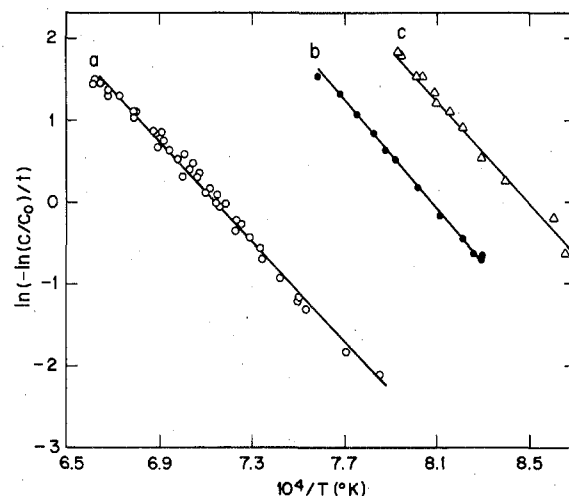


Figure 3. Arrhenius plots for (a) GeCl_4 , (b) SiBr_4 , (c) POCl_3 . The data for GeCl_4 include the results when the reaction time was varied from 0.35 to 1.25 s. The data for SiBr_4 and POCl_3 are for a single reaction time (0.50 s).

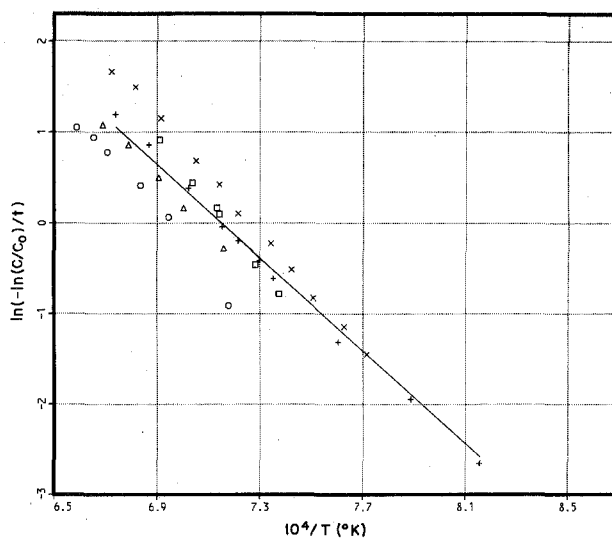


Figure 4. Arrhenius plots for GeCl_4 from five experiments in which the initial concentration of GeCl_4 varied as follows: \times , 0.0013; \square , 0.0033; $+$, 0.0050; Δ , 0.0062; \circ , 0.0076 atm.

different initial concentrations (Figure 4) do not fit eq 7 as well as similar data in the case of SiCl_4 . The data indicate that, at each temperature and initial concentration, the fraction remaining decreases exponentially with time as expected for a first-order reaction. The rate constant, however, appears to decrease with increasing concentration. For the range of initial concentrations tested, the activation energy is about 60 kcal/mol in each experiment. The decrease in rate constant appears to be due to a decrease in the preexponential factor.

POCl₃. POCl_3 reacts at a lower temperature than any of the other reagents tested in this study. Under our reaction conditions, the reaction initiates near 850 °C. The Arrhenius plot indicates a good fit to eq 7 with an activation energy of about 62 kcal/mol (Figure 3c).

BCl₃. The data for the reaction of BCl_3 with oxygen do not fit eq 7. It is clear that our assumption of a single rate-controlling step involving a first-order reaction cannot be supported by these data. Figure 5 shows the effect of varying the initial concentration of BCl_3 . The greatest deviations of these plots from each other are at the lower temperatures. Although this is suggestive of a high-temperature first-order mechanism with some competing low temperature reaction, the data are insufficient to

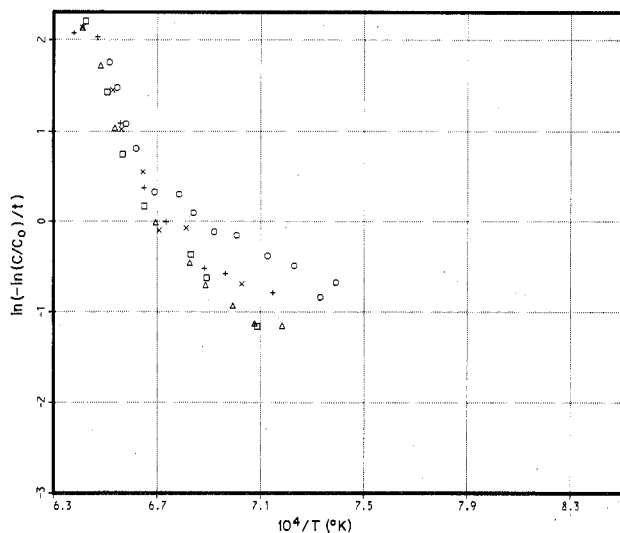


Figure 5. Arrhenius plots for BCl_3 from five experiments in which the initial concentration was varied as follows: \square , 0.0025; \circ , 0.0022; Δ , 0.0019; $+$, 0.0016; \times , 0.0013 atm.

TABLE I: Activation Energy and Preexponential Factors (MCVD Reactions)

reactant	E_a , kcal/mol	preexponential, s^{-1}
SiCl_4	98	8×10^{14}
SiBr_4	67	5×10^{11}
GeCl_4	64	2×10^{10}
POCl_3	62	3×10^{11}

confirm such a suggestion. Geiss and Fröschle have studied the kinetics of the BCl_3 reaction as a function of oxygen concentration.³ They found a third-order dependence on O_2 concentration, but they have not offered a proposed reaction mechanism.

Simultaneous Reactions. In the results above, we have been testing each reagent with oxygen to discover whether it is first order with respect to temperature, initial concentration, and reaction time. In each case where good fits to eq 7 were obtained, we determined an activation energy. These values are listed in Table I and the data are compared in Figure 6.

During the fabrication of an actual preform, however, the reagents are not usually present separately, but rather two or more halide reagents are combined so that a mixture of oxides can be obtained. In order to discover whether the presence of one halide reagent had an effect on the kinetics of the reaction of another oxygen, we have studied mixtures of SiCl_4 and GeCl_4 as well as mixtures of SiCl_4 and SiBr_4 . Some results are shown in Figure 7.

In the experiments with SiCl_4 and GeCl_4 combined, the GeCl_4 causes SiCl_4 to react at lower temperatures with an activation energy of about 60 kcal/mol. This can be compared to an activation energy of 100 kcal/mol for SiCl_4 alone or 60 kcal/mol for GeCl_4 alone. In the combined experiments, the reactions of GeCl_4 is shifted to higher temperatures than for GeCl_4 alone.

Similar results are observed for SiCl_4 combined with SiBr_4 , except that SiBr_4 reaction kinetics are less affected.

Discussion

The data presented here are insufficient to deduce complete reaction mechanisms. The data are consistent with a chain reaction in which the slow step involves only one SiCl_4 (or other reagent halide) molecule. This might be a chain initiation step involving the thermal decomposition of the reagent molecule, or involving the reaction with oxygen to form an oxychloride reactive intermediate.⁴

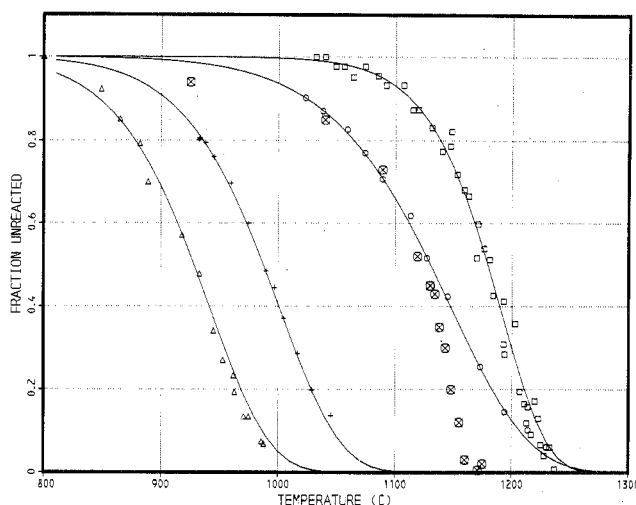


Figure 6. Comparison of the reactions of SiCl_4 , \square ; GeCl_4 , \circ ; BCl_3 , \otimes ; SiBr_4 , $+$; POCl_3 , Δ , with reaction times of 0.5 s. The solid lines are calculated from eq 8 and the data in Table I.

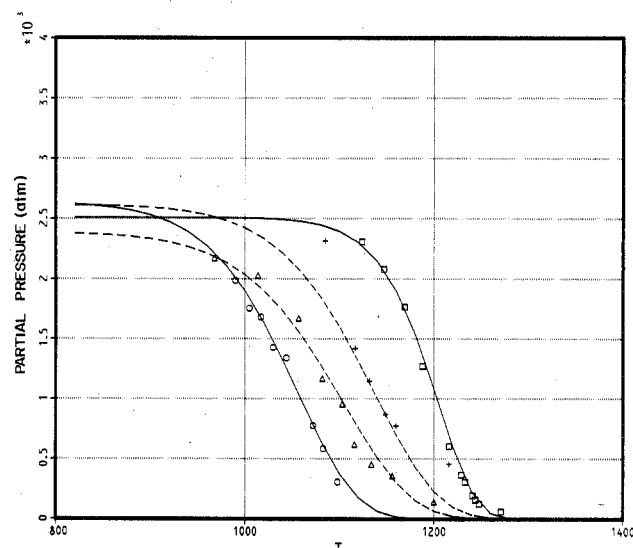


Figure 7. Comparison of the reactions of SiCl_4 or GeCl_4 with O_2 alone to the reaction when SiCl_4 and GeCl_4 are mixed together; \square , SiCl_4 alone (line drawn with $E_a = 110$ kcal/mol); \circ , SiCl_4 in the presence of GeCl_4 ($E_a = 62$ kcal/mol); Δ , GeCl_4 alone ($E_a = 60$ kcal/mol); $+$, GeCl_4 in the presence of SiCl_4 ($E_a = 64$ kcal/mol).

Such a chain initiation step can help explain the changes in kinetic behavior when more than one reactant is present. Consider the data in Figure 7. When SiCl_4 is present alone, the reaction with oxygen initiates near 1100 °C when the chain initiation step begins to occur with an activation energy of about 100 kcal/mol. When GeCl_4 is present, the chain initiation step involving GeCl_4 can begin near 950 °C. Once the chain reaction is started, the free radical intermediates can react with either SiCl_4 or GeCl_4 . This explains the coincidence of the activation energy for the SiCl_4 reaction in the presence of GeCl_4 with the activation energy for the reaction of GeCl_4 alone. The chain initiation (rate determining) step is the same in both cases. The inhibition of the consumption of GeCl_4 may be explained if the chain-propagating reactions involving SiCl_4 are faster than those involving GeCl_4 .

Conclusions

The data presented here are sufficient to show that the reactions with oxygen used in the glass deposition process (except those involving BCl_3) are first order with respect to the halide reagent concentration. The strong interaction of the reaction of one halide reagent with the reaction of

another can tend to cause the oxides to be deposited simultaneously. If that interaction did not occur, preferential deposition of one of the oxides would occur as the gas stream traverses the hot zone. (This would be especially pronounced in the case of POCl_3 and SiCl_4 mixtures.)

We have also shown that the reactions will go to completion under normal glass fiber fabrication conditions. This information serves to define the problem of increasing deposition efficiency as one involving the collection of reaction products, rather than one involving incomplete reaction.

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References and Notes

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Gas Phase Photolysis of Ethyl Bromide at 253.7 nm

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The photolysis of ethyl bromide was studied at 100 Torr and 23 °C using 253.7-nm radiation. In the pure system between 60 and 90 s at an absorbed light intensity of 8.3×10^{13} quanta/cm² s the major products and their respective quantum yields are as follows: hydrogen bromide, 0.26; ethane, 0.40; ethylene, 0.028; 1,1-dibromoethane, 0.102; 1,2-dibromoethane, 0.0092; vinyl bromide, 0.009; 1,1,2-tribromoethane, 0.0027; methane, 0.00052; and methyl bromide, 0.00091. When 5 mol % oxygen is added, the quantum yields in this time period become the following: hydrogen bromide, 0.47; ethane, 0.00032; ethylene, 0.0081; 1,1-dibromoethane, 0.0040; 1,2-dibromoethane, 0.022; vinyl bromide, 0; 1,1,2-tribromoethane, 0; methane, 0.0001; and methyl bromide, 0.091. Bromine is also formed with a quantum yield of 0.22. At long photolysis times the HBr and C_2H_4 go into a stationary state, and the main photolysis products are C_2H_6 and 1,1- $\text{C}_2\text{H}_4\text{Br}_2$ with quantum yields of 0.24 and 0.17, respectively. The behavior of the system is interpreted based on a model involving C-Br rupture as the main primary process ($\phi = 0.8$) with a substantial contribution of HBr elimination ($\phi = 0.2$). Primary $\text{C}_2\text{H}_5\cdot$ and Br· fragments abstract hydrogen from the substrate to produce mainly the 1- $\text{C}_2\text{H}_4\text{Br}\cdot$ radical. Net product formation involves reaction of radical species with Br_2 (present at low, steady-state concentration $<10^{-6}$ M), Br atoms, or HBr. The dynamic behavior of the system was investigated by computer simulation and compared with experimental results.

I. Introduction

The present study is an outgrowth of a parallel investigation of the mechanism of the γ radiolysis of ethyl bromide vapor at room temperature.¹ We undertook an investigation of the photolysis of this compound since all previous gas-phase photolysis studies were carried out at high temperatures and/or in the presence of various additives. Roof and Daniels² investigated the 313-nm photolysis of ethyl bromide-acetaldehyde mixtures at 310 °C. Results were interpreted in terms of the formation of $\text{C}_2\text{H}_5\cdot$ and Br·; the former was assumed to catalyze the decomposition of the acetaldehyde. Friedman, Bernstein, and Gunning³ studied the photolysis of ethyl bromide in the presence of mercury and excess cyclopentane, over a temperature range of 30–250 °C. Ethane was formed with a quantum yield of nearly unity, but only a small amount of ethylene was detected; results were interpreted on the basis of C-Br bond scission as the major primary photolytic event in the wavelength range 210–260 nm. Barker and Maccoll⁴ photolyzed gaseous ethyl bromide at 253.7 nm over the temperature range 150–300 °C. At these rather high temperatures, they reported a radical chain reaction forming C_2H_4 and HBr.

Gurman, Dubinski, and Kovalev⁵ studied the photolysis of liquid ethyl bromide at 253.7 nm and room temperature. Major products were ethane, dibromoethane, and bromine,

as well as a small amount of ethylene. They made no mention of the presence of hydrogen bromide.

The present investigation is concerned with the 253.7-nm photolysis of ethyl bromide vapor at 100 Torr pressure and 23 °C. Quantum yields are reported for several products both in the absence and in the presence of oxygen, added as a free radical scavenger. Only the major features of the photolytic decomposition of the compound are reported here and these are discussed in light of a computer simulation of the reaction mechanism. Further details of the reaction mechanism are described elsewhere.⁶

II. Experimental Section

Baker reagent grade ethyl bromide was dried with Drierite and fractionated through a 4-ft glass-helix packed Todd still. The middle cut boiling at 38.3 ± 0.1 °C was degassed on a mercury-free vacuum line, vacuum distilled through a 25-cm column of barium oxide, and stored in the dark at -196 °C. This material showed no observable impurities by flame ionization gas chromatography. Matheson hydrogen bromide used in actinometry experiments was passed through columns of P_2O_5 and copper filings; research grade oxygen was dried with silica gel. Gas chromatography standards and other miscellaneous reagents were used as received in the best available grades.