Hydrazinium salts of 2,4-dichlorophenylacetic acid, phenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, diphenylacetic acid, cinnamic acid, and picolinic and nicotinic acids have been prepared by accomplishing neutralization of aqueous hydrazine hydrate with the respective acids. Formation of these hydrazinium salts has been confirmed by analytical, IR spectral, and thermal studies. IR spectra of the salts register N–N stretching frequencies of $\text{N}_2\text{H}_5^+$ ion in the region 963–951 cm$^{-1}$ and the frequencies of $\text{N}_2\text{H}_6^{2+}$ ion in the region 1047–1026 cm$^{-1}$. Thermal decomposition studies show that the hydrazinium salts undergo melting followed by endothermic decomposition into carbon residue as the endproduct.

1. Introduction

Hydrazine is the simplest diamine and forms salt with mineral and carboxylic acids [1–5]. The monoprotonated hydrazine, the hydrazinium cation still retains a basic site and hence capable of coordination with various metal ions. However, many hydrazinium complexes reported in the literature contain hydrazinium ion as a mere charge neutralizing species [6, 7]. The complexes containing coordinated hydrazinium ion are used as very good precursor for the preparation of nanoparticles [8] with nearly uniform particle size. Some of these salts are used as flame-retardants [9, 10] and proton conductors [11]. Preparation and thermal behaviour of some salts from few aliphatic acid [12, 13] and aromatic carboxylic acids [14, 15] have been reported. There is no literature citation about hydrazinium salt of aromatic substituted acetic acids, aromatic unsaturated acids, and heteroacids except hydrazinium salt of pyrazine mono and dicarboxylic acids [16, 17]. It is therefore, considered interesting to prepare hydrazinium salt of aromatic-substituted acetic acids.

2. Experimental

All the salts reported have been prepared by the neutralization of the respective acids in aqueous medium with hydrazine hydrate (99–100%) in appropriate molar ratios.

2.1. Preparation

2.1.1. Hydrazinium Salts of 2,4-Dichlorophenylacetate, Phenoxyacetate, 2,4-Dichlorophenoxyacetate, and Diphenylacetate. These are prepared by mixing hydrazine hydrate and acids in 2:3 molar ratio in 50 mL of distilled water. The resulting turbid solution is heated over water bath to obtain clear solution and concentrated to nearly 20 mL. Then it was allowed to crystallize at room temperature. The crystals are filtered off and washed by using benzene and dried in air.

2.1.2. Hydrazinium Cinnamate Hydrate. These are prepared by mixing hydrazine hydrate and diphenylacetic acid or cinnamic acid in 1:1 molar ratio in 50 mL of water. The contents of the beaker are heated on water bath. Then
the undissolved acid is removed by filtration. The resulting clear solution is concentrated on water bath to 20 mL. Then it is allowed to crystallize at room temperature; they are filtered off, and washed by using alcohol and air dried.

2.1.3. Hydrazinium Picolinate and Hydrazinium Nicotinate. These are prepared by mixing hydrazine hydrate and picolinic acid or nicotinic acid with 1:1 molar ratio in 50 mL of distilled water. The resulting clear solution is concentrated on water bath to 20 mL. Then it is allowed to crystallize in a vacuum desiccator over calcium chloride. Salts are separated out after 2 days, filtered, and washed by using ether.

3. Results and Discussion

The analytical data (Table 1) of the salts are consistent with the proposed formulae for them.

3.1. Infrared Spectra. The important IR bands of the salts are listed in Table 2.

The IR spectra of the hydrated salts display absorption bands in the region of 3346–3330 cm\(^{-1}\) due to O–H stretching of water molecule. In hydrazinium 2,4-dichlorophenoxyacetate hydrate and hydrazinium phenoxyacetate, the band due to O–H stretching frequency overlaps with the band due to N–H stretching frequency. The bands in the region of 1390–1323 cm\(^{-1}\) and 1598–1521 cm\(^{-1}\) for these salts correspond to symmetric and asymmetric stretching frequencies of the carboxylate ions. The N–N stretching frequencies of N\(_2\)H\(_5\)\(^{+}\) ion appear in the range of 963–951 cm\(^{-1}\) [1, 11, 12] and the N–N stretching frequencies of N\(_2\)H\(_6\)\(^{2+}\) ion show bands in the region of 1043–1029 cm\(^{-1}\).

3.2. Thermal Analysis. See Table 3.

3.2.1. Hydrazinium 2,4-Dichlorophenylacetate Hydrate (Scheme 1). The thermogram of this salt indicates that the decomposition of the salt takes place in three steps. In the first step, dehydration takes place with endothermic peak at 99\(^\circ\)C. In the second step the carboxylate intermediate decomposes to formic acid with endothermic peak at 211\(^\circ\)C and an exothermic peak at 269\(^\circ\)C. Finally, it decomposes to carbon residue at 305\(^\circ\)C.
Table 3: TG-DTA data.

<table>
<thead>
<tr>
<th>S. no</th>
<th>Compound</th>
<th>DTA peak temp. (°C)</th>
<th>Thermogravimetry (TG)</th>
<th>Decomposition product</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Obsd</td>
<td>Cald</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temp. range °C</td>
<td>Mass loss (%)</td>
</tr>
<tr>
<td>1</td>
<td>Hydrazinium 2,4-dichlorophenylacetate hydrate</td>
<td>99 (+)</td>
<td>25–133</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>211 (+)</td>
<td>133–286</td>
<td>79.43</td>
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<td></td>
<td></td>
<td>269 (−)</td>
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<tr>
<td></td>
<td></td>
<td>99 (+)</td>
<td>25–90</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
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<td>90–234</td>
<td>50.41</td>
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<td></td>
<td></td>
<td>265 (−)</td>
<td>234–344</td>
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<td></td>
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<td>327 (−)</td>
<td>103–225</td>
<td>18.21</td>
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<tr>
<td>3</td>
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<td>225–528</td>
<td>96</td>
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<td></td>
<td></td>
<td>488 (−)</td>
<td>106 (+)</td>
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<td></td>
<td>186 (−)</td>
<td>86–354</td>
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<td></td>
<td>233 (−)</td>
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<td></td>
<td></td>
<td>484 (−)</td>
<td>92 (+)</td>
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<td>150 (+)</td>
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<td></td>
<td>458 (−)</td>
<td>121 (+)</td>
</tr>
<tr>
<td>5</td>
<td>Hydrazinium cinnamate hydrate</td>
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<td>99–218</td>
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<td>Hydrazinium picolinate</td>
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<tr>
<td>7</td>
<td>Hydrazinium nicotinate</td>
<td>183 (−)</td>
<td>127–304</td>
<td>90.20</td>
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</table>

3.2.2. *Hydrazinium Phenoxyacetate Hydrate* (Scheme 2). This compound undergoes decomposition in three steps. In the first step, compound undergoes melt with endothermic peak at 99°C. Then the compound decomposes to phenol with exothermic peak at 149°C and 265°C. Finally, at 327°C it decomposes to carbon residue.

3.2.3. *Hydrazinium 2,4-Dichlorophenoxyacetate Hydrate* (Scheme 3). The thermogram of this salt indicates that the decomposition of the salt takes place in two steps. In the first step, both dehydration and dehydrazination occur simultaneously showing a sharp endotherm at 170°C. In the second step, the acid intermediate decomposes exothermally at 285°C and 488°C to carbon residue.
Figure 1: Hydrazinium phenoxyacetate hydrate.

Figure 2: Hydrazinium 2,4-dichlorophenoxyacetate hydrate.

Figure 3: Hydrazinium diphenylacetate hydrate.

Figure 4: Hydrazinium cinnamate hydrate.

Figure 5: Hydrazinium picolinate.

Hydrazinium 2,4-dichlorophenylacetate hydrate

\[
\text{Cl} \quad \text{Cl} \quad \text{O-CH₂-COO}^- \quad \text{N₂H₅}^+·\text{H₂O}
\]

Scheme 3

Hydrazinium diphenylacetate hydrate

\[
\text{CH-COO}^- \quad \text{N₂H₅}^+·\text{H₂O}
\]

Scheme 4

Hydrazinium cinnamate hydrate

\[
\text{CH=CH-COO}^- \quad \text{N₂H₅}^+·\text{H₂O}
\]

Scheme 5
3.2.4. Hydrazinium Diphenylacetate Hydrate (Scheme 4). This undergoes decomposition in three steps. First step shows an endothermic peak at 106°C corresponding to the removal of moisture. In the second step, both dehydration and dehydrazination occur simultaneously showing two exothermic peaks at 186°C and 233°C to form formic acid. In the final step, formic acid completely decomposes to carbon residue.

3.2.5. Hydrazinium Cinnamate Hydrate (Scheme 5). This compound also undergoes three steps of decomposition. First step shows an endothermic peak at 92°C corresponding to liberation of water molecule. Second step shows on endothermic peak at 150°C due to the elimination of one molecule of hydrazine. In the third step, complete decomposition to carbon residue takes place.

3.2.6. Hydrazinium Picolinate and Nicotinate (Scheme 6). Both compounds undergo two step decomposition. First step is the removal of moisture with endothermic peaks at 121°C and 117°C, respectively. In the second step, the compound completely decomposes to carbon residue.

TG-DTA curves of some compounds are given (Figures 1, 2, 3, 4, and 5) as representative examples.

4. Conclusions

2,4-dichlorophenylacetic acid, phenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, diphenylacetic acid, and cinnamic acid formed as hydrazinium(+1) salts, whereas picolinic and nicotinic acid formed as hydrazinium(+2) salts.

All compounds undergo two- or three-step exothermic or endothermic decomposition through various intermediates and decompose completely to carbon residue as the final product.

References


