

## COMMUNICATIONS

## LETTERS

Photochlorination Reaction of Trichlorosilane ( $\text{SiHCl}_3$ ) at 337.1 nmKyung-Hoon Jung<sup>†</sup>, Jang Soo Shin and Young Sik Choi\**Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150 Chongryangni Seoul 131, Korea (Received June 5, 1984)*

In this communication we report the successful attainment of two separate objectives: (a) The use of the rotating sector technique for the kinetic study of photochlorination of  $\text{SiHCl}_3$  system; and (b) the test of a new means of purification of  $\text{SiCl}_4$  by adopting photochlorination technique at 337.1 nm to its major impurity, *i.e.*,  $\text{SiHCl}_3$ .

Almost all results reported to date on the study of photochlorination involving gas phase polyatomic molecules have been limited to the studies of carbon compounds.<sup>1-8</sup> In recent years the importances of silane compounds in semiconductor industry and its chlorinated compounds in optical fibre industry have attracted some attentions<sup>9-11</sup> but has never been thoroughly studied the present system. We now report a successful demonstration of the technique in the photochlorination of  $\text{SiHCl}_3$  at 337.1 nm.

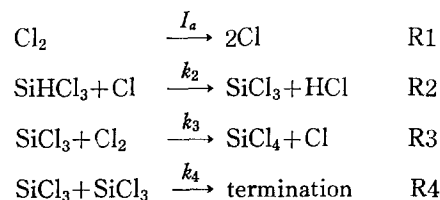
The photochlorination was performed at the temperature range of 22–70°C in a 309.09 cm<sup>3</sup> Pyrex reaction vessels equipped with a flat Pyrex window and was thermostated in an aluminum block furnace. Parts of vacuum line and reservoir flasks were painted black to prevent the dark reaction by the room light. The light source was a 150W high pressure Xe arc lamp (Oriel Co, XBO-150W) and 337.1 nm light was selected by a monochromator (Spex Industries Inc., Minimate 1670). The light beam from the monochromator was introduced into the reaction vessel in a homogenous and parallel light through a beam expander which was composed of two quartz lenses. Both slits of the monochromator had target dimensions of 1.5mm diameter which corresponds to spectral band width of 6 nm. The photon intensity entering the reaction vessel was determined to be  $I_0 = 1.25 \times 10^{14}$  quanta/sec on the basis of potassium ferrioxalate actinometry<sup>12</sup> and azomethane actinometry.<sup>13,14</sup> The absorption coefficient,  $\kappa$ , of  $\text{Cl}_2$  was calculated using Beer-Lambert law and found to be  $6.75 \times 273/T$  (atm.  $T.K$ )<sup>-1</sup>cm<sup>-1</sup>.<sup>13,15</sup> In the intermittent illumination, a variable speed mechanical light chopper

(EG & G Princeton Applied Research, Model 125A) was used. Its aperture wheel was opened for 90° of rotation and one of them was closed with black paper to increase the ratio of dark to light period. The reaction product,  $\text{SiCl}_4$ , was analyzed by HP 5880A gas chromatograph equipped with a TCD and a 1/8' × 7.0m × 20 % OV 101/80–100 mesh Chromosorb W s.s. column at 60 °C using He as carrier gas.

From our separate study where the variation of  $\text{SiCl}_4$  has been measured in terms of the pressures of  $\text{Cl}_2$  and  $\text{SiHCl}_3$  at constant light intensity, we have obtained Eq.(1) as the rate expression when  $\text{SiHCl}_3$  pressure is much greater than that of  $\text{Cl}_2$ .

$$d(\text{SiCl}_4)/dt = k_T^0(\text{Cl}_2)I_a^{1/2} \quad (1)$$

where  $k_T^0$  is the overall rate constant at  $T^0\text{K}$  and  $I_a$  is the light intensity absorbed by  $\text{Cl}_2$ . The most plausible reaction mechanism compatible with the above empirical reaction rate (Eq. 1) can be expressed by the following reactions.<sup>1,16</sup>



The detailed rate law derived from this mechanism by applying the stationary state approximation to  $\text{SiCl}_3$  and  $\text{Cl}$  is then,

$$d(\text{SiCl}_4)/dt = k_3 k_4^{-1/2} (\text{Cl}_2) I_a^{1/2} \quad (2)$$

Since Eq. (1) and Eq. (2) are identical,  $k_T^0 = k_3 k_4^{-1/2}$ .

The irradiation time dependence of the product,  $\text{SiCl}_4$ , at 4 different temperatures was measured and given in Table 1 and plotted in Figure 1. The overall rate constants at each temperature were calculated from the slopes of Figure 1. The absorbed light intensities and the concentrations of  $\text{Cl}_2$  are given in Table 2 and displayed in Figure 2. The evaluated  $\log k_T^0$ , the activation energy,  $E_a$ , and the pre-exponential

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factor,  $A$ , of the overall reaction from Figure 2. found to be  $(7.96 \pm 0.96) - (8670 \pm 850)/4.58T$ ,  $8.67 \pm 0.85 \text{ kcal mol}^{-1}$ , and  $(9.13 \pm 0.69) \times 10^{71/2} \text{ mol}^{-1/2} \text{ sec}^{-1/2}$ , respectively.

In the stationary state the lifetime of the chain carrier,  $\tau$ , is given by  $1/2(I_a k_4)^{-1/2}$  and was determined to be  $(1.65 \pm$

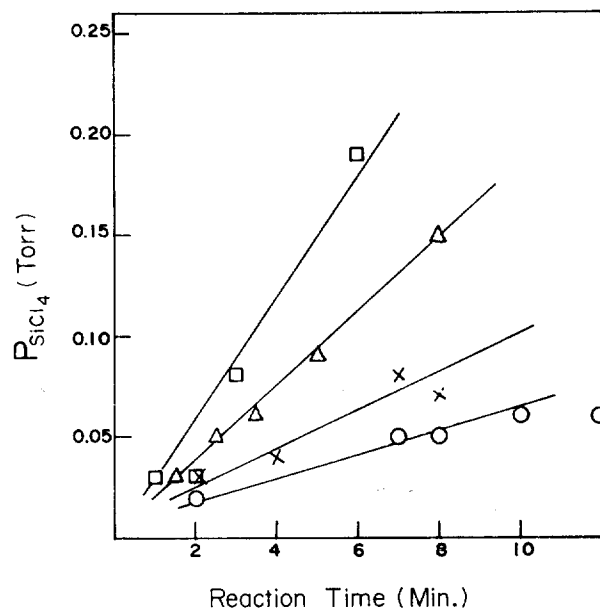


Figure 1. Variation of product with reaction time  $0.22^\circ\text{C}$ ; X,  $38^\circ\text{C}$ ;  $\Delta$ ,  $50^\circ\text{C}$ ;  $\square$ ,  $70^\circ\text{C}$ .

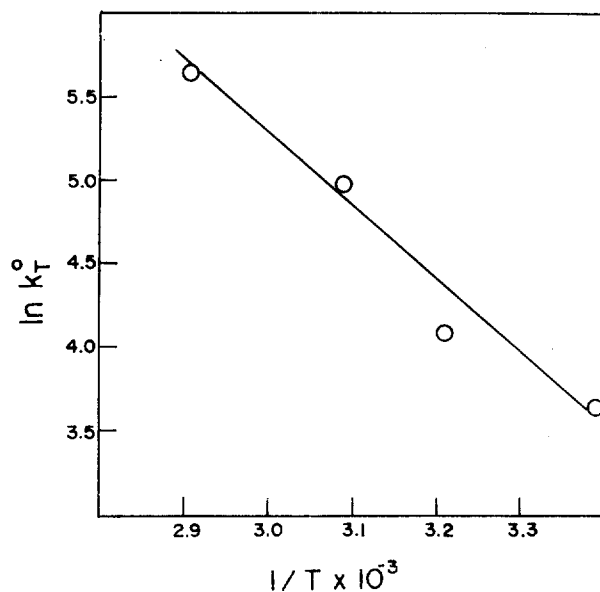


Figure 2. Arrhenius plot for the overall reaction.

$0.50) \times 10^{-2} \text{ sec}$  with the rotating sector technique.<sup>17</sup> Therefore, the rate constant of  $k_4$  was able to be calculated and was  $5.42 \times 10^{13} \text{ mol}^{-1} \text{ sec}^{-1}$ . Since the activation energy of the overall reaction is given by  $E_a = E_3 - \frac{1}{2}E_4$  and  $E_4$  must be zero, which is a usual value for the recombination of radicals in photochlorination processes,<sup>1</sup>  $E_3$  becomes  $8.67 \pm 0.85 \text{ kcal mol}^{-1}$  and  $\log k_3$  is then  $14.8 - 8670/4.58T$ .

The activation energy of R3 and Arrhenius pre-exponential factors of R3 and R4 obtained in this study are somewhat larger than those of the photochlorination of  $\text{CHCl}_3$ .<sup>1</sup> These differences of  $\text{SiHCl}_3$  from its carbon counterpart may be due to the contribution of silicon  $d$ -orbitals.<sup>18</sup> Because of the scarcity of kinetic data on the silicon compounds, it is little premature to draw any definite conclusion at this stage. The more clear explanations on the kinetic behavior of silanes due necessary further studies for the photochlorination of silanes.

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TABLE 1: Product with Reaction Time at Various Temperatures<sup>a</sup>

Run No.	Rxn Temp. ( $^\circ\text{C}$ )	Irr. Time (Min.)	$P_{\text{Cl}_2/\text{He}}$ (Torr)	$P_{\text{SiHCl}_3}$ (Torr)	$P_{\text{SiCl}_4}$ (Torr)
1	22	2.00	5.58	16.44	0.02
2		7.00	5.32	15.80	0.05
3		8.00	5.80	16.54	0.05
4		10.00	5.69	15.42	0.06
5		12.00	5.49	15.63	0.06
6	38	2.00	6.01	15.09	0.03
7		4.00	5.63	15.53	0.04
8		7.00	5.88	16.26	0.08
9		8.00	5.51	16.12	0.07
10	50	1.50	5.34	16.44	0.03
11		2.50	5.60	16.32	0.05
12		3.50	5.72	17.02	0.06
13		5.00	5.66	15.46	0.09
14		8.00	5.60	15.84	0.15
15	70	1.00	5.57	14.96	0.03
16		2.00	5.51	16.51	0.03
17		3.00	5.48	15.73	0.08
18		6.00	5.57	16.44	0.19

<sup>a</sup>  $I_0 = 1.25 \times 10^{14} \text{ quanta/sec}$ ; Dilution factor ( $\gamma$ ) of  $\text{Cl}_2/\text{He}$  are 0.086 at  $22^\circ\text{C}$ , 0.099 at  $38^\circ\text{C}$ , 0.098 at  $50^\circ\text{C}$ , and 0.098 at  $70^\circ\text{C}$ .

Table 2. Overall Rate Constant at Various Temperatures<sup>a</sup>

Rxn Temp. (K)	$\bar{P}_{\text{Cl}_2/\text{He}}$ (Torr)	$\gamma$	$\kappa$ (atm $T^\circ\text{K}$ ) <sup>-1</sup> mol <sup>-1</sup>	$R \times 10^4$ (Torr sec <sup>-1</sup> )	$I_a \times 10^{-12}$ (quanta sec <sup>-1</sup> )	$k_T^0$ ( $l^{1/2}\text{mol}^{-1/2}\text{sec}^{-1/2}$ )
295.15	5.58	0.086	6.25	0.70	8.57	38.66
311.15	5.76	0.099	5.93	1.35	9.62	59.22
323.15	5.58	0.098	5.71	3.07	8.91	145.77
343.15	5.53	0.098	5.37	5.72	8.33	283.57

<sup>a</sup>  $\kappa$ , absorption coefficient;  $R$ , Slope obtained from Figure. 1 by the least square analysis.

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## The Photochemistry of Co(III) Complex of Glycinemethylester

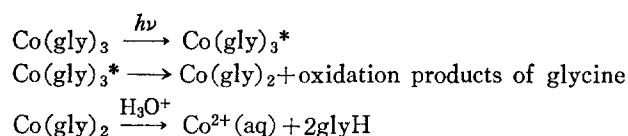
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Photochemical reactions of Co(III) complexes have often been described in terms of mechanisms involving an excited state of the metal ion which is charge transfer in character.<sup>1,2</sup> Ligand field excited states play important roles in the photoreactions of transition metal complexes especially with regard to photodegradation of complexes by ligand labilization.<sup>3,4</sup> Charge transfer irradiation promotes an intramolecular oxidation-reduction reaction which may be schematized as follows using the glycinate complex as an example<sup>5</sup>



In accordance with the intramolecular character of the photoreaction, the quantum yield was not affected by the acidity of the solution and only showed a small dependence on the glycinate and the steric arrangement of the complex.

The electronic spectra of Co(III) glycinate complexes suggest that there are significant interactions between ligand field states of the Co(III) centers. From the study of photochemical processes in Co(III) glycinate complexes, it is possible to elucidate the reactivity of different excited states

and to provide insight into nature of bonding in Co(III) methylester complexes.

In this paper we examine whether the photoreactivity is localized at the Co(III) center delocalized over the ligand-metal bonds. The photochemical behaviors of the complex will also be correlated with theoretical predictions based on the electronic absorption spectra of Co(III) glycineester complexes.

The complex,  $[\text{Co}(\text{gly})_2(\text{glycinemethylester})\text{Cl}]\text{Cl}_2$  was prepared by the published method.<sup>6</sup> The crude product was recrystallized from hot water by adding sequentially methanol, absolute ethanol, and ether, and dried in vacuo over Mg  $(\text{ClO}_4)_2$ . The spectral properties (UV-Vis, IR, <sup>1</sup>H nmr) of this compound prepared were identical with those reported.

Photolysis was carried out in aqueous HClO<sub>4</sub> solutions (pH 1-3). Irradiations ( $\lambda_{\text{irr}}=254\text{ nm}$ ) were utilized in an apparatus equipped with a Hanovia low-pressure mercury lamp. Light intensities were determined by ferrioxalate actinometry.<sup>7</sup>

The electronic structure of Co(III) glycineester complex was calculated by the CNDO/2 method with semiempirical integrals as described previously.<sup>8</sup>

Atomic cartesian coordinates of the molecular system