#### Laser Pyrolysis of Trichlorosilane. Kinetics and Mechanism

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# introduction

A series of papers<sup>1-5</sup> on silane chlorination reactions has recently been published. Vibrationally excited chlorosilane molecules play a substantial role in such processes since their dissociation is assumed to be responsible for chain branching. In the present work, kinetic parameters for the unimolecular dissociation of trichlorosilane, SiHC1<sub>3</sub>, have been determined by using laser pyrolysis.<sup>6-8</sup>

# Experimental

A commercial tunable CO<sub>2</sub>-laser (Apollo - 550) was used in the range  $_10$  W to  $_6$  W with a laser beam cross section  $_0.25$  cm<sup>2</sup>. A wavelength of 9.4  $\mu$  (P34) was employed. A glass reaction cell 10 cm long and 4 cm in diameter, with NaCl windows was mounted coaxially with the laser beam. Radiation was directed into the cell via a NaCl lens (f = 70 cm) placed at a distance of 45 cm from the cell inlet window.

Quantitative analysis was performed on a UR-20 IR-spectrometer (absorption bands 2260 cm<sup>-1</sup> (SiHCl), 2224 cm<sup>-1</sup> (N<sub>2</sub>O), and 1454 cm<sup>-1</sup> (c-C<sub>4</sub>H<sub>4</sub>F<sub>4</sub>)) and an MH-1303 mass-spectrometer. The irradiation time was varied from 30 s to 2 hours, the substance loss changing from 10% to 90%. No quantitative change in the sensitizer, SiF<sub>4</sub>, has been observed by mass spectra of the mixtures of irradiated and non-irradiated cells. Experiments on N<sub>2</sub>O dissociation in the absence of SiHCl<sub>3</sub> (5 Torr of H<sub>2</sub>O, 45 Torr of SiF<sub>4</sub>, up to  $_{\sim}$  300 Torr of Ar) showed no detectable loss of N<sub>2</sub>O.

#### **Results and Discussion**

According to the silylene mechanism<sup>9,10</sup> HCI must be the only detectable primary product of SiHCl<sub>3</sub> dissociation under the conditions employed:

SiHCl<sub>3</sub> ----> SiCl<sub>2</sub> + HCl, 
$$\Delta H_{298} = 240 \text{ kJ mol}^{-1} \frac{11}{2}$$
. (1)

SiHCl<sub>3</sub> depletion and HCl formation were observed by IR-spectra, the amount of HCl formed being equal to the SiHCl<sub>3</sub> loss within experimental error. The walls and windows of the reactor were coated by a white powder, the result of the SiCl<sub>2</sub> polymerization.<sup>9</sup> N<sub>2</sub>O, added to scavenge SiCl<sub>2</sub>, was found not to affect the measured rate constants for SiHCl<sub>3</sub> reaction, demonstrating that SiCl<sub>2</sub> does not influence the rate of reaction of the parent molecule.

In laser pyrolysis, the unimolecular dissociation rate constant, keff, is given by:6-8

$$k_{eff} = \frac{V_{eff}}{V_o} \cdot k_o \cdot exp \left(-\frac{E}{RT_{max}}\right)$$

where  $V_{eff}$  is the volume of the reaction zone,  $V_0$  is the total volume of the reactor,  $k_0$  is the pre-exponential factor, E is the activation energy and  $T_{max}$  is the maximum temperature in the "hot" zone. The Arrhenius parameters  $k_0$  and E for the unknown reaction can be obtained by comparison with a reference reaction which serves as an internal thermometer.<sup>8</sup> The rate constants of both the reactions determined under the same conditions are related as follows:

$$lgk_{2eff} = \frac{E_2}{E_1} \cdot lgk_{1eff} + B$$
(1)  

$$B = lg \frac{V_{eff}}{V_0} + lgk_{02} - \frac{E_2}{E_1} lg \frac{V_{eff}}{V_0} - \frac{E_2}{E_1} lgk_{01},$$
(11)

where the subscript "1" is used for "reference" reaction and "2" for reaction under investigation.

 $V_{eff}$  was determined by irradiating a Br<sub>2</sub>: SiF<sub>4</sub>: Ar mixture and observing the luminescence caused by Br recombination which characterises the "hot" zone volume. A visual estimate of the luminescent volume gave  $V_{eff} \sim 0.2 \text{ cm}^3$ ,  $V_{eff}/V_0 \sim 2.10^{-3}$ . The two channel dissociation of 1, 1, 2, 2-tetrafluorocyclobutane (c-C<sub>4</sub>H<sub>4</sub>F<sub>4</sub>) was used as a reference reaction.<sup>14</sup>

$$c-C_4H_4F_4 ---->2C_2H_2F_2$$
;  $E_a = 292.0 \pm 0.8$  kJ/mol;  $lgk_0 = 15.34 \pm 0.05$   
 $c-C_4H_4F_4 ----> C_2H_4 + C_2F_4$ ;  $E_a = 308.1 \pm 0.9$  kJ/mol;  $lgk_0 = 15.27 \pm 0.06$ 

Overall rate parameters,  $lgk_0 = 15.48 \pm 0.06$ ,  $E_a = 293.8$  kJ mol<sup>-1</sup> were employed.

The maximum temperature in the "hot" zone,  $T_{max}$ , estimated by the observed c-C<sub>4</sub>H<sub>4</sub>F<sub>4</sub> dissociation rate constant, varied from  $_{2}$  940 K to  $_{2}$  1070 K.

Fig. 1 shows a plot of lgk<sub>2eff</sub> (SiHCl<sub>3</sub>) vs lgk<sub>1eff</sub> (c-C<sub>4</sub>H<sub>4</sub>F<sub>4</sub>) (c.f. eqn I).



A least squares analysis gives:

$$\frac{E_2}{E_1} = 1.005 \pm 0.047; \qquad B = -1.11 \pm 0.13$$

Substituting these values into expressions (I) and (II), we obtain the Arrhenius parameters of the SiHCl<sub>2</sub> dissociation rate constant:

 $E_a = 295 \pm 12 \text{ kJ/mol}; \quad |gk_o = 14.4 \pm 0.8$ 

The activation energy,  $E_a$ , was obtained in the fall-off region and needs correction if the threshold energy  $E_o$  is to be estimated. Calculations based on Troe's formalism<sup>15,16</sup> suggest that  $E_o - E_a \sim 15 - 17 \text{ kJ mol}^{-1}$ , giving  $E_o = 312 \text{ kJ mol}^{-1}$ . This value may be compared with the reaction endothermicities reported by Ho et al. of 385 kJ mol<sup>-1</sup> and 469 kJ mol<sup>-1</sup> for the Si — H and Si — CI bond dissociation channels respectively.

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