

# CHAPTER I

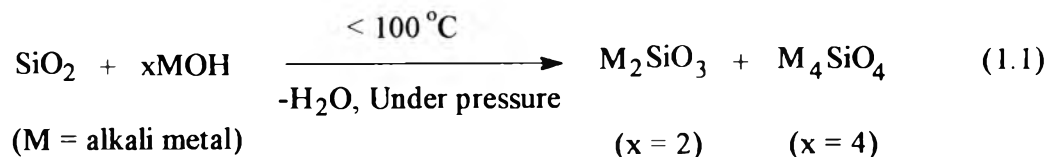
## INTRODUCTION

### 1.1 Background

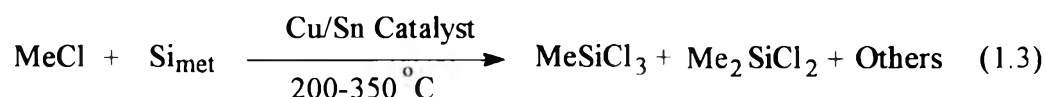
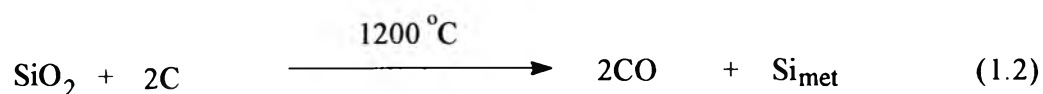
The potential role of organometallic silicon compounds in the development of new chemical reagents, polymers glasses and ceramic is limited at present by the paucity of simple silicon-containing starting material, whereas industrial carbon-based chemistry can draw on the diversity of compounds produced from crude oil, coal or other natural sources. Moreover, silicon chemistry (Kirk-Othemer, Encyclopedia of Chemical Technology, 1979) relies almost exclusively on the carbothermal reduction of  $\text{SiO}_2$  to silicon, which is then transformed into feedstock chemicals.

The widespread availability of  $\text{SiO}_2$  and its extremely low cost, make  $\text{SiO}_2$  an ideal starting material to many silicon feedstock chemicals. However, the primary problem with developing any large scale industrial process based on  $\text{SiO}_2$  is that the Si-O bonds in  $\text{SiO}_2$  are some of the strongest in nature (128 kcal (535 kJ)/mol). As a result, it is difficult to manipulate chemically.

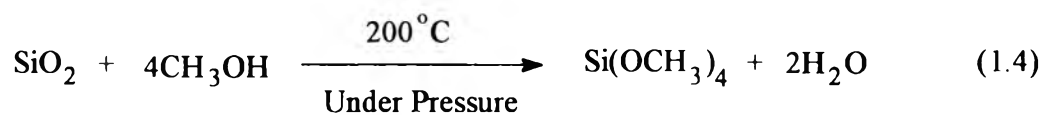
The primary silicon-based feedstock chemicals are derived from two relatively mature processes (Kirk-Othermer Encyclopedia of Chemical Technology, 1979). The first, the dissolution of  $\text{SiO}_2$  in strong base, provides access to a wide variety of inorganic silicates, as illustrated in equation (1.1) (Iler, R. K., 1979).



The second, carbothermal reduction of  $\text{SiO}_2$  to metallurgical grade silicon ( $\text{Si}_{\text{met}}$ ), equation (1.2), provides access to organosilicon compounds via reaction of  $\text{Si}_{\text{met}}$  with alkyl or aryl chlorides in the presence of catalysts, as shown in equation (1.3).

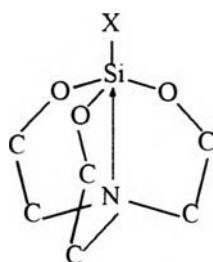


Kitahara and Asano (1973) showed that  $\text{SiO}_2$  dissolves to a higher extent in anhydrous methanol than in water, as shown in equation (1.4).



## 1.2 Literature Survey

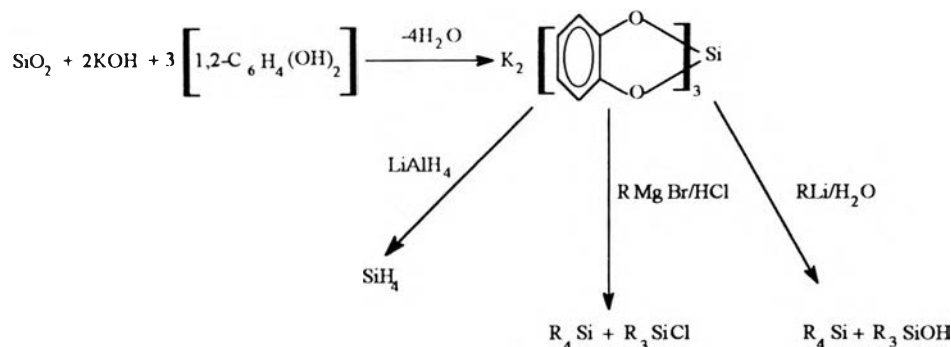
The first silatranes complexes, as shown in scheme 1-1 (with  $X = C_6H_5$  and  $C_2H_5O$ ), were patented by Finestone in 1960, who at that time suggested the existence of the  $Si \leftarrow N$  transannular dative bond in the silatrane molecule synthesized (Finestone A. B., 1960). In 1961, Frye, Vogel, and Hall reported a number of new, 1-substituted silatrane, scheme 1-1 [ $X = H, CH_3, n-C_{18}H_{37}, C_6H_5(CH_3)CH$  and etc.].



Scheme 1-1

They described the 1-ethoxy and 1-phenylsilatranes (melting points =  $100-102^{\circ}C$  and  $208-209^{\circ}C$ , respectively) and reported some data in support of intramolecular transannular dative bonds in silatrane complexes.

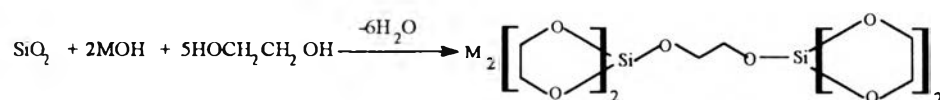
Rosenheim et. al. (Rosenheim A., 1931) reported that silica, sand, and quartz powder could also be employed to react with alkali catecholates to give hexacoordinate silicate complexes. However, Courrie's group demonstrated that these catechol silicate complexes were quite unstable. They could only be modified usefully by reacting with strong nucleophile to obtain tri- and tetrasubstituted products, which were necessary in industry primarily for polymer synthesis, as shown in scheme 1-2 (Corriu R. J. P., 1988).



M = Li, Na, K or Cs

**Scheme 1-2**

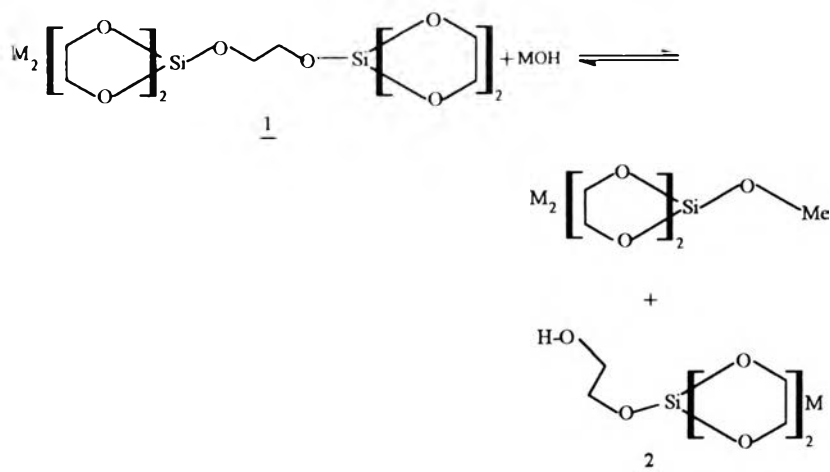
R.M. Laine and coworkers (Laine et. al., 1991) discovered the new synthetic routes to organosilicon compounds. By reacting  $\text{SiO}_2$  with ethylene glycol in the presence of an alkali base, highly reactive pentacoordinate silicates were obtained, as shown in scheme 1-3.



M = Li, Na, K or Cs

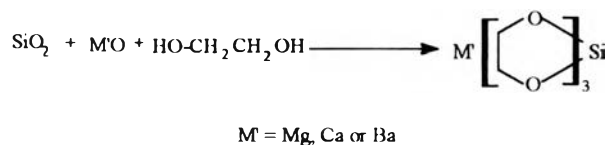
**Scheme 1-3**

The elemental analysis of the above products showed that if M was Li, Na, or K, the product was dimeric pentacoordinate species, labeled 1 in scheme 1-4. However, if Cs was used, the product acted as monomeric species, labeled 2. These results were confirmed by FTIR peak found for  $\nu_{\text{O-H}}$  at  $3,300 \text{ cm}^{-1}$ .



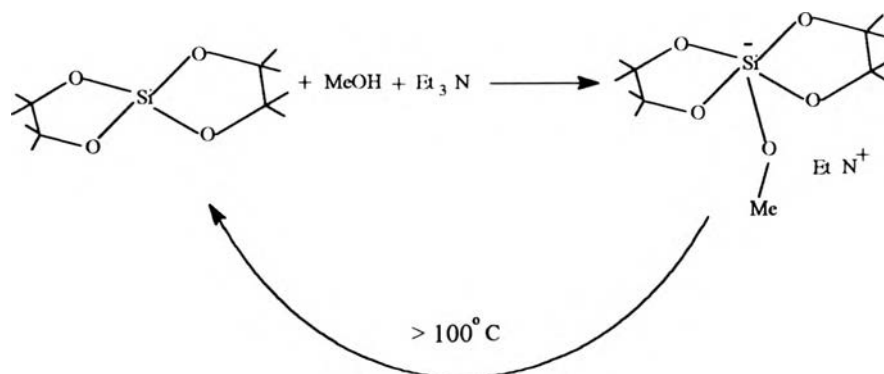
**Scheme 1-4**

Furthermore, hexacoordinate silicate complexes were obtained when reacting  $\text{SiO}_2$  with group II oxide in ethylene glycol, as shown in scheme 1-5.



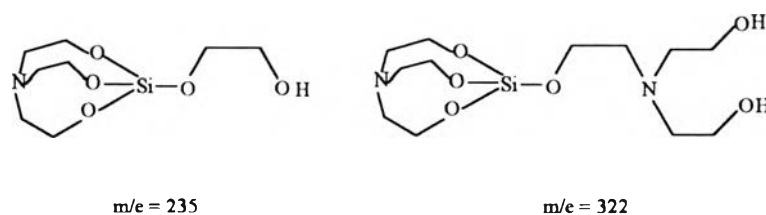
**Scheme 1-5**

Frye's observation (Frye C. L., 1970 : 1971) indicated that spiro-silicates could react with MeOH and amine base (e.g.  $\text{Et}_3\text{N}$ ) to form pentacoordinate, anionic silicate with ammonium counterion at ambient temperature. These species were not stable above  $100^\circ\text{C}$ , reverting to the tetracoordinate spiro-silicate, as shown in scheme 1-6.



**Scheme 1-6**

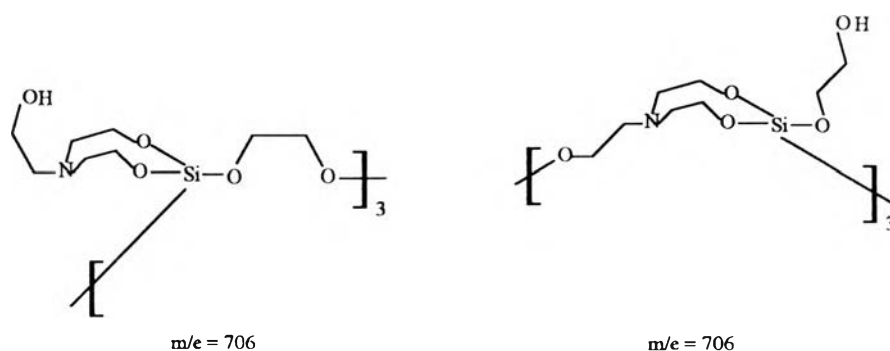
This observation prompted Laine's group to try with higher boiling (bp. > 200°C) amine base in place of group I or II hydroxides or oxides. Triethylenetetramine (bp. 266°C, TETA) and triethanolamine [N(CH<sub>2</sub>-CH<sub>2</sub>-OH)<sub>2</sub>, bp. 270°C (15 torr), TEA] were used as either catalyst and reactant, respectively. They found that TETA did not promote the formation of stable ammonium pentacoordinate silicates, confirmed by <sup>29</sup>Si NMR peaks of the product at -78, -79, -80 and -82 ppm. If TEA was used in place of TETA, similar product was obtained, depending on the amount of TEA. With up to two equivalents of TEA, the product had two silatrane species suggested by FAB<sup>+</sup>-MS, as shown in scheme 1-7.



**Scheme 1-7**

If one equivalent of TEA or less was employed, the primary product was the ethylene glycoloxysilatrane. <sup>29</sup>Si-NMR of this complex gave a single

peak at -96.2 ppm, which is typical of Si in silatrane (VS. TMS). TGA data gave %ceramic yield of 25.6. When the product was further dried under vacuum, higher M.W. oligomers were obtained, characterized by FAB<sup>+</sup>-MS, see scheme 1-8.



**Scheme 1-8**

Recently, Prakaipetch synthesized organosilicon complexes by reacting SiO<sub>2</sub> with TEA in EG in the presence and absence of TETA. The FAB<sup>+</sup>-MS results indicated that the product was oligomeric with a repeating unit equal to 235 Da, see scheme 1-7. She also studied the kinetics of formation of silatrane complexes by using the integral method to determine the reaction order. She found that the overall reaction was pseudo second order. The activation energy from Arrhenius's equation was equal to 64 ± 8 kJ/mol or 15 ± 2 kcal/mol.

### 1.3 Kinetic Theory

Chemical kinetics is the study of the chemical reaction rates. In this case, we focused on a way of obtaining and analyzing reaction rate data to obtain the rate constant for a specific reaction. Four methods of analyzing rate data are presented, the differential, the integral, the initial rate, and the half-life methods. The methods of half-lives and initial rates require experiments

under many different conditions to determine the reaction order and the specific reaction rate. With either the integral or differential method, it is possible to carry out only one experiment to find the specific reaction rate and the reaction order, with respect to one of the reactants. This research focused on the integral method to determine the reaction rate constant and reaction order, as detailed below [Fogler H. S., 1992, Moore W. J., 1993, Alberty R. A. and Silbey R. J., 1993, Sommer L. H. and Bennett O. F., 1957].

### 1.3.1 *Integral Method*

To determine the reaction order by the integral method, we must first assume the reaction order and integrate the differential equation used to model the batch system. If the order we assume is correct, the appropriate plot of concentration determined from this integration and corresponding to a particular rate law should be linear. For a reaction  $A \rightarrow \text{Product}$  with all experiments carried out in a constant-volume batch reactor, the combined rate law is

$$\frac{dC_A}{dt} = -r_A \quad (1.5)$$

For a zero-order reaction (Fig 1-1) the combined rate law is

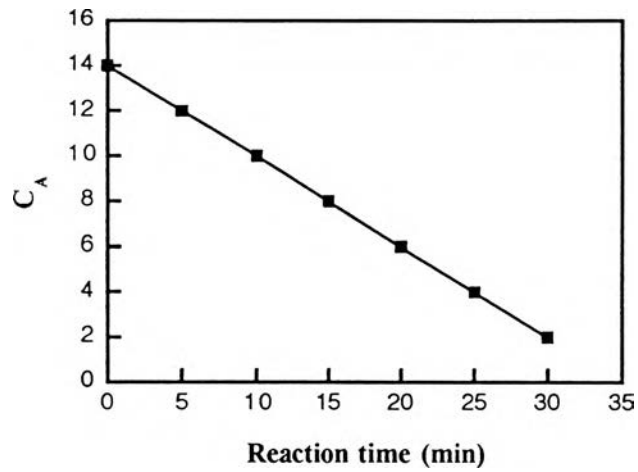
$$\frac{dC_A}{dt} = -k \quad (1.6)$$

Integrating with  $C_A = C_{A0}$  at  $t = 0$ , the following is obtained;

$$C_A = C_{A0} - kt \quad (1.7)$$



A plot of the A concentration as a function of time will be linear with slope  $(-k)$  for a zero order reaction.



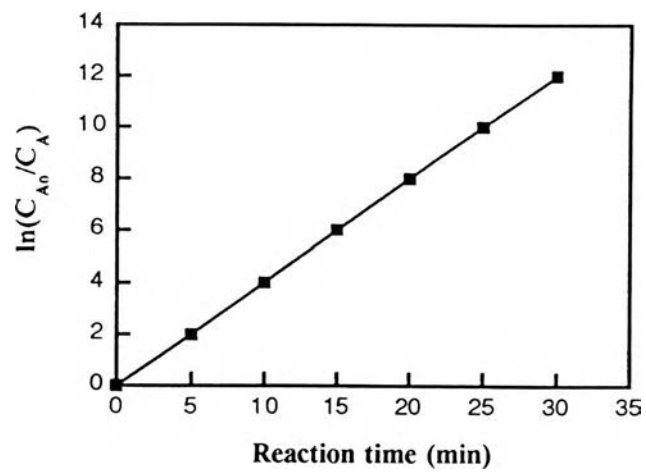
**Fig 1-1** Zero-order reaction.

If the reaction is first-order (Fig 1-2), the rate law will be

$$-\frac{dC_A}{dt} = kC_A \quad (1.8)$$

The limit  $C_A = C_{A0}$  at  $t = 0$  gives, on integration;

$$\ln \frac{C_{A0}}{C_A} = kt \quad (1.9)$$



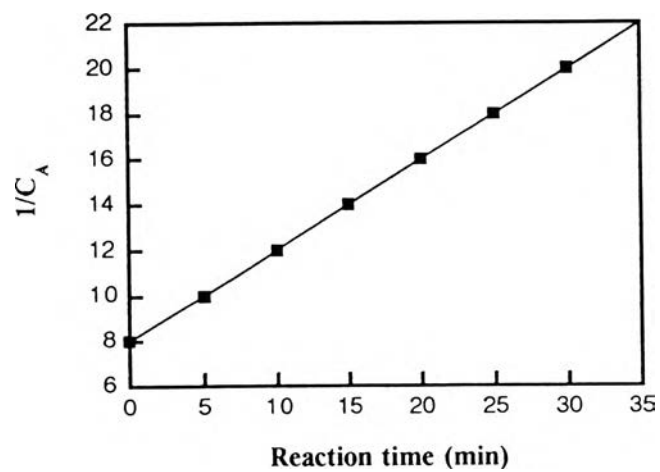
**Fig 1-2** First-order reaction.

If the reaction is second-order ( Fig 1-3 ), then the rate law is

$$-\frac{dC_A}{dt} = kC_A^2 \quad (1.10)$$

Integrating with  $C_A = C_{A0}$  (initial) yields

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \quad (1.11)$$



**Fig 1-3** Second-order reaction.

For the case, where  $aA + bB \rightarrow \text{products}$ , the rate expression and the integrated equation can be written :

$$-d \frac{C_A}{C_{A_0}} = k C_A C_B \quad (1.12)$$

$$\ln \frac{C_A}{C_B} = \ln \frac{C_{B_0}}{C_{A_0}} + (aC_{B_0} - bC_{A_0})kt \quad (1.13)$$

In the case where the initial concentrations of both reactants are equal and react at the same rate, the rate expression and integrated rate law can be reduced to equations (1.10) and (1.11). The plot of reciprocal concentration of A against time should give a straight line with the slope equal to the rate constant.

### 1.3.2 Factors influencing reaction rates

A number of variables are recognized to influence the rate of a reaction. The major factors are the following;

- 1). Concentration of reactants and product
- 2). Reaction temperature
- 3). Solvent properties, such as viscosity and dielectric constant.

Each of the variables will be considered in turn, and in this case we emphasized the concentration and reaction temperature variables.

Kinetic experiments were conducted on the dissolution rate of  $\text{SiO}_2$  as a function of

- : TIS concentration
- :  $\text{SiO}_2$  concentration
- : Reaction time
- : Reaction temperature

The reaction rate constant,  $k$ , depends upon temperature in an exponential fashion per Arrhenius :

$$k(T) = Ae^{-E_a/RT} \quad (1.14)$$

where the preexponential factor,  $A$ , and activation energy,  $E_a$  (in unit J/mol or cal/mol) are adjustable parameters, whereas  $R$  is gas constant =  $8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$  or  $1.987 \text{ calmol}^{-1} \text{ K}^{-1}$ , and  $T$  is absolute temperature in the unit of K.

The activation energy,  $E_a$ , has been equated to the minimum energy that must be possessed by reacting molecules before a reaction can occur. From the kinetic theory of gases, the factor  $e^{-E_a/RT}$  gives the fraction of the collisions between molecules that together have this minimum energy,  $E_a$ .

The activation energy is determined experimentally by using the following equation :

$$\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right) \quad (1.15)$$

Plots of  $\ln k$  versus  $1/T$  should be a straight line with the slope proportional to the activation energy.

#### **1.4 Research Objectives**

This research work was aimed at the synthesis of silatrane complexes (preceramic oligomers) directly from  $\text{SiO}_2$  and triisopropanolamine. Characterization of products was carried out using TGA, DSC,  $\text{FAB}^+$ -MS, FTIR and NMR. Kinetic studies of the dissolution reaction were investigated to determine the reaction rate, reaction order, and activation energy.