Solid state electrical conductivity and thermal degradation studies on some phenothiazine derivatives

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Abstract

Electrical conductivity and thermal degradation studies of promethazine hydrochloride (PH); 2-chlorophenothiazine (CP); diethazine hydrochloride (DH) and trifluoperazine dihydrochloride (TFP) are reported. The activation energies are evaluated based on their electrical conductivity study conducted over the temperature range 30-150 °C. These energies for PH, CP, DH and TFP are found to be 0.86, 1.02, 0.68 and 1.08 eV, respectively. The materials are analyzed for the kinetic parameters like the activation energies for decomposition and the Arrhenious pre-exponential factors in the Horowitz-Metzger methods. Using these factors and the standard thermodynamic parameters such as enthalpy, entropy and free energies are calculated. Thermogravimetric study on these phenothiazine derivatives in air indicated that their stabilities are in the order CP > TFP > PH > DH.

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1. Introduction

The first synthesis of phenothiazine was reported by Bernhasen in the year 1883 [1], since then many significant results have been reported which are of interest not only for the workers in the field of phenothiazines but also for the entire heterocyclic chemistry. New phenothiazines are widely known for their important pharmacological actions [2–5]. Phenothiazine and its derivatives are excellent electron donors [6,7]. Karrmann et al.[6] have stated that electron-donating properties of the compound are associated with the phenothiazine part of the molecule Brown and Aftergut [8] have shown that phenothiazine itself is a semiconductor with an energy gap of 1.6.eV [8]. A thorough literature survey revealed that work done on the electrical conductivity and thermogravimetric studies is meager [9,10]. Gutmann and Keyzer [11,12] have reported electrical measurements only on a few thiazine bases. Few authors have reported the solution conductivity of phenothiazine [13,14]. Solid state galvanic cells based on semiconducting charge transfer materials with mixed conduction (electronic–ionic) have been fabricated and tested by Singh et al. [15]. They have carried out electrochemical characterization such as open-circuit voltage, short-circuit current, time dependence and rechargability of these cells. The composite of phenothiazine was reported date back in 1969. This prompted us to carry out the electrical conductivity and thermogravimetric studies on promethazine hydrochloride (PH); 2-chlorophenothiazine (CP); diethazine hydrochloride (DH) and trifluoperazine dihydrochloride (TFP) phenothiazine derivatives. Electrical conductivity and thermal degradation study of phenothiazines are expected to give interesting results. The anticipated applications of phenothiazines as conducting materials are in the field of semiconductors [16–18], solid electrolyte batteries [19,20], synthesis of conducting polymers [21,22], fabrication of photogalvanic cells [23–25] as well as solar energy storage devices [26] and the like. The present study is hoped to throw more light on the properties of the phenothiazine derivatives, which may
help to use the same, in the above cited applications in a better way.

2. Experimental

Phenothiazine derivatives; PH (M & B, India), CP (S. K. & F, India Ltd.), diethazine hydrochloride (M & B, India) and TFP (S. K. & F, India Ltd) were used as such without further purifications. Elemental analysis for carbon, hydrogen, nitrogen and sulfur were done using Vario EL III CHNS analyzer, Germany. UV-Visible spectra were recorded in double distilled water except in the case of CP which was recorded in ethyl alcohol, using Systronics-117 Spectrophotometer Ahmedabad, India, with 1.0 cm quartz cells. IR spectra were taken using JASCO FTIR-460 PLUS spectrophotometer, Japan.

For conductivity measurements, all the samples were compressed into pellets of 1.30 cm diameter and thicknesses ranging around 0.1–0.2 cm using Perkin-Elmer KBr die under a pressure of 250 kg cm\(^{-2}\). The TSI Techno search instruments, Thane (w) 400602, Maharashtra, India, KBr press model-15 ton capacity was used for applying pressure. Conducting silver paint was coated on both flat surfaces of the pellets and electrical contacts with the electrodes were made by using the same paint. The resistance measurements were done using DOT-402 Digital Milli Ohm Meter and DOT-425 Insulation resistance tester, Bhandari Electronics and electricals, Bangalore, India.

Thermogravimetric analysis were performed in air atmosphere using TGA-7 Analyzer, Perkin-Elmer, from ambient temperature to 600 °C at the heating rate of 10 °C /min and with an air flow of 100 mL min\(^{-1}\).

3. Results and discussion

The structures of the phenothiazine derivatives, PH, CP, DH, and TFP are shown in Fig. 1. Two of the phenothiazine derivatives studied are 2–10 substituted where as PH and DH is substituted only at position 10.

![Structure of phenothiazines](image)

The analytical data of elemental, UV-Visible and FTIR studies are presented in Table 1.

The elemental analysis of all the phenothiazine derivatives for carbon, hydrogen, nitrogen and sulfur agreed very well with the theoretical values, indicating the high purity of the samples. UV-Visible electronic absorption spectra are recorded for the derivatives over the wavelength range 200–400 nm. The electronic spectra of PH, DH and TFP are recorded in aqueous medium. The derivative CP is not soluble in water but soluble in ethanol and hence its spectrum is recorded in ethanol medium. All the phenothiazine derivatives showed absorption bands around 250 and 300 nm. The absorption bands around 250 nm may be assigned to \(\pi -\pi^*\) transitions which are expected due to the benzene nuclei of the phenothiazine molecule. In addition, absorption peak at 205 nm observed for CP in alcohol solvent may also be assigned to \(\pi -\pi^*\) transition, also originating due to the benzene nuclei of the phenothiazine molecule. But this peak is not observed in the spectra of other phenothiazine derivatives as it may be taking below 200 nm. The absorption peaks observed in the region 296–322 nm may be assignable to \(\pi -\pi^*\) transitions. The wavelength of maximum absorption and the log-e values are in good agreement with the earlier reported values [27–29]. The characteristic IR spectral bands
assignable to phenothiazine ring system are observed at 1591–1600, 1568–1570, 925–930 and 731–744 cm⁻¹. The absorption bands observed in the range 1568–1600 cm⁻¹ are due to the aromatic structure of the phenothiazine ring. The absorption bands observed in the range 731–772 cm⁻¹ are due to the out-of-plane bending vibrations of the hydrogen atoms of the aromatic ring structure of phenothiazine derivative. The strong broad absorption bands observed between 2000 and 2500 cm⁻¹ in the case of PH, DH and TFP are due to the characteristic of → N * H ion combined with C=O. A sharp absorption band with medium intensity at 3334 cm⁻¹ observed in the case of CP may be assigned to N-H stretching.

3.1. Thermal studies

Thermogravimetric studies are done using the analytical parameters indicated in the experimental section. The maximum decomposition temperatures (DTmax) are presented in Table 2. The nature of TGA curves indicates that all the four phenothiazine derivatives PH, DH, CP and TFP degrade in three steps. The major amounts of degradations observed for PH (75%), TFP (75%) and DH (92%) are in the first step. CP degrades nearly 50% in the first step and the remaining 45% degrades mainly in the third step. The weight losses in the second step degradation were found to be very small, to the extent of 1–4% in all the phenothiazine derivatives. These four phenothiazine derivatives PH, DH, CP and TFP degrade completely at 580, 530, 600 and 590 °C, respectively. The analytical curves are presented in Fig. 2.

The aim of the kinetic study of thermal analysis data is to find the most probable kinetic model which best describes the process and allows the calculation of reliable values for the parameters. Many methods exist to characterize the degradation kinetics of various materials [30–35]. We have employed Broido’s, Coats–Redfern (C–R) and Horowitz–Metzger (H–M) methods for the evaluation of decomposition kinetics and to compare the results obtained by the three methods [36–38]. In Broido’s method, the thermal degradation process is considered to be of first order and the calculations are done accordingly. In the case on C–R and H–M methods the curve having the highest correlation coefficient values among the reactions of different orders are considered. The different equations employed to evaluate the degradation kinetics are as below

Broido’s method: \[ \ln[-\ln y] = -\frac{E_a}{RT} \]

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>PH</th>
<th>PH</th>
<th>DH</th>
<th>DH</th>
<th>CP</th>
<th>CP</th>
<th>TFP</th>
<th>TFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order (n)</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>Broido’s</td>
<td>1</td>
<td>0.25</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Coats–Redfern</td>
<td>1.25</td>
<td>0.50</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Horowitz–Metzger</td>
<td>530</td>
<td>791</td>
<td>527</td>
<td>527</td>
<td>803</td>
<td>551</td>
<td>786</td>
<td></td>
</tr>
<tr>
<td>Ea (kJ mol⁻¹)</td>
<td>128.87</td>
<td>66.51</td>
<td>110.82</td>
<td>48.55</td>
<td>96.74</td>
<td>112.5</td>
<td>36.66</td>
<td></td>
</tr>
<tr>
<td>Coats–Redfern</td>
<td>126.12</td>
<td>18.62</td>
<td>72.83</td>
<td>41.24</td>
<td>42.40</td>
<td>80.65</td>
<td>14.13</td>
<td></td>
</tr>
<tr>
<td>Horowitz–Metzger</td>
<td>146.66</td>
<td>131.49</td>
<td>83.13</td>
<td>49.18</td>
<td>65.94</td>
<td>72.70</td>
<td>27.29</td>
<td></td>
</tr>
<tr>
<td>ΔH (kJ mol⁻¹)</td>
<td>12.03</td>
<td>59.93</td>
<td>106.96</td>
<td>44.17</td>
<td>90.0</td>
<td>107.92</td>
<td>30.16</td>
<td></td>
</tr>
<tr>
<td>Coats–Redfern</td>
<td>127.78</td>
<td>12.04</td>
<td>68.45</td>
<td>36.86</td>
<td>35.72</td>
<td>76.07</td>
<td>7.60</td>
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<tr>
<td>Horowitz–Metzger</td>
<td>148.06</td>
<td>24.91</td>
<td>78.75</td>
<td>44.80</td>
<td>59.26</td>
<td>68.12</td>
<td>20.76</td>
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<tr>
<td>ΔG (kJ mol⁻¹)</td>
<td>-15.57</td>
<td>239.44</td>
<td>159.88</td>
<td>161.44</td>
<td>246.48</td>
<td>161.88</td>
<td>235.43</td>
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<tr>
<td>Coats–Redfern</td>
<td>-268.44</td>
<td>224.44</td>
<td>137.02</td>
<td>166.19</td>
<td>223.69</td>
<td>153.18</td>
<td>232.51</td>
<td></td>
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<tr>
<td>Horowitz–Metzger</td>
<td>-263.98</td>
<td>260.64</td>
<td>164.06</td>
<td>166.39</td>
<td>259.83</td>
<td>178.80</td>
<td>266.43</td>
<td></td>
</tr>
<tr>
<td>ΔS (J K⁻¹ mol⁻¹)</td>
<td>-59.45</td>
<td>-226.94</td>
<td>-93.10</td>
<td>-194.77</td>
<td>-194.87</td>
<td>-97.96</td>
<td>-261.26</td>
<td></td>
</tr>
<tr>
<td>Coats–Redfern</td>
<td>-268.44</td>
<td>-268.52</td>
<td>-130.11</td>
<td>-245.40</td>
<td>-234.09</td>
<td>-139.94</td>
<td>-286.14</td>
<td></td>
</tr>
<tr>
<td>Horowitz–Metzger</td>
<td>-38.33</td>
<td>-298.02</td>
<td>-161.89</td>
<td>-230.72</td>
<td>-249.83</td>
<td>-200.88</td>
<td>-304.25</td>
<td></td>
</tr>
<tr>
<td>A (sec⁻¹)</td>
<td>86.7 × 10⁴</td>
<td>23.02</td>
<td>1.51 × 10⁷</td>
<td>26.12</td>
<td>11.1 × 10⁴</td>
<td>87.7 × 10⁴</td>
<td>36.9 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Coats–Redfern</td>
<td>10.5 × 10⁴</td>
<td>15.5 × 10⁻²</td>
<td>17.6 × 10⁵</td>
<td>1.67</td>
<td>9.90</td>
<td>5.62 × 10⁵</td>
<td>18.5 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Horowitz–Metzger</td>
<td>10.99 × 10⁴</td>
<td>44.7 × 10⁻⁴</td>
<td>38.4 × 10⁵</td>
<td>9.75</td>
<td>1.50</td>
<td>3.69 × 10⁵</td>
<td>21 × 10⁻⁹</td>
<td></td>
</tr>
</tbody>
</table>
Coats - Redfern method:
\[
\frac{-\ln y}{T^2} = \ln \frac{AR}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) \quad \text{for } n = 1,
\]
\[
\frac{1 - y^{1-n}}{T^2(1 - n)} = \ln \frac{AR}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) \quad \text{for } n \neq 1.
\]

Horowitz - Metzger
\[
\ln(-\ln y) = \frac{E_a \theta}{R(DT_{\text{max}})} \quad \text{for } n = 1.
\]
\[
\ln \left[ \frac{1 - y^{1-n}}{(1 - n)} \right] = \frac{E_a \theta}{R(DT_{\text{max}})} \quad \text{for } n \neq 1.
\]

The following notations were used in the above equation, \( E_a \) is the activation energy (J/mol), \( R \) the universal gas constant (8.314 J/mol·K), \( T \) the Absolute temperature (°K), \( DT_{\text{max}} \) the maximum decomposition temperature, \( A \) the Arrhenius pre-exponential factor (sec^{-1}), \( n \) the reaction order, \( \beta \) the heating rate (°C min^{-1}), \( \theta = T - DT_{\text{max}} \), \( y = (w_i - w_\infty) / (w_0 - w_\infty) \), where \( w_0 \), \( w_i \) and \( w_\infty \) are the weights of sample before degradation, at time \( t \) and after total decomposition, respectively.

The graphical plots of \( \ln[\ln(1/y)] \) versus 1000/T obtained for PH, DH, CP and TFP are presented in Fig. 3. The value of \( y \) represents the compound remaining at temperature \( T \) (°K). The slopes of the plots are determined and used to evaluate the activation energies and the data are presented in Table 2. The values of \( n \) reported in the table are the best fit values having the highest correlation coefficient.

The activation energy and pre-exponential factors observed are in the order PH > DH > TFP > CP. The activation energy depends on the chemical structure and the crystalline nature of the material. Greater the crystalline nature, greater will be the activation energy [39]. The thermodynamic properties like change in enthalpy (\( \Delta H \)), entropy (\( \Delta S \)), free energy (\( \Delta G \)) and frequency factor (\( A \)) are calculated using the standard equations as explained elsewhere [40,41], and the values are summarized in Table 2. The first order rate constant is determined based on the weight changes with time in the linear degradation portion.
of the thermogravimetric curve and used for the evaluation of entropy change.

3.2. Electrical conductivity

The study of solid state electrical conductivity of PH, DH, CP and TFP is very important in view of their applications in pharmacology, electrical and semiconducting devices [16–26]. The conductivity measurements are made on the powdered samples of the above phenothiazine derivatives after compounding them into pellet form using sufficient pressure. In order to evaluate the nature of variations of electrical conductivity with temperature, electrical conductivity is measured from ambient to suitable high temperature. The higher temperature limit selected for the electrical conductivity measurements are well within the melting point and decomposition temperatures of the phenothiazine derivatives. The values of the electrical conductivity are calculated using the equation

\[ \sigma = \sigma_0 \exp(-E/AT) \]

where \( E \) is the activation energy, \( k \) the Boltzman constant, \( T \) the temperature in K and \( \sigma_0 \) the constant. The logarithmic conductivity values were plotted for each phenothiazine derivative versus \( 1000/T \). Dependence of electrical conductivity of the phenothiazine drugs with temperature are shown in Fig. 4, and the relevant data are summarized in Table 3.

The observed electrical conductivity values at 30°C for PH, DH, TFP and CP are \( 3.99 \times 10^{-12}, 12.57 \times 10^{-12}, 2.73 \times 10^{-7} \) and \( 2.20 \times 10^{-13} \) S/cm respectively. The variations of electrical conductivity over the temperature ranges 30–125, 30–130, 30–140 and 30–150°C are studied for DH, CP, TFP and PH, respectively. The plots indicate that these drugs differ with respect to their ambient and temperature dependent electrical conductivities. The variations of electrical conductivities of these drugs with temperature showed both metallic and semi conducting natures except in the case of DH. The activation energies are calculated for the linear dependence of the electrical conductivity with temperature and included in Table 3. Though all the molecules are having the same phenothiazine structure,
Table 3
Electrical conductivity data of PH, CP, DH, and TFP

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conductivity (σ S cm⁻¹)</th>
<th>$E_1$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>$1.07 \times 10^{-12}$</td>
<td>0.43 (120-145°C)</td>
</tr>
<tr>
<td></td>
<td>$1.47 \times 10^{-10}$</td>
<td>0.43 (95-115°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.34 (30-75°C)</td>
</tr>
<tr>
<td>DH</td>
<td>$1.25 \times 10^{-12}$</td>
<td>0.35 (75-110°C)</td>
</tr>
<tr>
<td></td>
<td>$2.2 \times 10^{-10}$</td>
<td>0.41 (35-60°C)</td>
</tr>
<tr>
<td>CP</td>
<td>$2.06 \times 10^{-12}$</td>
<td>0.52 (90-130°C)</td>
</tr>
<tr>
<td></td>
<td>$2.4 \times 10^{-10}$</td>
<td>0.32 (30-80°C)</td>
</tr>
<tr>
<td>TFP</td>
<td>$2.73 \times 10^{-7}$</td>
<td>0.39 (70-120°C)</td>
</tr>
<tr>
<td></td>
<td>$6.91 \times 10^{-7}$</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Electrical conductivity plots of PH, DH, CP and TFP.

they differ with respect to the substituents at $R_1$ and $R_2$ and also with respect to $X$ as shown in Fig. 1. The net electrical conductivities observed for these phenothiazine drugs are due to the intra molecular and inter molecular electrical conductivities. The nature of substituents at $R_1$ and $R_2$ and the molecules at $X$ play an important role in altering the inter molecular electrical conductivity. Higher electrical conductivities are expected in the organic molecules containing double bonds which are in conjugation. This accounts for the intra molecular electrical conductivity. The closer overlapping of the unsaturated sites between the molecules is required for higher inter molecular electrical conductivity. The main differences in the electrical conductivities arises, because these drugs are having different $R_1$, $R_2$ and $X$ which are expected to vary the inter molecular packing resulting in the electrical conductivity variations. For a better explanation regarding the variation of electrical conductivity X-ray study is desired for which experiments are underway and the findings would be communicated shortly.

The present study including thermal degradation and electrical conductivity on PH, CP, DH and TFP...
phenothiazine derivatives is highly helpful in judicial selection of these materials for the applications as semiconductor, solid electrolytes in batteries, synthesis of conducting polymers, fabrication of solar energy storage devices and the like.

Acknowledgment

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[20] Saito, Tetsu(Japan storage battery Co Ltd) Kokai Tokkyo Koho 102,526 (cl H01 M4/06).
[22] Iwahiro, Yamada Yutaka (Asahi glass Co Ltd) Kokai Tokkyo Koho JP 61 103 923 (86, 103. 923) (cl C08G 61/12).
Trifluoperazinium dipicrate

The title compound [systematic name: 1-methyl-4-[(3-(2-(trifluoromethyl)-10H-phenothiazin-10-yl)propyl)piperazine-1,4-dium bis(2,4,6-trinitrophenolate)], $C_{21}H_{26}F_{3}N_{2}S^{2-} \cdot 2C_{6}H_{2}N_{3}O_{7}^{-}$, belongs to a group of phenothiazine derivatives which exhibit tranquillizing activity. The dihedral angle between the two outer aromatic rings of the phenothiazine unit is 24.69 (7)°. The crystal packing is stabilized by N—H⋯O hydrogen bonds and several weak C—H⋯O contacts. The molecular conformation of the trifluoperazinium cation differs significantly from that in the hydrochloride.

Comment

Trifluoperazine is a highly potent antipsychotic drug (approximately 20 times more potent than chlorpromazine) (Martindale, 1977). The identification and differentiation of some phenothiazine picrates have been carried out (Yung & Pernarowski, 1963) and a review on various aspects of phenothiazines has been published (Kojilo et al., 2001). In a continuation of our work on phenothiazine picrates (Yathirajan et al., 2007), this paper reports the formation of a salt by the interaction between 10-[3-(4-methyl-1-piperazinyl)propyl]-2-(trifluoromethyl)-10H-phenothiazine hydrochloride and 2,4,6-trinitrophenol in an aqueous medium.

A perspective view of the structure of (I) is shown in Fig. 1. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.28, November 2006; Allen, 2002; Mogul, Version 1.1; Bruno et al., 2004). The dihedral angle between the two aromatic rings of the phenothiazine unit is 24.69 (7)°. The piperazine ring adopts a chair conformation with both substituents in equatorial positions. The crystal packing is stabilized by N—H⋯O hydrogen bonds and several weak C—H⋯O contacts (Table 2).

The crystal structure of trifluoperazine hydrochloride, (II), has been reported (McDowell, 1980). However, the conformation of (II) does not compare well with (I). In (II), the dihedral angle between the two outer aromatic rings of the phenothiazine unit is 38.9°. Furthermore, it is rather strange that the piperazine ring in (II) is almost planar. The torsion...
Figure 1
The molecular structure of the title compound, showing the atom numbering with displacement ellipsoids drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

Figure 2
Least-squares fit of the trifluoperazinium cations in (I) (full bonds) and (II) (open bonds). H atoms have been omitted.

angles of the six ring atoms range from $-5.2$ to $4.4^\circ$, and the sums of the bond angles at the two N atoms are $359.4$ and $359.8^\circ$. The conformation of the methylene chain connecting the ring systems is similar in (I) and (II). The torsion angles are $-167.8(2)$ and $-164.1(2)^\circ$ in (I) compared with $173.2$ and $-178.6^\circ$ in (II). However, the conformation of the bond connecting the methylene chain to the phenothiazine unit is different in (I) [$\text{C12} - \text{N1} - \text{C1} - \text{C2} = -85.2(3)^\circ$] from that in (II) ($138.0^\circ$). A least-squares comparison of the trifluoperazinium cations of (I) and (II) (r.m.s. deviation = 0.165 Å), fitting only the phenothiazine units, is shown in Fig. 2. As can be seen, the molecular conformation is significantly different in the two structures.

**Experimental**

Trifluoperazine dihydrochloride (0.9696 g, 0.02 M) and picric acid (0.4615 g, 0.02 M) were dissolved in water (100 ml) separately. The solutions were mixed and stirred in a beaker. The separated bright-yellow compound was washed well with distilled water, filtered off and dried in a vacuum desiccator over phosphorus pentoxide. It was observed that, regardless of the proportions in which the donor and acceptor were mixed, only the 1:2 complex was formed. The complex was recrystallized from dimethyl sulfoxide (m.p. 514 K).

**Crystal data**

$\text{C}_{20}\text{H}_{32}\text{F}_{3}\text{N}_{3}\text{S}_{2}^2 \cdot 2\text{C}_{6}\text{H}_{2}\text{N}_{3}\text{O}_{7}^{2-}$  
$y = 73.959(7)^\circ$  
$V = 1847.9(3)$ Å$^3$  
$Z = 2$

**Data collection**

Stoe IPDSII two-circle diffractometer  
19064 measured reflections  
6895 independent reflections  
$R_{int} = 0.078$

**Refinement**

$R(|F|^2 > 2\sigma|F|^2) = 0.055$  
$wR(F)^{2} = 0.149$  
$S = 1.01$

**Table 1**

Selected torsion angles (°).

<table>
<thead>
<tr>
<th>Torsion Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N1} - \text{C1} - \text{C2} - \text{C3}$</td>
<td>$-167.8(2)$</td>
</tr>
<tr>
<td>$\text{C1} - \text{C2} - \text{C3} - \text{N31}$</td>
<td>$-164.1(2)$</td>
</tr>
<tr>
<td>$\text{N36} - \text{N31} - \text{C32} - \text{C33}$</td>
<td>$55.6(2)$</td>
</tr>
<tr>
<td>$\text{N31} - \text{C33} - \text{C32} - \text{N34}$</td>
<td>$-55.6(2)$</td>
</tr>
<tr>
<td>$\text{C32} - \text{N31} - \text{C36} - \text{C35}$</td>
<td>$58.5(2)$</td>
</tr>
</tbody>
</table>

**Table 2**

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D - H - A</th>
<th>H - A</th>
<th>D - A</th>
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<td>$0.92(4)$</td>
<td>$1.79(4)$</td>
<td>$2.666(3)$</td>
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<tr>
<td>$\text{N33} - \text{O41}$</td>
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<td>$2.46(3)$</td>
<td>$3.041(3)$</td>
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<tr>
<td>$\text{N34} - \text{O321}$</td>
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<td>$2.33(3)$</td>
<td>$2.918(3)$</td>
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<tr>
<td>$\text{C16} - \text{O442}$</td>
<td>$0.95$</td>
<td>$2.39$</td>
<td>$3.147(3)$</td>
</tr>
<tr>
<td>$\text{C32} - \text{O51}$</td>
<td>$0.95$</td>
<td>$2.34$</td>
<td>$3.060(3)$</td>
</tr>
<tr>
<td>$\text{C35} - \text{O41}$</td>
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<td>$2.41$</td>
<td>$3.312(3)$</td>
</tr>
<tr>
<td>$\text{C36} - \text{O442}$</td>
<td>$0.99$</td>
<td>$2.45$</td>
<td>$3.318(3)$</td>
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H atoms were found in a difference map. The H atoms bonded to nitrogen were freely refined and all other H atoms were refined using...
a riding model, with C—H = 0.95–0.99 Å and $U_{eq}(\text{H}) = 1.2U_{eq}(\text{C})$ or 1.5$U_{eq}$(methyl C).

Data collection: X-AREA (Stoe & Cie, 2001); cell refinement: X-AREA; data reduction: X-AREA; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2003).

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Electrical measurements and thermal kinetics study of phenothiazine and a few of its derivatives

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Abstract

Electrical conductivity and thermal degradation studies of phenothiazine (PTZ), acetophenazine dimaleate (APM), methotiazine hydrochloride (MDH) and mepazine hydrochloride monohydrate (MH) are reported. The activation energies are evaluated based on their electrical conductivity study conducted over the temperature range 30-150 °C. These energies for PTZ, APM, MDH and MH are found to be 0.44, 0.41, 0.34 and 0.47 eV, respectively. MH showed unusual temperature dependence metallic and semiconducting electrical conductivity. The parent compound and other derivatives showed semiconducting behaviors. The materials are analyzed for the kinetic parameters like the activation energies for decomposition and the Arrhenius pre-exponential factors in their pyrolysis region using Brook's, Coats-Redfern and Horowitz-Metzger methods. Using these factors and the standard equations thermodynamic parameters such as enthalpy, entropy and free energies are calculated. Thermogravimetric study on these phenothiazine derivatives in air indicated that their stabilities are in the order APM > MDH > PTZ > MH.

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Keywords: Organic compounds; Semiconductors; Thermogravimetric analysis; Electrical conductivity

1. Introduction

Organic semiconductors with remarkable physical properties have been extensively studied in the past few decades. Potential applications offered by these materials have been tremendous in the development of new electronic devices. The domain of organic electronic materials continues to be of great scientific and commercial interest. Ever since the discovery of semiconducting properties of phenothiazine, a lot of attention has been paid to improve the material properties of these derivatives. The first synthesis of phenothiazine was reported by Bernthsen in the year 1883 [1], since then, many significant results have been reported which are of interest not only for the workers in the field of phenothiazines but also for the entire heterocyclic chemistry. Now phenothiazines are widely known for their important pharmacological actions [2-5]. Based on the calculations made by the MO-LCAO method, it was shown that the phenothiazine possesses well-defined electron donar properties [6,7]. Karremann et al. have stated that electron donating properties of the compound are associated with the phenothiazine part of the molecule [6]. Aftergut and Brown have shown that phenothiazine is a semiconductor with an energy gap of 1.6 eV [8]. Due to the absence of thorough knowledge concerning the effect of impurities on the electrical properties they had carried out resistivity measurements on a number of specimens of the same substance at various stages of purification. It is interesting to note that they had admitted to continue the work in order to confirm the value of the energy gap reported at various potential stresses. But so far, no data relating to electrical conductivity measurements on these derivatives are reported. Also, until now many of its properties have not been fully explored or understood. In 1972, Mercier and Dumont have studied about the influence of electron donating properties on the psychotropic activity of phenothiazine derivatives [9]. They have reiterated that phenothiazine displayed a high electron donating power and an essential part in the mechanism of psychotropic activity of the phenothiazine drugs is played by a positive radical ion. A thorough literature survey on the phenothiazines under study revealed that work done on the electrical conductivity is meagre and no thermogravimetric studies have been done [10,11]. Gutmann and Keyzer have reported electrical measurements only on few thiazine bases [12,13]. They have carried out direct current measurements at different heating rates and suggested that the anomalous behavior of the thiazine bases were
due to the presence of micro regions of glassy material causing persistent inter-boundary polarizations. Ionic conductances of some salts of N-substituted phenothiazine in aqueous solution at 21 °C have been done by Schreiber et al. [14]. In order to clarify the behavior of phenothiazine hydrochlorides as electrolytes in aqueous solution, electrical conductivity of their aqueous solution was measured by Nakagaki and Satoshi [15]. Arrufat et al. have reported semiconductivity of cation radicals of certain phenothiazine derivatives [16]. Solid state galvanic cells based on semiconducting charge transfer materials with mixed conduction (electronic-ionic) have been fabricated and tested by Singh et al. [17]. They have carried out electrochemical characterization such as open-circuit voltage, short circuit current, time dependence and rechargeability of these cells. The polymer composite of phenothiazine was reported in the year 1969 [18]. In the present investigation, the electrical conductivity and thermogravimetric studies on phenothiazine (PTZ), acetophenazine dimaleate (APM), methdilazine hydrochloride (MDH) and mepazine hydrochloride monohydrate (MH) are presented for the first time. Electrical conductivity and thermal degradation study of phenothiazines are expected to give interesting results. The anticipated applications of the above phenothiazines, as thermally stable conducting materials are in the field of semiconductors [19-21], solid electrolyte batteries [22,23], synthesis of conducting polymers [24,25], fabrication of photogalvanic cells [26-28] as well as solar energy storage devices [29] and the like. The present study is hoped to throw more light on the properties of the phenothiazine derivatives, which may help to use the same, in the above cited applications in a better way.

2. Experimental

Phenothiazine (Rhone Poulenc) and its derivatives: acetophenazine dimaleate (Fluka, AG Switzerland), methdilazine hydrochloride (Glassemiehtline Pharmaceuticals) and mepazine hydrochloride monohydrate (May and Baker) were used as received without further purifications. Elemental analysis for carbon, hydrogen, nitrogen and sulphur were done using Vario EL III CHNS analyzer, Germany. UV spectra were recorded in double distilled water, using Systronic 2717 Spectrophotometer Ahmedabad, India, with 1.0 cm quartz cells. IR spectra were taken using JASCO FTIR-460 PLUS spectrophotometer Japan.

For conductivity measurements, all the samples were compressed into pellets of 1.30 cm diameter and thickness ranging around 0.1-0.2 cm using Perkin-Elmer KBr Die under a pressure of 250 kg cm⁻². The TSI Techno Search Instruments, Thane (w), Mahara.shu:a, India. KBr press model-12onne capacity using Systronic 17 Spectrophotometer Ahmedabad, India, with 1.0 cm quartz cells. IR spectra were taken using JASCO FTIR-460 PLUS spectrophotometer Japan.

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Fig. 1. Phenothiazine and its derivatives [APM, MDH and MH].

3. Results and discussion

The structures of the phenothiazine derivatives PTZ, APM, MDH and MH are shown in Fig. 1. APM is 2-10 substituted whereas MDH and MH are substituted only at position 10. The analytical data of elemental, UV and FTIR studies are presented in Table 1.

The elemental analysis of all the phenothiazine derivatives for carbon, hydrogen, nitrogen and sulphur agreed very well with the theoretical values, which indicated that the samples used are of very high purity. These phenothiazine derivatives do not have absorption peaks in the visible region and so the UV electronic absorption spectra are recorded over the wavelength range 200–400 nm. The electronic spectra of APM, MDH and MH are recorded in aqueous medium. Phenothiazine is not soluble in water but in ethanol and hence its spectrum is recorded in ethanol medium. Mainly two peaks are observed, for all the phenothiazines in which one is very intense in the region 250–265 nm and another less intense in the region 300–325 nm. Exact locations of these peaks in both the regions are dependent mainly on the nature of the substituents in 2-position. In the case of MDH and MH derivatives, only small 1–2 nm hypsochromic shift has been observed of the most intense π → π⁺ transition in the 250–265 nm region. Also, for the same derivatives, the intense n → π⁺ transitions are found to show hypsochromic shifts to a greater extent of 18–19 nm in comparison to the parent phenothiazine due to the substituent at position 2 [30]. The corresponding peaks for APM showed hypsochromic shifts to still a greater extent of 13 and 44 nm, respectively. This is because, in addition to the substituent at position 1, the presence of an electron withdrawing group at the position 2 which influenced the tricyclic Π-system either through its N (as a meta effect) or S (as a para effect) atom [31].

The wavelength of maximum absorption and the log ε values are in good agreement with the earlier reported values [32-34]. The characteristic IR spectral bands assignable to phenothiazine ring system are observed at 1550-1600, 1200-1470 and 1000–750 cm⁻¹. The sharp absorption bands observed in the range 731–772 cm⁻¹ are due to the out-of-plane bending
Table 1
Elemental, UV and FTIR analytical data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Elemental analysis in % (theoretical)</th>
<th>UV-vis absorptions $\lambda_{max}$ (nm)</th>
<th>log $\varepsilon$</th>
<th>FTIR spectral data (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTZ</td>
<td>C, 72.10 (72.32)</td>
<td>252</td>
<td>4.64</td>
<td>3340, 1595, 1572, 1465, 1377, 1307, 1242, 1078, 1035, 926, 743</td>
</tr>
<tr>
<td>APM</td>
<td>H, 4.35 (4.55)</td>
<td>320</td>
<td>3.66</td>
<td>3432, 3009, 2960, 2880, 1674, 1574, 1471, 1358, 1229, 1080, 924, 869, 743, 651</td>
</tr>
<tr>
<td>MDH</td>
<td>H, 5.63 (5.79)</td>
<td>239</td>
<td>4.46</td>
<td>3407, 1590, 1569, 1456, 1328, 1284, 1251, 1230, 1035, 753</td>
</tr>
<tr>
<td>MH</td>
<td>C, 62.80 (62.53)</td>
<td>250</td>
<td>4.62</td>
<td>3451, 1682, 1604, 1519, 1351, 1334, 1325, 1221, 1037, 752</td>
</tr>
<tr>
<td></td>
<td>H, 6.93 (6.90)</td>
<td>302</td>
<td>3.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N, 7.52 (7.68)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S, 8.92 (8.78)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1. Thermal studies

Thermogravimetric studies are done using the analytical parameters as indicated in the experimental section. The temperatures at which maximum decomposition of the compounds take place in the DTG curve ($DT_{max}$) are presented in Table 2. Information about the thermal decomposition of phenothiazine derivatives is rather poor. It is supposed that the thermal degradation in presence of air proceeds due to the oxidation of sulphur atom in the ring to sulphoxide, for the majority of these compounds [35]. The nature of TGA curves indicates that the phenothiazine degrades in two steps, APM and MDH degrade in four steps and MH degrades in three steps (Fig. 2).

PTZ degrades nearly 45% in first and 55% in second step. In the case of APM 25%, 20%, 10% and 35% degrades in steps I, II, III and IV, respectively. MDH degrades nearly 80% in I step and the remaining 6%, 10% and 35% degradation accounts for steps II, III and IV, respectively. MH degrades nearly 5% in the first step, 80% in the second step and 15% in the third step. The weight losses in the III step, II and IV steps and step I of APM, MDH and MH is found to be very small. Hence the kinetic parameters could not be calculated as the linear degradation portion of the TGA curve is very small. The major amounts of degradations observed for MDH (80%) and MH (80%) are in the first and second steps, respectively. In the case of MH the first step weight loss could be due to the loss of one molecule of water at 100 °C. PTZ, APM, MDH and MH degraded completely at 615, 644, 620 and 612 °C, respectively. The aim of the kinetic study of thermal analysis data is to find the most probable kinetic model which best describes the process and allows the calculation of reliable values for the parameters like, the order of the reaction, activation energy, enthalpy of reaction, entropy of the reaction, Gibbs’s free energy changes and the frequency factor. TGA curves which offer an effective short cut to the accumulation of considerable kinetic data must be treated with great caution if they are not to add more confusion than enlightenment. Many methods exist to characterize the degradation kinetics of various materials [36-44]. The three methods Broido’s [42], Coats–Redfearn (C-R) [43] and Horowitz–Metzger (H-M) [44] which are the most acceptable and commonly employed, are used to obtain thermodynamic parameters and the data obtained are presented in Table 2 for comparison.

In Broido’s method, the thermal degradation process is considered to be of first-order and the calculations are done accordingly. In the case of C-R and H-M methods the curve having the highest correlation co-efficient values among the reactions of different orders are considered. The different equations employed to evaluate the degradation kinetics in three different methods are given below:

Broido’s method

$$\ln \left( - \ln y \right) = - \frac{E_a}{RT}$$

Coats–Redfearn method

$$\ln \left( \frac{- \ln y}{T^2} \right) = \ln \left( \frac{AR}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) \right) - \frac{E_a}{RT}$$ for $n = 1$
A comparative thermogravimetric analytical and kinetic data of PTZ, APM, MDH and MH

<table>
<thead>
<tr>
<th>Order (n)</th>
<th>PTZ step I</th>
<th>PTZ step II</th>
<th>APM step I</th>
<th>APM step II</th>
<th>APM step IV</th>
<th>MDH step I</th>
<th>MH step II</th>
<th>MH step III</th>
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<td>Brodo</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Coats–Redfern</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>0.75</td>
<td>0</td>
<td>1.25</td>
<td>0</td>
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<tr>
<td>Horowitz–Metzger</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>0.75</td>
<td>0</td>
<td>1.50</td>
<td>0</td>
</tr>
<tr>
<td>DT_{\text{max}} (K)</td>
<td>503</td>
<td>824</td>
<td>463</td>
<td>583</td>
<td>829</td>
<td>565</td>
<td>538</td>
<td>751</td>
</tr>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>60.03</td>
<td>96.11</td>
<td>54.87</td>
<td>25.11</td>
<td>71.92</td>
<td>99.27</td>
<td>130.94</td>
<td>40.41</td>
</tr>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>55.85</td>
<td>89.26</td>
<td>51.02</td>
<td>20.26</td>
<td>65.03</td>
<td>94.57</td>
<td>126.42</td>
<td>34.17</td>
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<tr>
<td>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>153.13</td>
<td>241.22</td>
<td>141.12</td>
<td>185.41</td>
<td>245.39</td>
<td>165.94</td>
<td>155.67</td>
<td>210.45</td>
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<tr>
<td>$A$ (s$^{-1}$)</td>
<td>83 x 10</td>
<td>40 x 10$^2$</td>
<td>31.6 x 10$^2$</td>
<td>19.4 x 10$^{-1}$</td>
<td>74.70</td>
<td>29.7 x 10$^6$</td>
<td>16.2 x 10$^6$</td>
<td>85.2 x 10$^{-1}$</td>
</tr>
</tbody>
</table>

3.2. Electrical conductivity

The study of solid state electrical conductivity on PTZ, APM, MDH and MH is very important in view of their applications in pharmacology, electrical and semiconductor devices [19–28].

[$\ln \left( \frac{1 - y^{-n}}{1 - n} \right) = \ln \left( \frac{AR}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) \right) - \frac{E_a}{RT}$, for $n \neq 1$

Horowitz–Metzger method

$\ln [\ln (1/y)] = \frac{E_a \theta}{R(DT_{\text{max}})^2}$, for $n = 1$

$\ln \left( \frac{1 - y^{-n}}{1 - n} \right) = \frac{E_a \theta}{R(DT_{\text{max}})^2}$, for $n \neq 1$

where $E_a$ is the activation energy (J mol$^{-1}$); $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$); $T$ is the absolute temperature (K); $DT_{\text{max}}$ is the maximum decomposition temperature; $A$ is the Arrhenius pre-exponential factor ($s^{-1}$); $n$ is the reaction order; $\beta$ is the heating rate (°C min$^{-1}$); $\theta = T - DT_{\text{max}}$; $\nu = (w_i - w_{\text{oo}})/(w_{\text{oo}} - w_{\text{oo}})$, where $w_{\text{oo}}$, $w_i$, and $w_{\text{oo}}$ are the weights of sample before degradation, at time $t$ and after total decomposition, respectively.

The graphical plots of $\ln [\ln (1/y)]$ versus $1000/T$ obtained for PTZ, APM, MDH and MH are presented in Fig 3. The value of $y$ represents the compound remaining at temperature $T$ (K). The slopes of the plots are determined and used to evaluate the activation energies. The order of reaction with respect to a certain reactant is defined, in chemical kinetics, as the power to which its concentration term in the rate equation is raised. It is not necessarily related to stoichiometry of the reaction, unless the reaction is elementary. Complex reactions may or may not have reaction orders equal to their stoichiometric coefficients. The values of $'n'$, reaction order, reported in Table 2 are the best fit values having the highest correlation coefficient. The activation energies observed are in the order $MH > MDH > PTZH > APM$. It depends on the chemical structure and the crystalline nature of the material. Greater the crystalline nature greater will be the activation energy [45]. The thermodynamic properties like change in enthalpy ($\Delta H$), entropy ($\Delta S$), free energy ($\Delta G$) and frequency factor ($A$) are calculated using the standard equations as explained elsewhere [46,47] and the values are summarized in Table 2. The first-order rate constant is determined based on the weight changes with time in the linear degradation portion of the thermogravimetric curve and used for the evaluation of entropy change. The results obtained by the three methods are comparable except in few cases. This is because none of these methods is absolute one and the mathematical approach as well as the assumption.
The conductivity measurements are made using the two probe technique as explained in the experimental section on the powdered samples. In order to evaluate the nature of variations of electrical conductivity with temperature, electrical conductivity is measured from ambient to suitable high temperature. The higher temperature limit selected for the electrical conductivity measurements are well within the melting point and decomposition temperatures of the phenothiazine derivatives (Table 3). The values of the electrical conductivity are calculated using the equation:

\[ \sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right) \]

where \( E_a \) is the activation energy, \( k \) is the Boltzmann constant, \( T \) is the temperature (K) and \( \sigma_0 \) is the constant. The logarithmic conductivity values were plotted for each phenothiazine derivative versus 1000/T. Dependence of electrical conductivity of the phenothiazine drugs with temperature are shown in Fig. 4 and the relevant data are summarized in Table 3. The observed electrical conductivity values at 30°C for PTZ, APM, MDH and MH are 1.51 \times 10^{-13}, 9.20 \times 10^{-12}, 5.25 \times 10^{-11} and 1.66 \times 10^{-8} \text{ S cm}^{-1}, respectively. The variations of electrical conductivity over the temperature ranges 30–150, 30–150, 30–85 and 30–125°C are studied for PTZ, APM, MDH and MH, respectively. The plots indicate that these drugs differ with respect to their ambient and temperature dependent electrical conductivities. The variations of electrical conductivity of MH showed metallic behaviors at the temperature range 30–75°C and semiconducting behavior at the temperature range 90–125°C. This may be due to phase transition. At lower tem
perature the inter-molecular interaction may lead to the optimum
energy gap between conduction band and valence band for
metallic conduction. At higher temperature because of the phase
transition, the inter-molecular interaction is expected to result
the energy gap between the conduction band and valence band
suitable for semiconductors. But parent compound and other
derivatives showed semiconducting behavior. The activation
energies are calculated for the linear dependence of the electrical
conductivity with temperature and included in Table 3.

Though all the molecules are having the same phenothiazine
structure, they differ with respect to the substituents at R1 and
R2 and also with respect to X as shown in Fig. 1. The conductivity
mechanism is generally thought of as being an inter-molecular
phenomenon. Though aromatic nucleus is a conductor and yet
it exhibits considerable resistance in the bulk material. The
main problem seems to be one of transferring the charge carrier
from molecule to molecule. The net electrical conductivities
observed for these phenothiazine drugs are due to the intra-
and inter-molecular electrical conductivities. The structure of
the molecule is of paramount importance. The nature of sub-
stituents at R1, R2 and the molecules at X play an important role
in altering the inter- and intra-molecular electrical conductivi-
ties. Higher electrical conductivities are expected in the organic
molecules containing double bonds which are in conjugation
All of the so-called organic semiconductors are conjugated sys-
tems. Pohl and Engelhardt have discussed the importance of
the degree of conjugation [48]. They have stated that the size
of a set of conjugated double and single bonds is larger than
some number (about 10-15 double—single bond pairs) then the
molecule acquires unusual characteristics. This accounts for the
intra-molecular electrical conductivity. The activation energy in
organic semiconductors probably is a function of both intra-
and inter-molecular barriers, and therefore is a composite of
both. The closer overlapping of the unsaturated sites between
the molecules is required for higher inter-molecular electrical
conductivity. Donald et al. have studied the effect of structure
on the electrical conductivity of organic compounds [49]. They
have stated that, electron donating or withdrawing properties of
the substituents on an aromatic system affects the electrical con-
ductivity. Also the availability of the orbitals seems important to
the conductivity mechanism. The main differences in the electri-
cal conductivities arises, because these drugs are having different
R1, R2 and X which are expected to vary the inter-molecular
packing resulting in the electrical conductivity variations. A few
literatures are available about the crystal structure of pheno-
thazine and its analogs [50-55]. A cumulative opinion about the

Fig. 3. Graphical plots of ln[ln(1/y)] versus 1000T for PTZ, APM, MDH and MH

Please cite this article in press as: Achar, B.N. and Ashok, M.A. Electrical measurements and thermal kinetics study of phenothiazine and a few of
structure is that it exhibits anisotropy. For a better explanation regarding the variation of electrical conductivity X-ray study is desired for which experiments are underway and the findings would be communicated shortly.

4. Conclusions

The electrical conductivity studies on PTZ, APM, MDH and MH indicated that these phenothiazine derivatives showed interesting electrical properties. The conductivities of phenothiazine and its derivatives fall in the insulator region at 30 °C. The activation energies are calculated at the appropriate linear regions of the temperature range. Based on the thermogravimetric analysis in air, thermodynamic parameters relating to the decompositions of these derivatives are evaluated. All the materials reported here are thermally stable up to 125 °C. The data are useful for the applications of these derivatives in the field of semiconductor electronics.

Acknowledgements

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Fig. 4. Electrical conductivity plots of PTZ, APM, MDH and MH.
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