

CHAPTER I

INTRODUCTION

1.1 Background

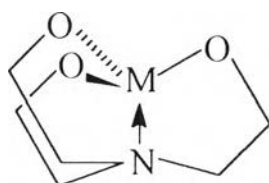
Aluminum, Al, atomic number 13, atomic weight 26.981, is the third most abundant element in the earth's crust (8.8 mass%) [KIRK-OTHEMER (1979); COTTON AND WILKINSON, (1967)] occurring widely in nature in silicate minerals, such as micas and feldspars, as the hydroxide (bauxite), and as cryolite (Na_3AlF_6)

Bauxite, weathered rock that consists mainly of aluminum hydroxide minerals, is the raw material for all manufactured aluminum compounds. The Bayer process (see scheme 1) is the commercial method used to produce alumina (Al_2O_3) and aluminum hydroxide ($\text{Al}(\text{OH})_3$) from bauxite. All bauxite refineries share six common process steps: bauxite mining, raw material preparation, bauxite digestion, separation, washing, and disposal of insoluble bauxite residues, aluminum hydroxide (trihydrate) precipitation, and calcination to anhydrous alumina [BAYER, (1988)]

Stoichiometrically, alumina is the only oxide of aluminum, however, it has several important hydrated forms corresponding to the stoichiometries $\text{AlO}(\text{OH})$ and $\text{Al}(\text{OH})_3$. Adding ammonia to a boiling solution of an aluminum hydroxide produces a form of $\text{AlO}(\text{OH})$ known as boehmite [Eisch, (1967)]. A second form of $\text{AlO}(\text{OH})$ occurs in nature as the mineral diaspore [Eisch, (1967)]

1.2 Literature Survey

Metallatranes, or simply atranes, are intramolecular complex cyclic ester or alkoxides of tris(2-hydroxyalkyl)amines having a skeleton of general structure I,



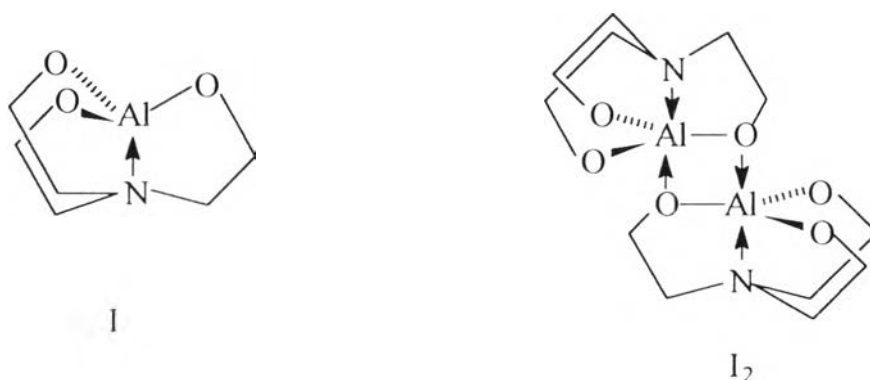
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where M is an n-valent element having inorganic or organic substituents when $n > 3$. The term metallatranes, proposed by VORONKOV and ZELCHAN in 1965, is an abbreviation used for aminotrialkoxy derivatives of different elements that contain the above skeleton (I). For example, aminotrialkoxyphosphoranes, aminotrialkoxyboranes and aminotrialkoxysilanes give phosphatranes, boratranes and silatranes, respectively. Atrane structures are generally characterized by the tricyclic model wherein a transannular $M \leftarrow N$ bond is assumed to be present.

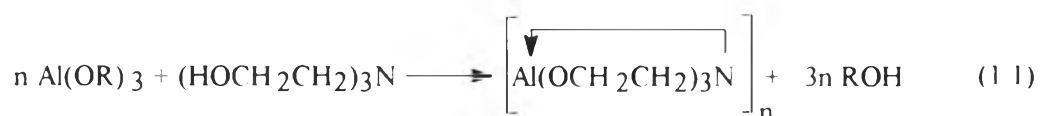
Metallatranes with $M = B, Al, Si, Ge, Sn, Pb, P, Ti, V, Mo$, etc. have been synthesized and studied during the last three decades [VORONKOV et al., (1968); BRADLEY et al., (1978)]. These compounds are of interest because of their cage structure, physical/chemical properties, and especially biological activity.

The behavior of monomer I and oligomeric alumatrane has been described previously [HEIN and ALBERT (1952); MEHROTRA (1962); MEHROTRA (1962); SHKLOVER et al., (1984); BRADLEY et al., (1978);

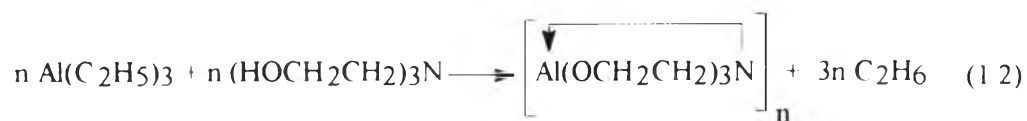
VORONKOV and BARYSHOK (1982); MEHROTRA and RAI (1991)]. In benzene solution, cryoscopy [HEIN and ALBERT (1952)] and ebullioscopy [MEHROTRA (1962)] indicate octameric and hexameric behaviors. A mass spectroscopic (EI 70 eV) study [MEHROTRA (1962)] showed the stability of the dimer I_2 in the gas phase.



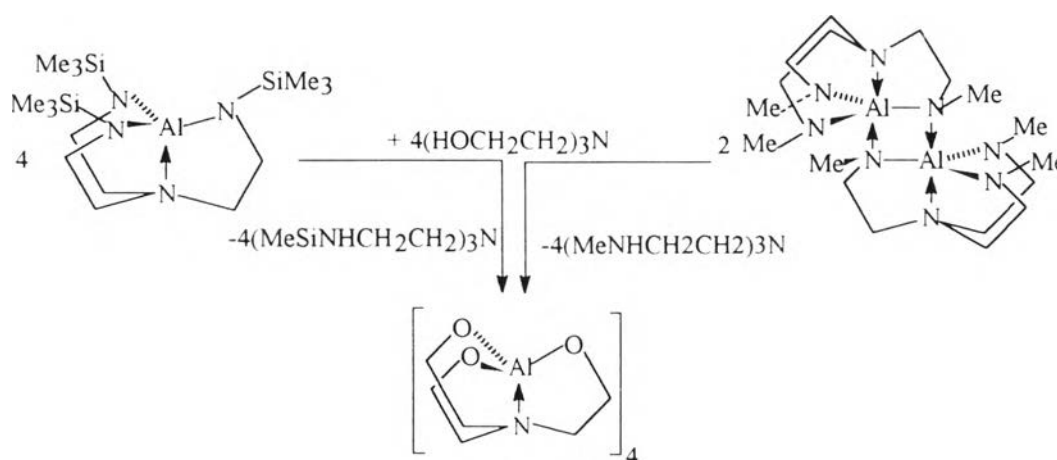
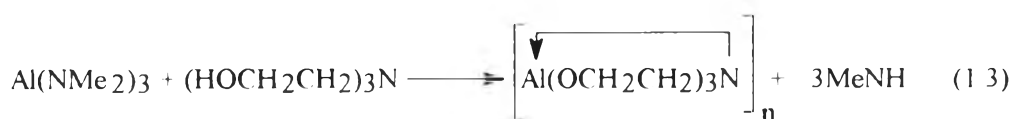
There are several methods to prepare alumatranes. The simplest alumatranes were prepared in high yield by the reaction of aluminum alkoxide with triethanolamine in an aromatic solvent (benzene [MEHROTRA (1962)], toluene [THOMAS et al., (1961)]) or with no solvent [HEIN et al., (1952); ICKEN et al., (1964); STANLEY (1968); ELBING et al., (1964)] according to eq 1.1



Triethylaluminum also reacts with triethanolamine in toluene or hexane at -78°C to form alumatranes [HIGASHI et al., (1968)] see eq. 1.2

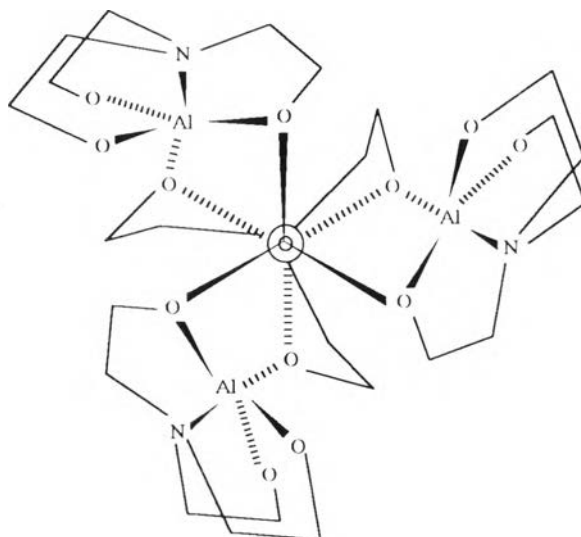


VERKADE et al., (1993) used the alcoholysis of tris-(dimethylamido) aluminum with triethanolamine (eq 1.3) and also the transligation of monomeric and dimeric alumazatrane with triethanolamine (Scheme 1.2)



Scheme 1.2 Transligation of Monomeric and Dimeric Alumazatrane with Triethanolamine.

According to ²⁷Al-, ¹H-, and ¹³C-NMR data, they found tetramers in solution and mass spectra revealed the stable tetramer (Scheme 1.3) in the gas phase.



Scheme 1.3 Newman Projection Down the Al-N Bond from an X-ray Crystallographic Determination of Tetrameric Alumatrane.

The starting materials to synthesize alumatrane complexes, aluminum alkoxides $[\text{Al}(\text{OR})_3]$ or aluminum alkyls $[\text{Al}(\text{R})_3]$, are expensive and the syntheses are multistep. LAINE et al. have developed an inexpensive way to convert metal oxides, namely, alumina and silica, into novel materials ranging from ion conducting (CHEW et al. submitted for publication), liquid crystalline polymers (RAY et al., 1992), to oligomeric and polymeric precursors.

LAINE et al. found that higher boiling point amine bases (b.p. $>200^\circ\text{C}$), such as triethanolamine and triethylenetetramine can be used either in catalytic or stoichiometric quantities to dissolve SiO_2 . Moreover, they also found that approximately stoichiometric quantities of TEA will effectively dissolve $\text{Al}(\text{OH})_3$. The “Oxide One Pot Synthesis Process (OOPS)” for alkoxyalanes was developed after it was discovered that stoichiometric amounts of TEA

would dissolve aluminum hydroxide, the source material for most pure alumina [KIRK-OTHEMER (1979); COTTON and WILKINSON (1967)].

Recently, PETCHSUK, DHUMRONGVARAPORN, and LAINE (1994) synthesized alumatrane directly from $\text{Al}(\text{OH})_3$ and TEA, and found pentamer, tetramer, trimer and the most stable species, dimer from mass spectroscopic data, ^1H -, ^{13}C - and ^{27}Al -NMR. Moreover when TETA, stronger base than TEA, was used, mass spectroscopic data indicated the same mixture of oligomers. The integral method is used to study the reaction kinetics. The reaction of $\text{Al}(\text{OH})_3$ and TEA is second order overall, first order with respect to $\text{Al}(\text{OH})_3$ and first order with respect to $[\text{TEA}]$. The activation energy for this reaction was obtained using the Arrhenius' equation and it was estimated to be $62 \pm 5 \text{ kJ mol}^{-1}$.

1.3 Kinetic Theory

There are four methods for analyzing kinetic data, namely, the differential, the integral, the initial rate, and the half-life methods [FOGLER (1992)]. The methods of half-lives and initial rates require experiments at many different initial conditions to determine the reaction order and the specific reaction rate, whereas with either the integral or differential method of analysis, 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. In this study, the integral method is used to determine the reaction rate and order.

1.3.1 Integral Method

The integral method is most often used when the reaction order is known and it is desired to evaluate the specific reaction rate constants at different temperatures to determine the activation energy. A differential equation for the reaction order, used to model the batch system, is integrated. If the assumption is correct, the appropriate plot determined from this integration should be linear.

The rate law for a first-order reaction can be written as

$$-\frac{dC_A}{dt} = kC_A \quad (1.4)$$

Thus, the integrated rate expression is,

$$\ln \left[\frac{C_A}{C_{A0}} \right] = -kt \quad (1.5)$$

According to Eq 1.5, a plot of $\ln C_A$ against time must be linear with a slope of $-k$

The general equation for second order reaction can be written as follows;



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 written as follows;

$$-\frac{dC_A}{dt} = kC_A^2 \quad (1.6)$$

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + kt \quad (1.7)$$

In the case where the initial concentrations of both reactants are not equal, the reactivity ratio, r , is defined as:

$$r = \frac{C_{A_0}}{C_{B_0}}$$

and X = Conversion factor

$$X = \frac{[\text{Al(OH)}_3] \text{ at starting point} - \text{Unreacted } [\text{Al(OH)}_3]}{[\text{Al(OH)}_3] \text{ at starting point}}$$

the equation can be derived as follow;

Initially ; $t = t_0 = 0$; $C_A = C_{A_0}$; $C_B = C_{B_0}$

At any time; $t = t$; $C_A = C_{A_0}(1-X)$; $C_B = C_{B_0}(1-rX)$

$$\begin{aligned} \text{Rate law: } -\frac{dC_A}{dt} &= C_A \frac{dX}{dt} \\ &= k[C_A][C_B] \quad (k = \text{reaction rate constant}) \\ &= k[C_{A_0}(1-X)][C_{B_0}(1-rX)] \end{aligned}$$

$$\frac{1}{(1-X)(1-rX)} dX = kC_{B_0} dt$$

$$\int \frac{1}{(1-X)(1-rX)} dX = \int kC_{B_0} dt$$

(See Appendix I for the complete conversion of this integral process)

$$\ln \left[\frac{(1-rX)}{(1-X)} \right] = kC_{B_0}(1-r)t \quad (1.8)$$

For the case where $aA + bB \rightarrow$ products, the rate expression and the integrated equation can be written as;

$$-\frac{dC_A}{C_{A_0}} = kC_A C_B \quad (1.9)$$

$$\ln \left[\frac{C_A}{C_B} \right] = \ln \left[\frac{C_{B_0}}{C_{A_0}} \right] + (aC_{B_0} - bC_{A_0})kt \quad (1.10)$$

1.3.2 The Reaction Rate Constant

Typical Arrhenius behavior results in the following equation;

$$k(T) = A e^{-E_A/RT} \quad (1.11)$$

Where A = preexponential factor or frequency factor

E_A = activation energy, J/mol or cal/mol

R = gas constant = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

= $1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$

T = absolute temperature, K

The activation energy is determined experimentally by carrying out the reaction at several different temperatures. From the natural logarithm, the following equation is obtained:

$$\ln(k) = \ln A - \frac{E_A}{RT} \quad (1.12)$$

The plot of $\ln(k)$ versus $1/T$ should be a straight line whose slope is proportional to the activation energy, the Y-intercept gives the natural log of the preexponential factor.

1.4 Objectives

Alumatrane complexes can be synthesized directly from reactions of aluminum hydroxide ($\text{Al}(\text{OH})_3$) and triisopropanolamine (TIS). Product was characterized by FAB^+ -MS, TGA, DSC, FT-IR and NMR. Kinetics of product formation were also investigated. The integral method was used to study the reaction rate order, rate constant, and activation energy. Moreover, the effect of triethylenetetramine (TETA) on the reaction was studied, as well