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Formation and structure of tris(alumatranyloxy-*i*-propyl)amine directly from $Al(OH)_3$ and triisopropanolamine

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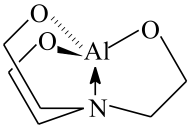
Abstract

Recently, a new one step method was developed for synthesizing a methyl substituted alumatrane directly from aluminum hydroxide [$Al(OH)_3$] and triisopropanolamine (TIS). The structure of TIS-Al was characterized using DSC, TGA, FAB$^+$-MS, NMR (^{1}H-, ^{13}C-, ^{27}Al-), and FTIR. Triethylenetetramine (TETA), a stronger base than TIS, was found to act as a catalyst to accelerate the $Al(OH)_3$ dissolution rate. The kinetics of TIS-Al formation were studied as a function of different conditions. The activation energy of reaction was 24 ± 2 kJ mol^{-1}. © 2001 Elsevier Science Ltd. All rights reserved.

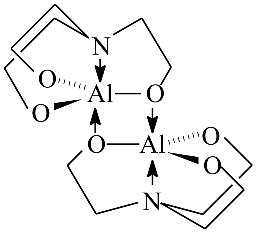
Keywords: Tris(alumatranyloxy-*i*-propyl)amine; Aluminum hydroxide; Triisopropanolamine; Kinetics

1. Introduction

Atranes, **I**, with M = B, Al, Si, Ge, Sn, Pb, P, Ti, V, Mo, etc. have been synthesized and studied extensively over the last three decades [1–5]. These compounds are of interest owing to their cage structure and physical/chemical properties. The behavior of alumatrane, where M = Al, 2,8,9-trioxa-5-aza-1-alumatricyclo [3.3.3.$0^{1,5}$] undecane, and oligomeric alumatrane has been described previously [6–9]. In benzene, cryoscopy and ebullioscopy indicate tetrahedral and octahedral behavior. A mass spectroscopic (EI 70 eV) study showed the stability of the dimer **I**′ in the gas phase.



I



I'

There are several methods of preparing alumatranes. Alumatrane is prepared readily in high yield by reaction of aluminum alkoxides with triethanolamine in an aromatic solvents [10,11] or with no solvent [12–14]. Triethylaluminum also reacts with triethanolamine in toluene or hexane at −78°C to form alumatrane [15]. Verkade [16] prepared alumatrane by the alcoholysis of tris-(dimethylamido) aluminum with triethanolamine

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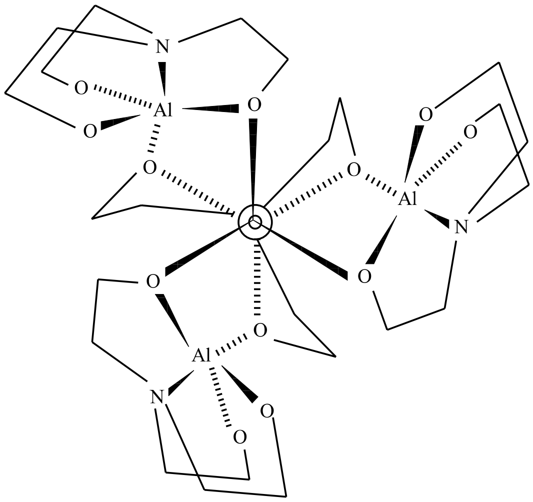
and also by transligation of monomeric and dimeric alumazatranes with triethanolamine.

According to ^{27}Al-, ^{1}H-, and ^{13}C-NMR data, they found tetramers, **II**, in solution and dimeric **I′** by mass spectra in the gas phase. Alumatrane precursors, aluminum alkoxides [Al(OR)$_3$] or aluminum alkyl [Al(R)$_3$] are expensive and the syntheses are multistep. Laine et al. have developed an inexpensive way to convert metal oxides or hydroxides, namely, Al(OH)$_3$ and silica, into novel materials ranging from ion conducting [17], liquid crystalline polymers [18], to oligomeric and polymeric precursors [19].



II

Laine also found that higher boiling point amine bases (b.p. >200°C), such as triethanolamine and triethylenetetramine (TETA) can be used either in catalytic or stoichiometric quantities to dissolve SiO$_2$. Moreover, they also found that approximately stoichiometric quantities of triethanolamine will effectively dissolve Al(OH)$_3$. The "oxide one pot synthesis process (OOPS)" for alkoxyalanes was developed after it was discovered that stoichiometric amounts of triethanolamine would dissolve Al(OH)$_3$, the source material for most pure alumina.

The purpose of this work is to extend previous efforts to reactions of Al(OH)$_3$ and triisopropanolamine (TIS), and study the kinetics of the product formation, which includes the reaction order, rate constant, and activation energy. Along with this, the effect of TETA on the reaction was also studied to improve the solubility of this novel aluminum alkoxide in non-polar solvents for use as a catalytic intermediate in the sol–gel processing.

2. Experimental

2.1. Materials

The starting materials and products are slightly moisture and air sensitive. Therefore, all operations were carried out with careful exclusion of air by purging with nitrogen gas.

UHP grade nitrogen; 99.99% purity was obtained from Thai Industrial Gases Public Company Limited (TIG). Aluminum hydroxide hydrate [$Al(OH)_3 \cdot xH_2O$] containing 57.5% Al$_2$O$_3$ as determined by TGA was purchased from Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG), used as solvent in the reaction, was purchased from Farmitalia Carlo Erba (Barcelona) and purified by fractional distillation at 200°C, under N$_2$ before use. TIS was obtained from Fluka Chemika-BioChemika (Switzerland) and used as received. TETA was obtained from Union Carbide Thailand Limited (Bangkok, Thailand) and distilled under vacuum (10^{-2} Torr) at 120°C. Acetonitrile and methanol were purchased from J.T. Baker Inc. (Phillipburg, USA) and purified by standard techniques.

2.2. Instrumentation

Mass spectra were obtained on a 707E-Fison Instrument (VG-Autospec, Manchester, England) with a VG data system, used in the positive fast atomic bombardment (FAB$^+$) mode. Thermal analysis was carried out on a Netzsch DSC 200 (Germany) and a Netzsch Gerätebue BmbH Thermal analysis TG 209 (Germany). ^{1}H- and ^{13}C-NMR spectra were obtained using a 500 MHz JEOL (JNM-A500) spectrometer at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University, using deuterated methanol (CD$_3$ OD) and tetramethylsilane (TMS) as the solvent and internal reference, respectively. ^{27}Al-NMR spectra were recorded on Bruker 360 MHz at the University of Michigan. Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad FT-45A FTIR spectrometer with a resolution of ±4 cm^{-1}.

2.3. Procedure

General procedures to obtain tris(alumatranyloxy-*i*-propyl)amine are as follows; Al(OH)$_3$, 50 ml of EG, and TIS were added to a 250 ml two-necked round bottomed flask. The reaction mixture was stirred and heated under N$_2$ in a thermostatted oil bath. When the oil bath temperature reached 200°C, the reaction was considered to have commenced. Fresh EG in the same amount as the distillate was added to maintain the total reaction volume until the reaction mixture turned clear, indicating reaction completion. After letting the reaction mixture stand without stirring overnight, white product precipitated out. After filtering, the product was stirred with dried acetonitrile overnight to remove excess TIS. The solid product was then filtered off and dried under high vacuum (10^{-2} Torr) at 120°C for 5 h. Dried products were then characterized by DSC, TGA, FTIR, FAB^+-MS and NMR.

Unreacted alumina recovered from a reaction was purified as follows: after the reaction mixture was cooled, unreacted $Al(OH)_3$ was filtered off, and stirred with dried methanol overnight to extract remaining product from unreacted $Al(OH)_3$. The unreacted $Al(OH)_3$ was filtered off, washed with 2 × 20 ml of dried methanol, and then oven dried at 120°C for 10 h. Finally, the dried $Al(OH)_3$ was calcined in the TGA to obtain the alumina content. The total unreacted $Al(OH)_3$ was recalculated to obtain reacted alumina.

2.4. Kinetic studies

The kinetic studies were conducted primarily on the dissolution of $Al(OH)_3$ as a function of changes in the reaction conditions, namely, the amount of TIS, the amount of $Al(OH)_3$, reaction temperature, and time. Each condition was repeated three times.

The optimum ratio of TIS was first studied by fixing the amount of $Al(OH)_3$ (57.5% Al_2O_3 content by TGA) at 22.7–10 mmol equivalent of Al_2O_3. The amount of TIS was varied from 0 to 50 mmol. The reaction time and temperature were fixed at 3 h and 200°C, respectively.

2.4.1. Dissolution rate as a function of $Al(OH)_3$

The amount of TIS was fixed at 3.83 g (20 mmol) and the amount of $Al(OH)_3$ was varied from 0.89 to 8.87 g (5–40 mmol). EG was added to make the total volume of the reaction mixture 50 ml. The reaction time and temperature were set at 1 h and 200°C, respectively. The relationship between mmol of unreacted alumina and mmol of alumina added was plotted.

2.4.2. Dissolution rate as a function of TETA concentration

To study the effect of TETA concentration on the rate of reaction, $Al(OH)_3$ and TIS quantities were fixed at 1.77 g (22.7 mmol) and 0.96 g (5 mmol), respectively. The concentration of TETA was varied from 0.00 to 4.39 g (0–30 mmol). The reaction time and temperature were fixed at 3 h and 200°C. The relationship between mmol dissolved alumina and mmol TETA added was then plotted.

2.4.3. Determination of the reaction rate constant and activation energy

Amounts of $Al(OH)_3$ and TIS were fixed at 1.77 g (22.7 mmol) and 0.96 g (5 mmol), respectively. The reaction time was varied from 15 to 120 min with increments of 15 min at 150°C, 170°C, 190°C, and 200°C. The relationship between mmol of unreacted alumina versus reaction time at each reaction temperature was then plotted to obtain the reaction rate constant (k). The activation energy was then calculated by plotting ln (k) versus $1/T$ (1 K^{-1}).

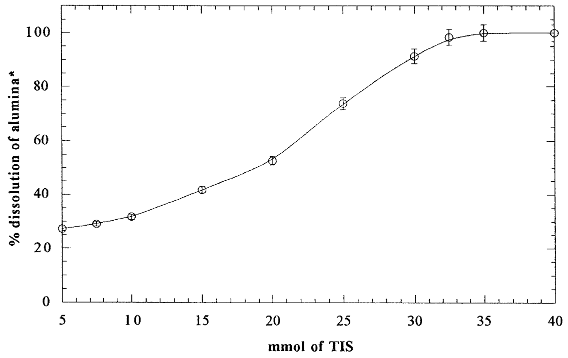
2.4.4. Dissolution rate as a function of time in the presence of TETA as a catalyst

The effect of time on the reaction of $Al(OH)_3$ and TIS with TETA as a catalyst was studied by fixing the amounts of $Al(OH)_3$, TIS, and TETA at 1.77 g (22.7 mmol), 0.96 g (5 mmol), and 0.18 g (1.25 mmol), respectively. The reaction temperature was fixed at 200°C and the reaction time was varied from 15 to 120 min. The mmol of unreacted alumina for each run were then plotted versus time.

3. Results and discussion

In this study, recovered $Al(OH)_3$ was thermally converted to α-alumina to determine the actual amount dissolved. $Al(OH)_3$ used at the beginning and left after the reaction was measured as Al_2O_3 using TGA ceramic yields.

As seen in Fig. 1, with a fixed amount of aluminum hydroxide hydrate at a reaction time and temperature of 3 h and 200°C, respectively, the reaction went very slowly for TIS quantities less than 20 mmol. However, it went to completion when 35 mmol of TIS was used. The addition of 10 mmol of TETA with 22.7 mmol of $Al(OH)_3$ and 35 mmol of TIS led to complete reaction within 2 h (see Fig. 6).



Reaction time : 3 h

Reaction temperature : 200°C

*Equivalent mmol of alumina calculated from $Al(OH)_3.xH_2O$ used

Fig. 1. Optimization of $Al(OH)_3$: TIS ratio for complete $Al(OH)_3$ dissolution.

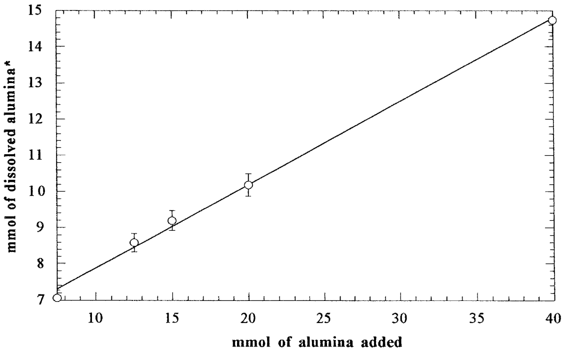
3.1. Dissolution rate as a function of $Al(OH)_3$

In this case, determination of a reaction rate, the so-called "method of initial rates", was based upon an accurate analysis of one product at a very early stage of reaction. Therefore, all reactions studied did not proceed to completion. The reaction time and temperature were thus set at 1 h and 200°C. The amount of alumina was varied from 7.5 to 12.5, 15, and 40 mmol while the TIS concentration was fixed at 20 mmol. The relationship between the dissolved and added alumina is nearly linear, (Fig. 2). Clearly, the reaction of $Al(OH)_3$ and TIS also depends on the amount of $Al(OH)_3$. The curve was nearly linear, suggesting that the reaction was first order with respect to $Al(OH)_3$ and first order with respect to TIS. It is worth noticing that the intercept of both curves are not equal to zero. This is because some unreacted $Al(OH)_3$ is lost during the recovery step.

3.2. Determination of the reaction rate constant and the activation energy

We used the integral method to determine the reaction order. The reaction order was first assumed to be second order overall. Plots of $\ln[(1-rX)/(1-X)]$ versus reaction time at each temperature are presented in Fig. 3 (note: the linearity of the data suggests that the reaction is most likely second order as assumed). The reaction rate constants were obtained from the slope of the plotted data, straight lines with different gradients. As expected, the higher temperatures showed higher gradients, meaning that higher reaction temperatures gave higher dissolution rate.

To determine the activation energy, the Arrhenius equation was employed. After obtaining the reaction rate constants (k), ln k was plotted versus $1/T$ as Fig. 4, which gives a straight line with the slope proportional to the activation energy. The slope obtained is equal to the activation energy divided by the gas constant (8.314 J mol^{-1} K^{-1}). As a result, the activation energy was 24 ± 2 KJ mol^{-1}.



Reaction time : 1 h
Reaction temperature : 200°C
*Equivalent mmol of alumina calculated from $Al(OH)_3.xH_2O$

Fig. 2. Dissolution rate as a function of $Al(OH)_3$ concentration.

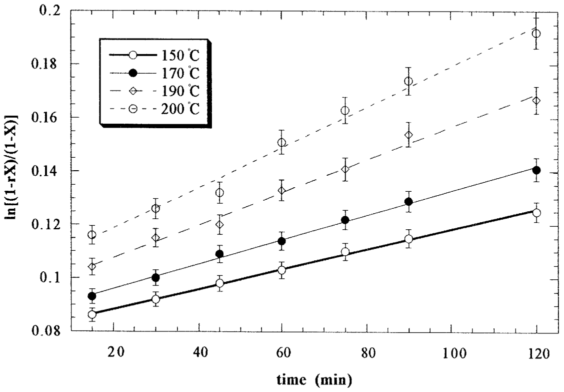


Fig. 3. The relationship of logarithm of conversion factor versus reaction time for each variation of reaction temperature.

3.3. Dissolution rate as a function of TETA concentration

The plot of the amount of dissolved $Al(OH)_3$ and amount of TETA is presented in Fig. 5. The higher the TETA concentration, the greater the amount of dissolved $Al(OH)_3$. At low TETA concentration (1.25–2.5 mmol), the amount of $Al(OH)_3$ dissolved increased significantly, as compared to the higher TETA concentrations. This is due to the role of TETA acting as solubilization catalyst to increase the surface area of $Al(OH)_3$.

3.4. Dissolution rate as a function of time in the presence of TETA, as a catalyst

Fig. 6 shows two plots of mmol of unreacted $Al(OH)_3$ versus reaction time comparing reactions with

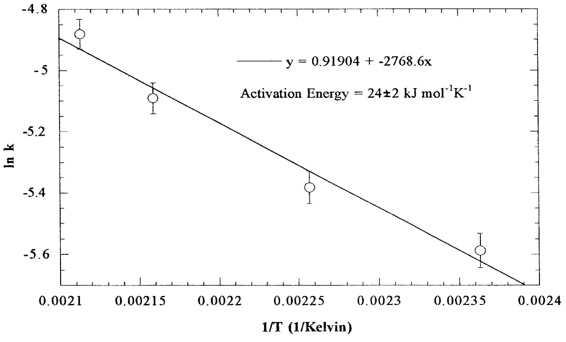
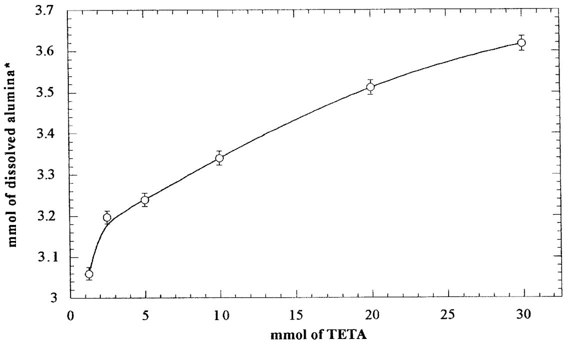


Fig. 4. The relationship of logarithm of rate constant and reaction temperature.



*Equivalent mmol of alumina calculated from $Al(OH)_3.xH_2O$ used

Fig. 5. Effect of the TETA concentration.

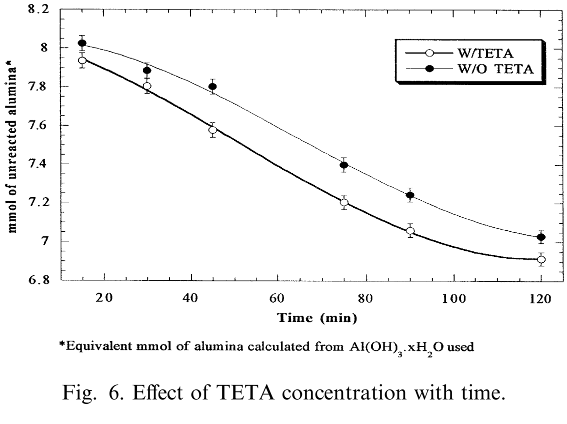
and without TETA. The dissolution reaction rate with TETA was faster than that without TETA because TETA increased solubility of $Al(OH)_3$, resulting in increasing its surface area which caused the reaction to go faster, as discussed previously.

3.5. Characterization

3.5.1. Thermogravimetric analysis

The TGA data for the product from the reaction without TETA shows two major regions of mass loss (see Fig. 7(a)). The first region between 180–260°C indicated the decomposition of TIS ligand while the second region occurred at about 260–550°C corresponding to the oxidative decomposition of carbon residues. The % ceramic yield of the product was 27.6%, which was higher than the theoretical ceramic yield (23.7%) owing to the incomplete combustion of the sample since the final ash was still gray in color.

Similarly, the TGA of the product synthesized in the presence of TETA (Fig. 7(b)) also showed two major mass losses at 180–250°C and 250–500°C corresponding to the decomposition of TIS ligand and the oxidative decomposition of carbon residues, respectively. The % ceramic yield of product was 31.9%, which was much higher than the theoretical yield. This can be explained along with the mass spectrum which indicated that the product synthesized from the batch containing TETA using as catalyst gave more smaller units, dimer (m/e 431), than the one without TETA. The more smaller unit, the higher ceramic yield. Moreover, the final ash was darker in color.



*Equivalent mmol of alumina calculated from $Al(OH)_3.xH_2O$ used

Fig. 6. Effect of TETA concentration with time.

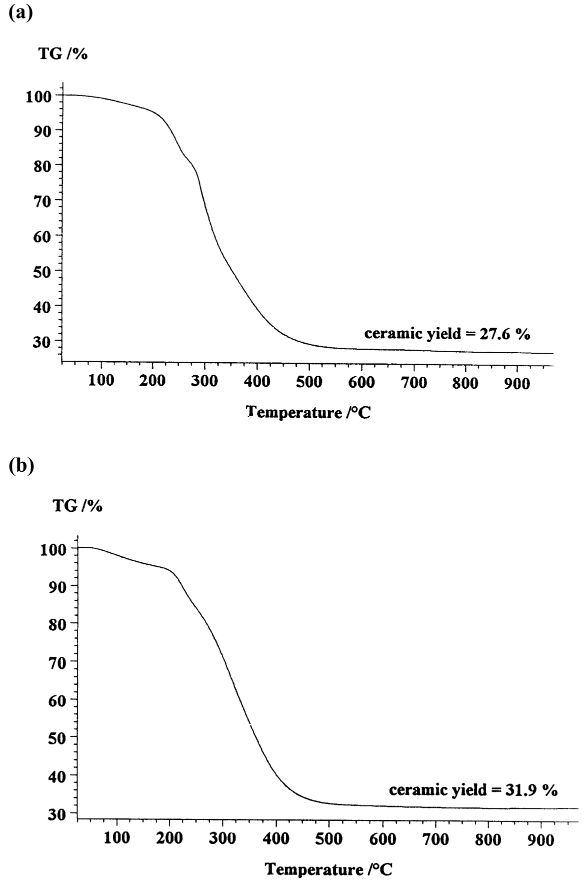


Fig. 7. TGA data of the products obtained from the reactions: (a) with and (b) without TETA.

3.5.2. Differential scanning calorimetry

The DSC of the product from the reaction without TETA, see Fig. 8(a), showed an exotherm at 250–280°C corresponding to the melting point immediately followed by the decomposition temperature of the product, the endotherm at 280–400°C. It is coincident with the result of its TGA. The T_g was observed at about 167°C.

Similarly, the DSC data of the product from the reaction with TETA, as shown in Fig. 8(b), indicated the

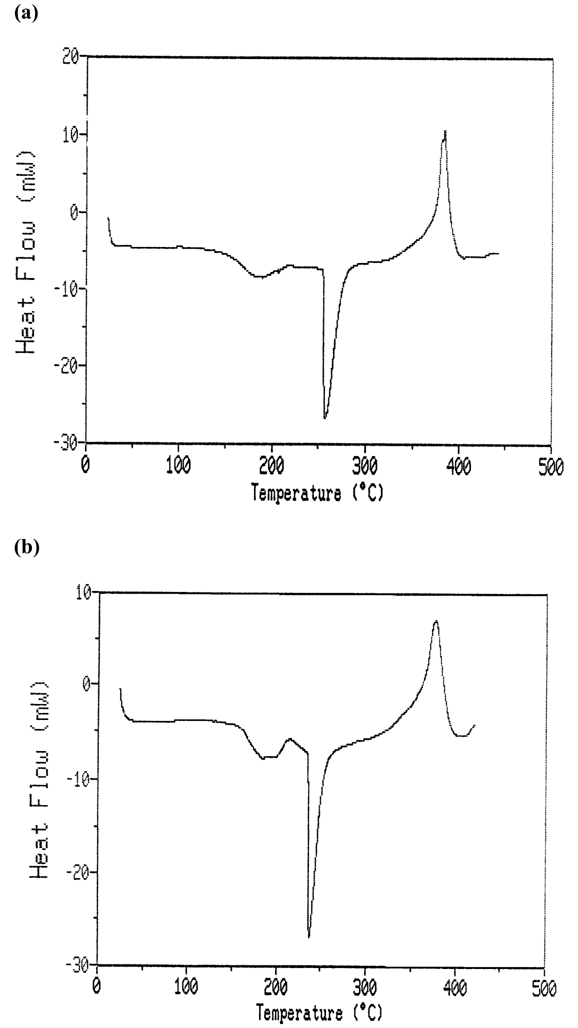


Fig. 8. DSC thermograms of the products obtained from the reactions (a) with and (b) without TETA.

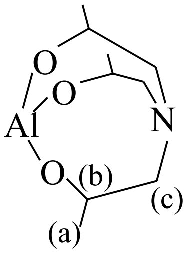
exotherm at about 220–260°C corresponding to the melting point followed by the decomposition of the product, the endotherm at about 260–380°C. It is worth noticing that the both temperatures are lower than those in Fig. 8(a). This is due to the more smaller units containing in the products obtained from the reaction with catalyst TETA. The T_g of this product occurred at about 166°C.

3.5.3. *Positive fast atomic bombardment mass spectroscopy*

Mass spectral analysis suggests that there are four different alumatrane complexes; hexamer (*m/e* 1292), the highest intensity pentamer plus one morpholine (*m/e* 1250) resulted from losing a molecule of water in TIS, trimer plus one ethylene glycol (*m/e* 707), and monomer plus one TIS (*m/e* 409) and the intensities of all proposed structures was shown in Table 1.

The fragmentation pattern of the product from the reaction with TETA gave higher intensities of the lower unit peaks at *m/e* 216 and 409, and lower intensity of the peak at *m/e* 1250. This result can obviously confirm that the reaction carried out without TETA gives the product containing higher molecular weight unit than the one run with TETA owing to the acceleration of TETA resulting in faster completion of the reaction.

3.5.4. *Nuclear magnetic resonance spectroscopy*

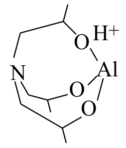
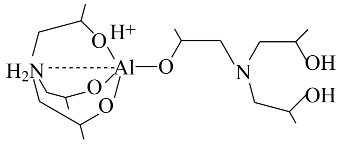
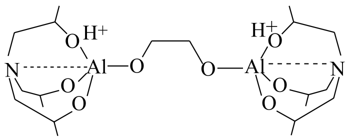
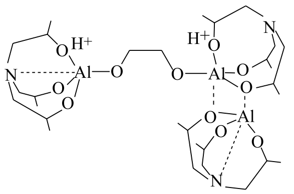
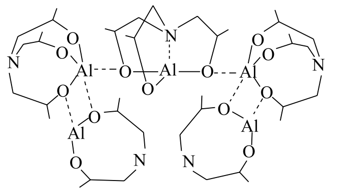
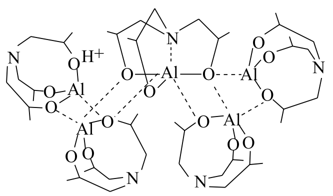


The NMR results showed that the products certainly contained several kinds of oligomers, such as monomer, dimer, etc., which are coincided with the mass spectroscopy results. The ^{1}H-NMR spectrum of the product from the reaction without TETA showed three multiple characteristics of quadrapolar coupling peaks indicating the presence of a few species in the product. The peaks at 1.1–1.4 ppm correspond to the $-CH_3$ group of TIS, position (a). The peaks at 2.4–3.1 ppm are assigned to the methylene group adjacent to the N-atom of TIS ($-N-CH_2$) at position (c). The peaks at 3.6–4.2 ppm are assigned to the tertiary carbon adjacent to the O-atom of TIS, position (b). The ^{1}H-NMR spectrum of the product from the reaction with TETA gave a similar one.

Similarly, the ^{13}C-NMR spectrum of the product from the reaction showed a multiple peak at 22.0 ppm corresponding to $-CH_3$ groups at position (a) coupled to itself and proton of the tertiary carbon. The sharp peak at 64.3 ppm belongs to the carbon adjacent to N-atom of TIS ($-N-CH_2$) at position (c). The multiple peak at 79.0 ppm is associated with the carbon adjacent to O-atom of TIS (position (b)) due to the coupling with $-N-CH_2$ and $-CH_3$. The spectrum of both reactions, with and without TETA, showed the similar positions.

The ^{27}Al-NMR spectra of the products from the reaction with and without TETA coincidentally showed three different peaks, as shown in Table 2, at around 65, 49 and 7 ppm at the ratio of 1:1:1. Again, these three peaks indicated the presence of both hexa- (at 7 ppm) and tetracoordinated (at 65 and 49 ppm) aluminum compounds.

Table 1
The proposed structures and fragmentation pattern of products

m/e	Intensities	Proposed structure
216	50	 $\mathrm{AlN(CH_2CH_2CH_3O)_3H^+}$
409	17.5	 $\mathrm{AlN(CH_2CH_2CH_3O)_3N(CH_2CH_2CH_3O)\ (CH_2CH_2CH_3OH)_2H^+}$
492	38.7	 $\mathrm{Al_2[N(CH_2CH_2CH_3O)_3]_2\ (OCH_2\ CH_2O)\ H_2^+}$
707	35.4	 $\mathrm{Al_3[N(CH_2CH_2CH_3O)_3]_2(OCH_2)_2H_2^+}$
959	7.9	 $\mathrm{Al_3[N(CH_2CH_2CH_3O)_3]_2Al_2[N(CH_2CH_2CH_3O)_2]_2}$
1076	15	 $\mathrm{Al_5[N(CH_2CH_2CH_3O)_3]_5H^+}$

(*continued on next page*)

Table 1 (*continued*)

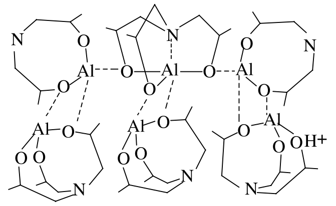
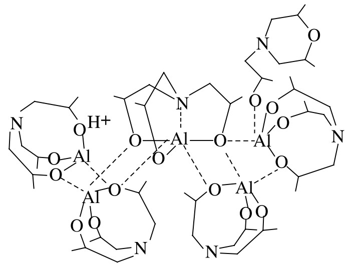
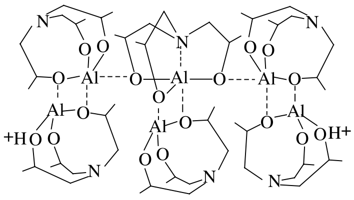
m/e	Intensities	Proposed structure
1175	46.3	 $Al_4(CH_2CH_2CH_3O)_3]_4Al_2[N(CH_2CH_2CH_3O)_2]_2H^+$
1250	100	 $Al_5[N(CH_2CH_2CH_3O)_3]_5N(CH_2CH_2CH_3O)_2CH_2CH_2CH_3H^+$
1292	7.8	 $Al_6[N(CH_2CH_2CH_3O)_3]_6H^+$

Table 2
Peak positions of ^1H-, ^{13}C-, and ^{27}Al-NMR of products

Compounds	^1H-NMR (ppm)	^{13}C-NMR (ppm)	^{27}Al-NMR (ppm)
Product w/o TETA	1.1–1.4 (a)	22.0 (a)	7.5, 49.6 and 66.0
	2.4–3.1 (c)	64.3 (c)	
	3.6–4.2 (b)	79.0 (b)	
Product w/o TETA	1.1–1.9 (a)	21.0 (a)	7.4, 48.8 and 64.9
	2.2–2.8 (c)	65.0 (c)	
	3.7–4.1 (b)	79.0 (b)	

Table 3
Peak position and assignments of FTIR spectra of products with/without TETA

Peak positions (cm^{-1})		Assignments
Al-TIS	TIS-Al-TETA	
3300–3700	3300–3700	*u* O–H
2750–3000	2750–3000	*u* C–H
1650	1630	O–H overtone; C–H bending
1450	1450	*δ* C–H
1000–1200	1000–1250	*u* C–N; O–H bending
500–800	500–800	*u* Al–O

3.5.5. Fourier transform infrared spectroscopy

The FTIR spectra of the products from the reactions with and without TETA show similar functional groups (Table 3). Due to the moisture sensitivity of the products, the $\nu_{\mathrm{O-H}}$ appears at 3300–3700 cm^{-1}, and the wave number at 2750–3000 cm^{-1} corresponds to $\nu_{\mathrm{C-H}}$. The single peak at about 1650 cm^{-1} is O–H overtone and C–H bending. The strong peak at 1000–1250 cm^{-1} results from the $\nu_{\mathrm{C-N}}$ and/or O–H bending. The broad peak at 500–800 cm^{-1} represents the $\nu_{\mathrm{Al-O}}$ of the product.

4. Conclusions

In this work, alumatrane complexes were synthesized directly from inexpensive starting material, $Al(OH)_3$, and TIS, via the one step process, called “OOPS” process. Mass spectra revealed that products were oligomers. The main product was pentamer bonded with TIS that lost one H_2O molecule. From TGA data, the % ceramic yields of the product from the reactions without and with TETA were 27.6 and 31.9%, respectively, which are higher value than the theoretical yield (23.7%). The higher percent ceramic yields were due to the small unit of oligomers in the product and the small amount of unreacted $Al(OH)_3$ remaining in the product.

The reaction order was second order overall, first order with respect to $Al(OH)_3$ and first order with respect to TIS. The dissolution rate increased when the reaction temperature increased. The activation energy of this reaction was about 24 ± 2 kJ mol^{-1}.

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