Kinetics of the “OOPS” Process of Silica and Triisopropanolamine to Tris (silatranyloxy-*i*-propyl)amine

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To identify the mechanism of the “OOPS” process, the conversion of silica and triisopropanolamine to tris(silatranyloxy-*i*-propyl)amine, studies were carried out on the reaction rate as a function of concentrations of silica and triisopropanolamine, the reaction order and the activation energy. The reaction orders are the first order with respect to both silica and triisopropanolamine. Overall, the reaction is second-order. The reaction rate increases with increasing reaction temperature. The activation energy for this reaction is 55 ± 4 kJ/mol. In the presence of catalytic amounts of triethylenetetramine, the reaction rate is approximately doubled.

Key words: Kinetics, tris(silatranyloxy-*i*-propyl)amine, silica, triisopropanolamine and silatrane.

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การเกิดสารทริส(ไซลาทรานิล็อกซี่ไอโซโพรพิล)อะมีน โดยผ่านกระบวนการ "OOPS"

สุจิตรา วงศ์เกษมจิตต์ ริชาร์ด เลน และ เพ็นศรี พิบูลย์ชัยสิทธิ์ (2544)

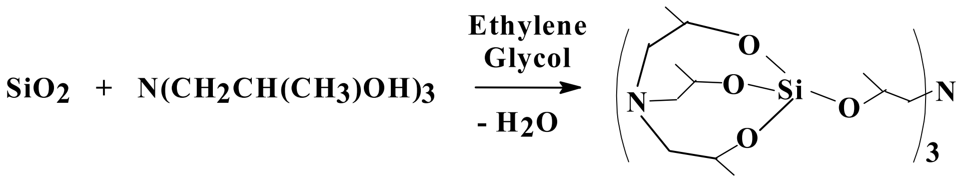
วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย **26(2)**

เพื่อเป็นการพิสูจน์กลไกของการเกิดสารทริส(ไซลาทรานิล็อกซี่ไอโซโพรพิล) อะมีน ซึ่งผลิตได้โดยตรงจากสารตั้งต้นซิลิกาและไตรไอโซโพรพานอลามีน โดยผ่านกระบวนการ "OOPS" นั้น จึงจำเป็นต้องมีการศึกษาอัตราการเกิดปฏิกิริยาที่เป็นฟังก์ชั่นกับความเข้มข้นของสารตั้งต้นแต่ละตัว ลำดับของปฏิกิริยาและพลังงานกระตุ้นที่ใช้ในการเกิดปฏิกิริยา จากการศึกษาพบว่าลำดับของปฏิกิริยานี้ เป็นลำดับที่หนึ่งเมื่อเทียบกับสารตั้งต้นซิลิกา และเป็นลำดับที่หนึ่งเมื่อเทียบกับสารตั้งต้นไตรไอโซโพรพานอลามีน นั่นคือลำดับของปฏิกิริยานี้โดยรวมแล้วเป็นปฏิกิริยาลำดับที่สอง อัตราการของการเกิดปฏิกิริยาเพิ่มขึ้นเมื่ออุณหภูมิที่ใช้ในการเกิดปฏิกิริยาเพิ่มขึ้น พลังงานกระตุ้นที่ศึกษาได้มีค่าเท่ากับ 55 ± 4 กิโลจูลล์ ต่อโมล ถ้ามีการเติมไตรเอทธิลีนเตตระมีน ซึ่งทำหน้าที่เป็นคะตะลิสต์สำหรับปฏิกิริยานี้ อัตราการเกิดปฏิกิริยาเกิดเร็วขึ้นเป็นสองเท่า

คำสำคัญ กลไกของการเกิดปฏิกิริยา สารทริส(ไซลาทรานิล็อกซี่ไอโซโพรพิล) อะมีน ซิลิกา

INTRODUCTION

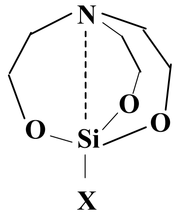
The "Oxide One Pot Synthesis (OOPS)" process, converting silica and triisopropanol-amine (TIS) using ethylene glycol as a solvent in the presence and absence of catalytic amounts of triethylenetetramine (TETA) to a silatrane derivative, tris(silatranyloxy-*i*-propyl) amine, was reported in a previous paper. (1) The reaction occurs according to equation (1);



(1)

The use of silica as the starting material to obtain a wide variety of silicon-containing compounds directly is the main objective of this research for overcoming the energy-intensive step from the carbothermal reduction of SiO_2 to silicon, which is then transformed into feedstock chemicals. (2)

The silatrane is generally a pentacoordinate silicon derivative forming a "transannular bond" between the Si and N atoms, as indicated by the dashed line in structure **I.** (3,4)



I

The length of this transannular bond is dependent upon the substituent bound to Si and structural modifications on the silatrane framework.(5,6) The distance is considerably shorter than the sum of the van der Waals radii of 3.5 Å for Si and N, yet longer than a conventional Si-N covalent bond length found in tetracoordinate Si compounds. The transannular bond can be considered to be a very weak bond. It is expected to shift a negative charge to the silicon by partial donation from the axial nitrogen lone pair. As a result, the silicon is less susceptible to attack by an incoming nucleophile.

It is known that siloxane bonds are susceptible to alcoholysis under suitable conditions. When the reaction was performed on organosilsesquioxane substrates with triethanolamine as the alcoholic reactant, the yield of silatrane was high.(7) In related work,(8) silica was observed to dissolve in excess triethanolamine at temperatures of 200°-250°C to obtain mono-, bis- and tris (silatranyloxy ethyl)amine. However, a parallel attempt with TIS was unsuccessful.

The purpose of this study is thus to obtain further understanding of the nature of the reaction in the "OOPS" process by measuring the reaction rate as a function of concentrations of silica, and TIS, the reaction order and the activation energy. Along with this, the effect of TETA on the reaction of SiO_2 and TIS is also studied since the addition of TETA is found to activate the reaction, as reparted in the previous paper. (1)

EXPERIMENT

Materials

All reactions were carried out under a N_2 atmosphere with careful exclusion of extraneous moisture and air since the product is slightly sensitive to moisture and air. The glassware used for these experiments was oven dried. Amorphous, precipitated silicon dioxide, SiO_2, with a multi-point BET surface area of 182 m^2/g, was donated by PPG Siam Silica Co., Ltd. and used as received. It was stored under dry conditions prior to use to prevent moisture adsorption. Ethylene glycol, EG, (99.5% Farmitalia Carlo Erba) used as a solvent for the reaction, was distilled before used by fractional distillations at 200°C. Triethylenetetramine, TETA, (Union Carbide, Thailand, Ltd.) used as a base catalyst, was distilled under vacuum prior to use. TIS was obtained from Fluka Chemical Company and used as received.

Procedure

Kinetic Studies on the Dissolution of SiO_2

The initial reaction rate as a function of change in the reaction conditions, such as the amount of TIS, reaction time, and reaction temperature, was studied, based upon a very early stage of the reaction. That is, all reactions studied did not proceed to completion. The optimum ratio of SiO_2 : TIS at fixed reaction temperature and time was again studied. The amount of unreacted and dried SiO_2 for each variable study was weighed to obtain relationships between factors. The reaction order and the activation energy were determined and calculated.

The appropriate ratio of SiO_2 : TIS used to study the kinetics was 1:1 or 30 mmol of SiO_2 : 30 mmol of TIS, with reaction time and temperature at 2 h. and 170°C (which was the temperature of silicone oil bath), respectively. For the case of the dissolution rate study as a function of time, the reaction time was varied from 1 to 75 min., and for the study of dissolution rate as a function of temperature, reaction temperatures were studied at 150°, 170°, and 190°C.

1. *The Procedure for Preparing the Mixture Solution*

The SiO_2, TIS, and EG were placed in a 250 mL two-necked flask, and stirred using a magnetic stirrer. At first the reaction flask was camped about 5 cm. over the oil bath set at the desired temperature using a 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). SiO_2 was slowly dissolved with continuous distillation of H_2O and EG. After a set time, the reaction was stopped, and the mixture was cooled to room temperature. The unreacted SiO_2 was filtered off and stirred with 75 mL of MeOH for 10 h. at room temperature to extract all soluble silatranes. The unreacted SiO_2 was again filtered, dried in an oven at 120°C for 10 h., and weighed. The unreacted SiO_2 was then converted to obtain the relationship between factors. Each experiment was repeated 3 times.

2. *Dissolution Rate as a Function of Amounts of TIS*

SiO_2 (1.803 g., 30 mmol), TIS which varied from 0 to 120 mmol (or 0 to 22.942 g), and 100 mL of EG were placed in a 250 mL two-necked flask, followed by the procedure described in section 1. The reaction temperature and time were fixed at 200°C and 2 h, respectively. The relationship of percentage of dissolved silica and TIS concentration, as well as the relationship between the mmol of dissolved SiO_2 versus mmol of TIS added were plotted.

3. Dissolution Rate as a Function of the Amount of SiO_2

The experiments were carried out by fixing the amount of TIS at 5.736 g (30 mmol) and varying the amounts of SiO_2 from 0 to 60 mmol (0-3.625 g). The procedure described in section 1 was again repeated by fixing the reaction temperature and time at 200°C and 2 h. respectively. The mmol of dissolved SiO_2 versus mmol of SiO_2 added was then plotted.

4. Dissolution Rate as a Function of Time

Amounts of SiO_2 and TIS were fixed at 1.803 g (30 mmol) and 5.736 g (30 mmol), respectively. The reaction time was varied from 1 to 75 min., followed by the procedure described in section 1 and fixing the reaction temperature at 150°C. The reciprocal (1/mmol) of unreacted SiO_2 concentration versus reaction time was then plotted.

5. Dissolution Rate as a Function of Temperature

The experiment was carried out by fixing the amounts of SiO_2 and TIS at 1.803 g (30 mmol) and 5.736 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 1 was repeated. The plot of 1/mmol of unreacted SiO_2 versus reaction time for each reaction temperature gave the reaction rate constant, k, which was equal to the slope of the curve. From the Arrhenius's equation, the plot of ln(k) versus 1/T (K^{-1}) resulted in the activation energy, Ea.

6. The Effect of TETA Concentration on the Reaction of SiO_2 and TIS

The reaction was carried out by fixing the amounts of SiO_2, TIS and TETA at 1.803 g (30 mmol), 5.736 g (30 mmol) and 0.0439 g (0.3 mmol), respectively. The reaction time was varied from 1 to 75 min., then followed by the procedure described in section 1 and fixing the reaction temperature at 170°C. The 1/mmol of unreacted SiO_2 versus reaction time was then plotted.

RESULTS AND DISCUSSION

Kinetic Studies on the Dissolution of SiO_2

These studies were directed to determine the rate constant, k, reaction order and activation energy of the reaction.

According to the previous work,(1) the characterized product approximately contained SiO_2 and TIS at the ratio of approximately 1:1. For the determination of the reaction order by the integral method, thus the assumption was made that the reaction of the silatrane complexes from SiO_2 and TIS was second order overall and first order respect to SiO_2 and first order with respect to TIS. The dissolution rate of SiO_2, R, can be expressed as;

$$\mathbf{R = k[SiO_2]\,[TIS]} \qquad \mathbf{(2)}$$

1. Dissolution Rate as a Function of Amounts of TIS

TIS concentration was varied from 0 to 120 mmol while fixing SiO_2 at 30 mmol and reaction temperature and time at 200°C and 2 h., respectively.

From Figure 1 and 2, the relationships between percentage of reacted SiO_2 and TIS concentration showed linearity until the amount of TIS reached 60 mmol, and the SiO_2 was completely dissolved. That is, the dissolution of SiO_2 depended on the TIS concentration. The non-zero interception for the reaction run without TIS was a surprising result. This was because SiO_2 can be slightly dissolved by ethylene glycol. The amount of unreacted SiO_2 lost during the recovery process may be another possible reason.

2. Dissolution Rate as a Function of Amounts of SiO_2

This study was conducted by fixing the amount of TIS at 30 mmol and varying the amounts of SiO_2 from 0 to 60 mmol. The plot of the relationship between the mmol of dissolved SiO_2 and amount of SiO_2 added also showed an increasing linearity when the amount of SiO_2 added was increased (Figure 3).

Figure 1. The Relationship of % Dissolved Silica for each amount of TIS.

Figure 2. Effect of TIS concentration.

Figure 3. Effect of SiO_2 Concentration on the Dissolution of SiO_2.

From both results, we can confirm that the reaction of SiO_2 and TIS was dependent on the amount of TIS and SiO_2. Both plots show a linear relationship, and we can thus conclude that the assumptions leading to equation(2) are correct. Furthermore, one mechanism can possibly be drawn, as illustrated in Figure 4.

3. Determination of the Reaction Order

As mentioned previously, the reaction order was determined by the integral method. Therefore, a particular reaction order was first assumed, and the resulting differential equation for the model was then integrated. If the reaction order assumed was correct, then the appropriate plot of concentration corresponding to a particular rate law which resulted from the integration should be linear as a function of time.

In this case, the reaction order was assumed to be second order overall, first order with respect to TIS and first order with respect to SiO_2. Because the experiment was carried out with initial concentration of both reactants being equal and reacting at the same rate, the rate expression and integrated rate law could therefore be obtained from the equations (3) and (4). The plot of reciprocal concentration of the unreaction of SiO_2 and reaction time should be linear with the slope equal to the rate constant.

$$-dC_A/dt = kC_A \qquad (3)$$

$$\ln C_{Ao}/C_A = kt \qquad (4)$$

The reactions were carried out by fixing the amounts of SiO_2 and TIS at 30 mmol. The reaction time was varied from 1 to 75 min. at 150°C. The relationship between the reciprocal of mmol of unreacted SiO_2 against time was obtained (Figure 5), showing a straight line, which confirmed that the reaction order of SiO_2 and TIS was second order overall, first order with respect to TIS and first order with respect to SiO_2, as assumed.

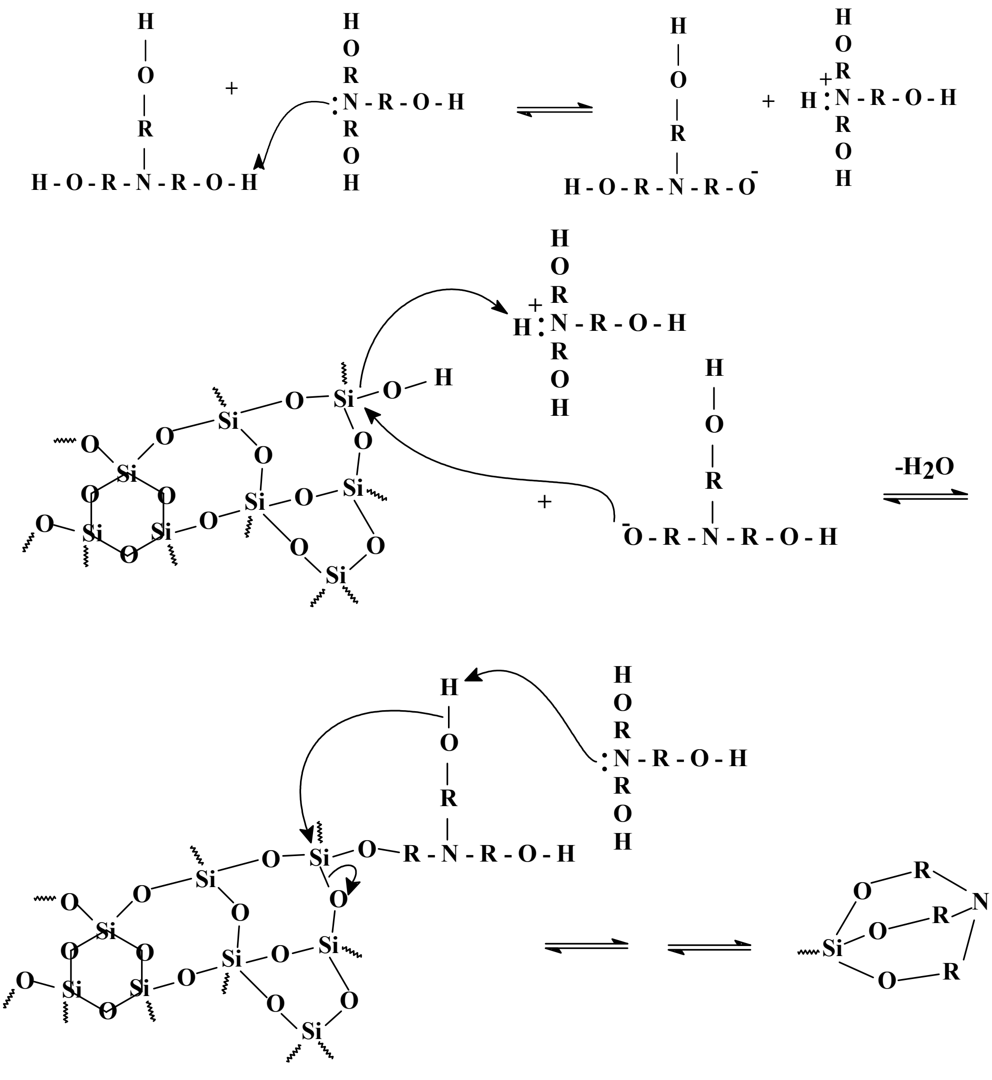


Figure 4. Possible Mechanism of the reaction of silica and tris(isopropanolamine).

Figure 5. Effect of Reaction time.

4. Determination of Reaction Rate Constant and Activation Energy

The reaction rate constant, k, is independent of the concentration of the species involved in the reaction. However, it is strongly dependent on temperature, as expressed in the Arrhenius equation.

The experiments were conducted by fixing the amounts of SiO_2 and TIS at 30 mmol. The reaction temperature was varied from 150°, 170°, to 190°C. For each reaction temperature, the reaction time was varied from 1 to 75 min. The plots between the reciprocal mmol of unreacted SiO_2 against reaction time of each temperature all showed straight lines with different rate constants, as shown in Figure 6 and Table 1. As expected, reactions run at higher temperatures exhibited higher rate constants.

Table 1 showed the calculated rate constants for each temperature obtained from the slopes of the plots, which were determined by eq.(4).

The activation energy could be obtained through the Arrhenius equation. After taking the natural logarithm of the Arrhenius equation the following equation was obtained;

$$\mathbf{\ln(k) = \ln A - E/R\ (1/T)} \qquad \mathbf{(5)}$$

The plot of ln(k) versus 1/T is shown in Figure 7. A straight line with slope corresponding to the activation energy was obtained. After multiplying the slope by the gas constant (8.314 $Jmol^{-1}k^{-1}$), the activation energy obtained was found to be ~55±4 J/mol.

Figure 6. Effect of Reaction Temperature on the Dissolution of SiO_2.

Table 1. The Reaction Rate Constants at Various Temperature.

Temp (°C)	**1/Temp (1/K)**	**k (1/mmol.min)**	**ln (k)**
150	0.002364	0.00013	-8.94668
170	0.002257	0.000244	-8.31638
190	0.002160	0.000503	-7.59397

Figure 7. Determination of the Activation Energy for SiO_2 Dissolution.

5. The Dissolution Rate of SiO_2 with TETA as a Function of Time

The reaction was carried out by fixing the amount of SiO_2, TIS, and TETA at 30 : 30 : 0.3 mmol and varying the reaction time from 1 to 75 min. The reaction temperature was fixed at 170°C. The plot of mmol of reacted SiO_2 versus the reaction time showed faster dissolution of SiO_2 than the one without TETA at the same conditions. The Dissolution of SiO_2 with TETA was about 2 times faster, as shown in Figure 8.

Figure 8. Effect of TETA on Dissolution of SiO_2.

CONCLUSIONS

In the kinetic studies on the dissolution of SiO_2, the dissolution process was a second order reaction overall, first order with respect to SiO_2 and first order with respect to TIS. The rate constant of the reaction, k, increased as the reaction temperature increased, which corresponds to the Arrhenius equation. The activation energy was determined experimentally by carrying out the reaction at several different temperatures. The plot of ln(k) and reciprocal of temperature gave the slope corresponding to the activation energy, Ea, which was 55 ± 4 kJ/mol. When 1% TETA was present, the reaction time was halved. Therefore, TETA can be used as a dissolution catalyst for this reaction.

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