

## CHAPTER II

### EXPERIMENTAL PROCEDURE

#### 2.1 General Material Handling

Since the silatrane complexes are slightly moisture and air sensitive, all operations were carried out with the careful exclusion of moisture and air by running reactions under N<sub>2</sub> atmosphere.

Silicon dioxide (SiO<sub>2</sub>) with a surface area of 320 m<sup>2</sup>/g (average particle size of 0.007 μm), was purchased from Aldrich Chemical Company. It was kept in a dry environment prior to use, to prevent moisture adsorption.

Ethylene glycol (EG, HOCH<sub>2</sub>CH<sub>2</sub>OH), was purchased from Carlo Erba Company and used as reaction solvent. EG was distilled by fractional distillation at 200°C under N<sub>2</sub> atmosphere. EG recovered from the reaction was also redistilled for recycle. Triisopropanolamine [TIS, N(CH<sub>2</sub>CHCH<sub>3</sub>OH)<sub>3</sub>] was obtained from Fluka Chemika Company and used as received. Commercial grade triethylenetetramine [TETA, H<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>NH)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>] supplied by Union Carbide (Thailand) was vacuum distilled at 150°C (10<sup>-2</sup> torr).

Methanol and acetonitrile, used as solvents for purification, were purchased from Baker Analyzed Company and purified by standard techniques under N<sub>2</sub> atmosphere (Vogel,1978). Acetonitrile was distilled from calcium hydride powder, whereas methanol was distilled from magnesium metal

activated with iodine. The distilled solvents were kept in glass bottles over molecular sieves prior to use.

Diethylether and dichloromethane, used as solvents for precipitation, were also purchased from Baker Analytical Co. and purified by standard techniques. Dichloromethane was distilled from anhydrous calcium chloride under N<sub>2</sub> atmosphere and diethylether was dried by adding anhydrous calcium chloride in ether, kept in a clear dry Winchester bottle, let stand for 24 h. with occasional shaking, and then filtered the dried ether through large, fluted filter paper into another clean, dry Winchester bottle.

All glassware is cleaned by soaking in a NaOH/*i*PrOH cleaning solution bath, followed by washing, rinsing with water, and then drying in an oven at 120 °C prior to use.

## **2.2 General Instrumental/Characterization Methods**

### *2.2.1 FAB<sup>+</sup>-MS spectroscopy (MS)*

Mass Spectra were obtained on a VG Autospec-ultima 707E from Fisons, using a direct probe of the positive fast atom bombardment (FAB<sup>+</sup>) mode. Cesium iodide (CsI) was used as a standard for peak calibration. The cesium gun beam, used as the initiator, was set at 2 μA for the optimum resolution. The range studied was set from *m/e* 20 to 3000. Solid samples were mixed with glycerol as a matrix, whereas liquid samples, being soluble in EG, were run directly without using the matrix.

### 2.2.2 *Thermogravimetric Analyses (TGA)*

Thermogravimetric Analyses were carried out using a Netzsch TG 209 instrument. Approximately 5-20 mg of sample was placed into an alumina pan and heated in air with heating rate of 20°C/min. The flow rate used was 10 ml/min. TGA was used to determine decomposition temperatures, product purities, and experimental ceramic yields.

### 2.2.3 *Differential Scanning Calorimeter (DSC)*

Differential Scanning Calorimeter. A Netzsch DSC 200, was used to measure phase transition temperatures;  $T_g$ ,  $T_d$ ,  $T_c$ , and  $T_m$ . A sample (5 to 20 mg) was placed in a hermetically aluminum pan. The pan was crimped to improve thermal contact between the sample and container. The temperature range was from ambient temperature to 450°C with a ramp rate of 10°C/min in a  $N_2$  environment. Liquid  $N_2$  was used as coolant for the heating-cooling program.

### 2.2.4 *Fourier Transform Infrared spectroscopy (FTIR)*

Fourier Transform Infrared spectra were obtained using a FT-IR 45 A Biorad spectrometer with a resolution of 4  $cm^{-1}$ . Solid powder samples were prepared by the pressed disc technique. A sample was thoroughly ground using 1.0 % sample to 99 wt % pure and dry crystalline potassium bromide, KBr and then hydraulically pressed. The sample disc was then placed in the chamber which was then purged with  $N_2$  for 20 min to remove  $CO_2$  atmosphere.

### 2.2.5 $^{13}\text{C}$ - and $^1\text{H}$ - NMR spectroscopy (NMR)

$^{13}\text{C}$ - and  $^1\text{H}$ - NMR spectra were obtained using a 500 MHz JEOL spectrometer at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University. A sample was dissolved in deuterated dimethyl sulfoxide ( $\text{d}_6$ -DMSO). Tetramethylsilane (TMS) was used as the internal reference for chemical shift measurements in both proton and carbon NMR.  $^1\text{H}$ -NMR spectra were recorded at a frequency of 10,000 Hz using 16 scans, a pulse width and pulse delay of 5.5 sec and 3.0 sec respectively, and sweep width of 16,000 Hz.  $^{13}\text{C}$ -NMR spectra were collected at 10,000 number of scans, using a pulse width of 4.75  $\mu\text{sec}$ , 1.5 sec pulse delay, and sweep width of 16,000 Hz.

### 2.2.6 $^{29}\text{Si}$ -NMR spectroscopy (NMR)

$^{29}\text{Si}$ -NMR spectra were obtained using a 500 MHz JEOL spectrometer. A  $\sim 50$  mg sample of precipitated powder was dissolved in  $\sim 3$  mL of  $\text{d}_6$ -DMSO. The clear solution was run using a pulse width of 5.0 sec, pulse delay 5  $\mu\text{sec}$ , a sweep width of 16,000 Hz, 64 scans with a 10 sec delay time, and 9,500 data point scans

### 2.3.1 Synthesis of Silatrane Complexes

Synthesis of silatrane complex was carried out by placing 6.09 g (100 mmol) of silicon dioxide ( $\text{SiO}_2$ ), 19.12 g (100 mmol) of triisopropanolamine (TIS) and 100 mL of ethylene glycol (EG) into a 250-mL,

two-necked reaction flask. The reaction mixture was stirred and heated to 200 °C to distill off EG and by-product, H<sub>2</sub>O, produced during the reaction. A thermostatted silicone oil bath was used as a heat source. During the course of a reaction, the same amount of fresh EG as distillate was added. This process of EG distillation and addition was repeated until the mixture turned clear, indicating that the reaction was complete. The reaction time was 10 h. Most of the remaining EG was removed by vacuum distillation (10<sup>-2</sup> torr) using an oil bath temperature of 100°C. The resulting product turned very viscous at this point. The viscous product was purified by precipitating with dried 10 % CH<sub>2</sub>Cl<sub>2</sub> in diethylether. The powder product was filtered off, dried in a vacuum oven at 50°C for 10 h., and then characterized by TGA, DSC, FAB<sup>+</sup>-MS, FTIR, and NMR.

### 2.3.2 *Kinetic Studies on the Dissolution of SiO<sub>2</sub>*

The method of initial rates of SiO<sub>2</sub> dissolution was used to study reaction kinetics. In these studies, reaction time, or reaction temperature, was varied whereas ratio of SiO<sub>2</sub> : TIS was fixed at 1 : 1. The amount of unreacted, dried SiO<sub>2</sub> for each variable examined was determined to obtain relationship between factors. The reaction order and the activation energy were determined and calculated.

#### 2.3.2.1 Procedure

The SiO<sub>2</sub>, TIS, and ethylene glycol were placed in a 250 mL, two-necked reaction flask, stirred magnetically. At first the reaction flask was clamped about 5 cm. above the oil bath set at the reaction temperature using the temperature controller for 10 minute. The reaction time was started after immersing the reaction flask into the oil bath (the reaction volume was kept

constant at 100 mL for every batch).  $\text{SiO}_2$  dissolved slowly with continuous distillation of  $\text{H}_2\text{O}$  and EG. After a set time, the reaction was stopped, and the mixture was cooled to room temperature. The unreacted  $\text{SiO}_2$  was filtered off and stirred with 75 mL MeOH for 10 h. at room temperature to extract all soluble silatranes. The unreacted  $\text{SiO}_2$  was again filtered, dried at  $120^\circ\text{C}$  for 10 h., and weighed. Each variable run was repeated three times.

#### 2.3.2.2 Conditions for the Kinetic Studies

The appropriate ratio of  $\text{SiO}_2$  : TIS used to study the kinetics was 1:1 or 30 mmol of  $\text{SiO}_2$  : 30 mmol of TIS, with reaction time and temperature at 2 h. and  $170^\circ\text{C}$  (temperature of silicone oil bath), respectively. For the dissolution rate studies as a function of time, the reaction time was varied from 1 to 75 min. For the dissolution rate as function of temperature, reactions were run at  $150^\circ$ ,  $170^\circ$ , and  $190^\circ\text{C}$ .

#### 2.3.2.3 The Procedure for Recovering Unreacted $\text{SiO}_2$

The following is the procedure for isolating unreacted  $\text{SiO}_2$ . After the reaction was cooled to room temperature, unreacted  $\text{SiO}_2$  was filtered off the EG and stirred with 75 ml of methanol for 10 h, to dissolve all soluble silatrane complexes. The unreacted  $\text{SiO}_2$  was again filtered off, washed with methanol, and oven dried at  $120^\circ\text{C}$  for 10 h. Finally, the dried  $\text{SiO}_2$  was weighed.

#### 2.3.2.4 Dissolution Rate as a Function of Amount of TIS

$\text{SiO}_2$  (1.80 g., 30 mmol), TIS varied from 0 to 120 mmol (or 0 to 22.94 g), and 100 mL of EG, were placed into a 250 mL two-necked

reaction flask, followed the procedure described in section 2.3.2.3. The reaction temperature and time were fixed at 200°C and 2 h, respectively. The relationship of percent dissolved silica as a function of TIS concentration was plotted in Fig. 3-9, as well as the relationship between the mmol of dissolved SiO<sub>2</sub> versus mmol of TIS added (Fig. 3-10).

#### 2.3.2.5 Dissolution Rate as a Function of the Amount of SiO<sub>2</sub>

The experiments were carried out by fixing the amount of TIS at 5.74 g (30 mmol) and varying the amount of SiO<sub>2</sub> from 0 to 60 mmol (0-3.63 g). The procedure described in section 2.3.2.3 was again repeated by fixing the reaction temperature and time at 200 °C and 2 h, respectively. The mmol of dissolved SiO<sub>2</sub> versus mmol of SiO<sub>2</sub> added was then plotted. (Fig. 3-11)

#### 2.3.2.6 Dissolution Rate as a Function of Time

Amounts of SiO<sub>2</sub> and TIS were fixed at 1.80 g (30 mmol) and 5.74 g (30 mmol) respectively. The reaction time was varied from 1 to 75 min., followed by the procedure described in section 2.3.2.3 at a reaction temperature of 150°C. The reciprocal (1/mmol) of unreacted SiO<sub>2</sub> concentration versus reaction time was then plotted. (Fig. 3-12)

#### 2.3.2.7 Dissolution Rate as a Function of Temperature

The experiment was carried out by fixing the amounts of SiO<sub>2</sub> and TIS at 1.80 g (30 mmol) and 5.74 g (30 mmol) respectively. The reaction temperature was varied from 150 to 190°C. For each reaction temperature

studied, the reaction time was varied from 1 to 75 min. Again the procedure described in section 2.3.2.3 was repeated. The plot of 1/mmol of unreacted SiO<sub>2</sub> versus reaction time for each reaction temperature gave the the reaction rate constant, k, which was equal to the slope of the curve (Fig.3-13). From the Arrhenius's equation, the plot of ln(k) versus 1/T (K<sup>-1</sup>) resulted in the activation energy, E<sub>a</sub> (Fig.3-14).

### 2.3.2.8 The Effect of TETA Concentration on the Reaction of SiO<sub>2</sub> with TIS

#### A. Synthesis

The effect of TETA concentration was studied by fixing the amount of SiO<sub>2</sub> and TIS at 6.09 g (100 mmol) and 19.12 g (100 mmol) respectively. TETA [0.15 g (1 mmol)] was then added. The ratio of SiO<sub>2</sub> : TIS : TETA for this case was 1:1:0.01. The procedure for the synthesis of silatrane complexes without TETA (section 2.3.1) was then repeated except that in this case TETA was employed. The reaction was complete in only 5 h.

#### B. Dissolution Rate of SiO<sub>2</sub> with TETA

The reaction was carried out by fixing the amounts of SiO<sub>2</sub>, TIS and TETA at 1.80 g (30 mmol), 5.74 g (30 mmol) and 0.04 g (0.3 mmol ) respectively. The reaction time was varied from 1 to 75 min., then followed by the procedure described in section 2.3.2.3 and fixing the reaction temperature at 170°C. The 1/mmol of unreacted SiO<sub>2</sub> versus reaction time was then plotted (Fig. 3-15).