International Journal of Engineering Research and Science & Technology

ISSN: 2319-5991
Vol. 2, No. 4
November 2013

www.ijerst.com

Email: editorijerst@gmail.com or editor@ijerst.com
KINETICS OF THERMOLYSIS OF NICKEL PERCHLORATE COMPLEX WITH 2-AMINOPYRIDINE LIGAND

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INTRODUCTION

Many complexes of transition metals having organic ligand and NO₃⁻ or ClO₄⁻ ions (Kumar et al., 2012, 2012; Singh et al., 2008, 2009; Dalvi et al., 2008; Konar et al., 2003;) have shown self catalyzed exothermic thermolysis, and may find application in rocket propellants (Singh et al., 2003, 2005), explosives and pyrotechnics (Fedoroff and Sheffield, 1966; Kopper and Jansen, 1970). These complexes when decompose gives corresponding metal oxide (Kumar et al., 2012) which may have exciting catalytic, magnetic and electrical ownership (Sawant et al., 2002). Transition metal oxides are good burning rate enhancer for composite solid propellants (Kung, 1998; Shen et al., 1993; Solymosi, 1977; Jacob and Whitehead, 1969; Patil et al., 1975). Thermal investigation of energetic complexes assists to perceive cleanly the safety in handling, thermal stability and storage. Kinetic studies furnish an easy access into the mechanism of thermal decomposition of...
a new energetic material. 2-Aminopyridine acts as a bidentate (El-ajaily et al., 2009; Deshpande et al., 2010; Li and Yuan, 2012) or as a monodentate (Mei et al., 2009; Kozlevcar et al., 2001).

In recent years, the study of polynuclear complexes of transition metals has endured dreadful progress due to their various applications and structural captivations. In this work, we submit an account of preparation, characterization and thermolytic studies of nickel perchlorate complex with 2-aminopyridine ligand. The complex is trinuclear and have coordinated water molecules along with 2-aminopyridine. Kinetic evaluation using isothermal TG data has been studied. Kinetics of fast decomposition (explosion) of complex has also been incorporated in this paper.

MATERIALS AND METHODS

Materials
Following analytical grade reagents nickel carbonate, perchloric acid, 2-aminopyridine (s.d. fine), ethanol (Changshu Yangyuan Chemical China), petroleum ether (Merck) were used without further purification.

Preparation and Characterisation of Complex
The complex was prepared by two step procedure. In first step nickel perchlorate was obtained by reacting nickel carbonate with 60% perchloric acid followed by recrystallization. Precipitate of reported complex was formed when ethanolic solution of 2-aminopyridine and nickel perchlorate reacts. Precipitate was washed 3 times with ethanol and dried in hot air oven. The complex was characterized by gravimetric estimation (Vogel et al., 1995), infra red (Miller and Wilkins, 1952; Robert, 1996; Nakamoto, 1978) (Perkin Elmer FT-IR spectrometer) and elemental analysis (Thermo Finnigan Flash EA 1112 CHNS analyzer). Various characterisation data are presented in Table 1.

| Table 1: IR Frequencies And Elemental Analysis Data of the Complex |
|---------------------|---------------------|---------------------|
| **IR ν (cm⁻¹)**     | **Assignments**     | **Element %, Observed/Calculated** |
| 414, 469            | M-N                 | C                   |
| 627                 | ClO₄⁻               | N                   |
| 772                 | Pyridine ring       | H                   |
| 1090                | ClO₄⁻               | Ni                  |
| 1330                | Aryl C-NH₂          |                     |
| 1490                | Aryl C=C            |                     |
| 1572                | N-H def.            |                     |
| 1625                | Aryl C=N            |                     |
| 2951                | C-H str.            |                     |
| 3363                | N-H str.            |                     |
| 3430                | O-H str.            |                     |

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Thermogravimetric (TG) in Air

Dynamic TG (Figure 1) was undertaken using an indigenously fabricated TG apparatus (Singh and Singh, 1978) in static air atmosphere. Gold crucible was used as sample holder (sample mass 20 mg, heating rate 10 °C/min).

Simultaneous TG-DTG-DTA

These curves were obtained at heating rate of 10 °C/min in flowing N₂ atmosphere (sample mass ~ 4 mg, N₂ flow rate 100 ml/min) in open crucible (Perkin Elmer Pyris Diamond TG/DTA). The curves are shown in Figure 2.

Isothermal TG

Isothermal TG (Figure 4) a complex was taken under static air using the same indigenously fabricated TG apparatus as mentioned earlier (Sample mass 10mg, particle size 200 mesh) at temperatures 160, 170, 180, 190, 200°C for 30% weight loss.

Kinetic Analysis of isothermal TG data

Usually a single step kinetic equation is employed for the kinetic analysis of solid state thermal decomposition (Brown and Dollimore, 1997; Kumar et al., 2012)

\[
\frac{d\alpha}{dt} = k(T)f(\alpha) \quad ...(1)
\]

where \(\alpha\) is the extent of conversion, \(t\) is the time and \(T\) is absolute temperature. \(k(T)\) is rate constant and \(f(\alpha)\) is the reaction model (Table 3) (Brown and Dollimore, 1997; Kumar et al., 2012). The Arrhenius equation can describe satisfactorily the temperature dependence of \(k(T)\). Substituting the value of \(k(T)\) in Arrhenius equation, gives

\[
\frac{d\alpha}{dt} = A \exp(-E/RT).f(\alpha) \quad ...(2)
\]

where \(A\) is the Arrhenius factor, \(E\) is the activation energy and \(R\) the gas constant.
Model Fitting Method

Equation (1) when rearranged and integrated, yield the following equation:

\[ g(\alpha) = k_j(T) t \quad ...(3) \]

where \( g(\alpha) = \int f(\alpha) \, d\alpha \) is the integrated form of reaction models (Table 3). Equation (3) gives the rate constant \( k_j(T) \) when a particular model is substituted in it. For a model, the rate constant at various temperatures \( T_i \) and Arrhenius parameters can be determined by using logarithmic form of following Arrhenius equation:

\[ \ln k_j(T_i) = \ln A_j - \frac{E_j}{R T_i} \quad ...(4) \]

Arrhenius parameters are shown in Table 3.

Isoconversional Method

This method makes possible to evaluate the activation energy as a function of extent of conversion (Vyazovkin and Wight, 1997, 1999) (Figure 5) which indicate towards multistep kinetics. According to isoconversional method, the reaction model is not dependent on temperature.
Table 2: TG-DTA Data of the Complex

<table>
<thead>
<tr>
<th>Step</th>
<th>TG Temperature Range/°C</th>
<th>% Decomposition</th>
<th>Peak Position/°C</th>
<th>Nature of Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>95-240</td>
<td>15</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>II</td>
<td>243-248</td>
<td>58</td>
<td>247</td>
<td>Exo</td>
</tr>
</tbody>
</table>

Table 3: Activation Energy (E), Arrhenius Factor and Correlation Coefficients (r) for the Isothermal Decomposition of the Complex

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Model</th>
<th>lnA</th>
<th>Slope</th>
<th>E/kJmole⁻¹</th>
<th>r</th>
<th>Mean Dev</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Power law⁴/³</td>
<td>2.330</td>
<td>1627.9</td>
<td>13.5</td>
<td>0.9929</td>
<td>2.890</td>
<td>3.047</td>
</tr>
<tr>
<td>2</td>
<td>Power law²/³</td>
<td>2.102</td>
<td>16.37.3</td>
<td>13.2</td>
<td>0.9931</td>
<td>2.782</td>
<td>2.934</td>
</tr>
<tr>
<td>3</td>
<td>Power law¹/²</td>
<td>1.798</td>
<td>1654.8</td>
<td>13.7</td>
<td>0.9933</td>
<td>2.684</td>
<td>2.793</td>
</tr>
<tr>
<td>4</td>
<td>Power law⁻¹/²</td>
<td>1.215</td>
<td>1726.5</td>
<td>14.3</td>
<td>0.9944</td>
<td>2.433</td>
<td>2.566</td>
</tr>
<tr>
<td>5</td>
<td>Power law⁻¹</td>
<td>1.140</td>
<td>1748.2</td>
<td>14.5</td>
<td>0.9947</td>
<td>2.418</td>
<td>2.550</td>
</tr>
<tr>
<td>6</td>
<td>Mampel (1-á)</td>
<td>-0.359</td>
<td>1986.8</td>
<td>16.5</td>
<td>0.9922</td>
<td>1.921</td>
<td>2.027</td>
</tr>
<tr>
<td>7</td>
<td>a-e⁴/³</td>
<td>1.934</td>
<td>1666.4</td>
<td>13.8</td>
<td>0.9946</td>
<td>2.729</td>
<td>2.877</td>
</tr>
<tr>
<td>8</td>
<td>a-e²/³</td>
<td>0.649</td>
<td>1994.7</td>
<td>16.6</td>
<td>0.9901</td>
<td>2.434</td>
<td>2.567</td>
</tr>
<tr>
<td>9</td>
<td>a-e¹/²</td>
<td>0.278</td>
<td>1997.4</td>
<td>16.6</td>
<td>0.9908</td>
<td>2.251</td>
<td>2.375</td>
</tr>
<tr>
<td>10</td>
<td>cs</td>
<td>1.158</td>
<td>1872.2</td>
<td>15.9</td>
<td>0.9937</td>
<td>2.559</td>
<td>2.689</td>
</tr>
<tr>
<td>11</td>
<td>T-d-diff</td>
<td>0.959</td>
<td>2040.1</td>
<td>16.9</td>
<td>0.9926</td>
<td>2.637</td>
<td>2.781</td>
</tr>
<tr>
<td>12</td>
<td>cc</td>
<td>1.234</td>
<td>1793.4</td>
<td>14.9</td>
<td>0.9941</td>
<td>2.513</td>
<td>2.650</td>
</tr>
<tr>
<td>13</td>
<td>P-T</td>
<td>-0.941</td>
<td>1977.1</td>
<td>16.4</td>
<td>0.9998</td>
<td>1.619</td>
<td>1.710</td>
</tr>
<tr>
<td>14</td>
<td>G-B</td>
<td>2.191</td>
<td>1853.9</td>
<td>15.4</td>
<td>0.9944</td>
<td>3.056</td>
<td>3.222</td>
</tr>
</tbody>
</table>

Figure 5: A Plot of Activation Energy (E) vs α

Table 4: Explosion Delay, Activation Energy for Thermal Explosion (E*) and Correlation Coefficient (r) of Complex

<table>
<thead>
<tr>
<th>Dₜ/s at Temperature/°C</th>
<th>220±1</th>
<th>230±1</th>
<th>240±1</th>
<th>250±1</th>
<th>260±1</th>
<th>E*/kJ mol⁻¹</th>
<th>r</th>
<th>lnk</th>
</tr>
</thead>
<tbody>
<tr>
<td>131</td>
<td>120</td>
<td>111</td>
<td>98</td>
<td>74</td>
<td>29.2</td>
<td>0.9518</td>
<td>-2.196</td>
<td></td>
</tr>
</tbody>
</table>

or heating rate. If we combine equation (3) and (4), we have

\[-\ln t_{\alpha_i} = \ln \left[ A_{\alpha_i} / g(\alpha_i) \right] - E_{\alpha_i}/RT_i \] …(5)
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**Explosion Delay Measurements**

Explosion delay ($D_E$) measurement was performed using tube furnace technique (Singh *et al.*, 1991), (sample mass ~10mg) at temperatures 220, 230, 240, 250, and 260°C with temperature accuracy of ±1°C (Table 4). The $D_E$ data was fitted in the equation (Kumar *et al.*, 2012)

$$D_E = A \exp \frac{E^*}{RT} \quad ... (6)$$

where $E^*$ is the activation energy for explosion, A plot of $D_E$ vs 1/T is presented in Figure 6.

**RESULTS AND DISCUSSION**

**Elemental and Spectral Description**

The analytical data given in Table 1, present a good agreement between calculated and observed percentage of the element C, H, N and Ni which certify the proposed molecular formula of the complex. In the IR spectra, a broad band at 3430 cm$^{-1}$ is due to O-H stretching vibration indicating the presence of coordinated water molecules in the complex. A peak at 1090 cm$^{-1}$ is specific of a non-coordinated ionic perchlorate and a sharp peak around 627 cm$^{-1}$ indicate the presence of ClO$_4^-$ ion having Td symmetry i.e. not coordinated to nickel. Peak at 414 and 469 cm$^{-1}$ is due to M-N stretching (Miller and Wilkins, 1952; Robert, 1996; Nakamoto, 1978) which confirms the nickel to ligand coordination. Other peaks shown in Table 1 are according to standard text.

**Thermal Analysis**

Thermogravimetric curve (TG) obtained in static air (Figure 1) shows that the complex decomposes in two steps. First step is slow (95-240°C) and second is rapid (243-248°C). First step of mass loss is due to loss of 10H$_2$O molecules (~15% mass; calculated % mass of 10H$_2$O = 14.7%). A close view of TG data shows that this first step is completed via two less distinct stages. In first stage, four water molecules leave the complex in the temperature range 95-180°C (~7% mass) and in second stage, rest of six water molecules also leave the complex in the temperature range 200-240°C (~9% mass) giving anhydrous complex. At 243°C the left residue ignited and given a sharp weight loss (~58%) which forms the second step of TG curve. Finally a residue (~28%) is left which may be due to nickel oxide (calculated 19%) and carbon (10.5% calculated).

In flowing nitrogen atmosphere also, the complex decomposed in two steps (Figure 2) of which first step is gradual and second is very rapid similar to static air TG. A DTG peak has been recorded for rapid step. Since first step is very gradual, no DTG peak has been obtained for this. In DTA thermogram (Figure 2), during 1st step of decomposition the curve is below the baseline (0.0) which indicates the endothermic elimination of water molecules. An exothermic peak at 247°C in DTA curve has been obtained due to ignition of...
residual mass (dehydrated complex) after first step decomposition.

Thus, the tentative mechanism of thermolysis of the complex may be given as:

\[
\text{[Ni}_3\text{(C}_5\text{H}_6\text{N}_2\text{)}_2\text{(H}_2\text{O})_{10}\text{]}\text{(ClO}_4\text{)}_6 \\
\rightarrow 10\text{H}_2\text{O} \\
\text{[Ni}_3\text{(C}_5\text{H}_6\text{N}_2\text{)}_2\text{]}\text{(ClO}_4\text{)}_6
\]

95-240°C

\[
\text{[Ni}_3\text{(C}_5\text{H}_6\text{N}_2\text{)}_2\text{]}\text{(ClO}_4\text{)}_6 \\
\rightarrow 243-248°C \\
\text{NiO+C + Gaseous products}
\]

Owing to the TG, the complex may contain 4\text{H}_2\text{O} molecule (~6%) as bridged ligand between two Ni atoms and 6\text{H}_2\text{O} molecule (~9%) may terminally coordinated, two on each Ni-atom. One 2-aminopyridine ligand coordinated to each terminal Ni-atoms in a bidentate fashion. Thus, each Ni-atom will be hexacoordinated and giving a trinuclear chain in which H-bonds between coordinated \text{H}_2\text{O} molecules could not be omitted (Figure 3). Several bridged polynuclear complexes of Ni with various ligands has also been reported in open literature in which Cl\text{–}, Br\text{–}, OH\text{–} and CO or other ligands bridges between Ni-atoms.

Very recently trinuclear and tetranuclear complexes of Ni have been reported (Xiao et al., 2011). In these complexes Ni is octahedrally coordinated and O-atom of 3,5-dichloro-2-hydroxy-benzylaminoacetic acid bridges between two Ni-atoms. A dinuclear perchlorate complex of Ni in which nickel (II) are bridged by alkoxide oxygen (Konar et al., 2012). Water bridged dinuclear cationic complexes of first row transition series are also reported in literature (Wilcox, 1996) in which cationic complexes are crucial in the model studies of metallocatecholases and metallohydrolases.

The kinetic analysis of 30% decomposition of initial mass which includes elimination of all the water molecules and 2-Apy ligands, has been studied using isothermal TG data in static air by applying model fitting and isoconversional method (Vyazovkin and Wight, 1997, 1999). Each model results approximately same activation energy (Table 3, average E = 15.2 kJ mole\(^{-1}\)). Since solid state decomposition is a complex process, isoconvensional method (Vyazovkin and Wight, 1997, 1999) has been applied to estimate the activation energy which will be independent of models. A perusal of Figure 5 shows that the activation energy changes with \(\alpha\) (degrees of conversion). Thus, this method evaluate the effective activation energy having a separate value at different \(\alpha\) which explore the multistep kinetics for such a complex solid state process. It is not easy to assign a benign value of activated energy to a particular process.

Complex is stable at room temperature, but in response to sudden high temperature it explodes. The activation energy of explosion was found to be 29.2 kJ mole\(^{-1}\) (Table 4). Exponential dependence of explosion delay on temperature was found. This shows that reactant changes significantly during pre-explosion reactions. The process of explosion is not a process of steady state. Freeman and Gorden (Freeman and Gorden, 1956) derived following equation:

\[
D_e = A\text{e}^{-\Delta H^*/RT}
\]

where \(\Delta H^*\) is the heat of activation and comparable to activation energy, \(E^*\) (equation 6).
CONCLUSION
Trinuclear nickel complex has been synthesized and characterized. Complex decomposes in two steps of which first step is slow and second is fast. Corresponding to second step an exothermic DTA peak has been obtained. Model fitting method applied on isothermal TG data yields a single value of activation energy whereas isoconversional method gives a series of $E$ values at different $\alpha$. Explosion delay exponentially depends on temperature.

ACKNOWLEDGMENT
Thanks to Secretary Board of Management, Head of the Department of Chemistry, DBS College, Kanpur, for providing laboratory facilities and University Grants Commission, New Delhi for financial assistance. Thanks are also due to STIC, Cochin University of Science and Technology for CHN & FT-IR analysis.

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