DOI : 10.15613/sijrs/2015/v2i1/80080
ISSN (Print): 2349–8919
ISSN (Online): 2350–0999
SciеXplore: International Journal of Research in Science, *Vol 2(1), 13–18, January–June 2015*

Preparation and Characterization of Some New Hydrazinium Carboxylates

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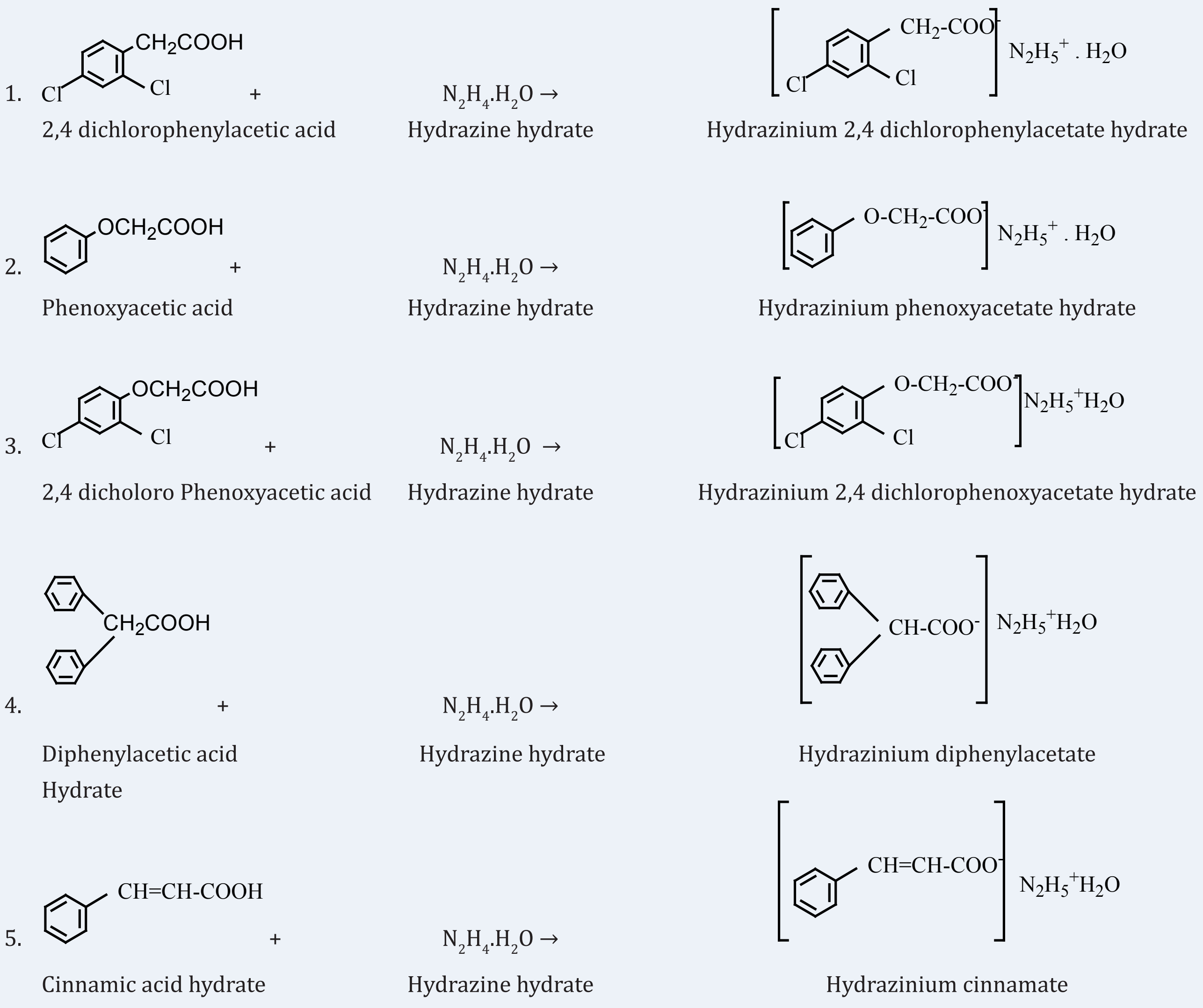
Graphical Abstract

The reaction between aryl carboxylic acids and hydrazine hydrate yields hydrazinium salts. Hydrazinium (+2) salts are separated from heterocyclic carboxylic acids, whereas other carboxylic acids yields hydrazinium (+1) salts.



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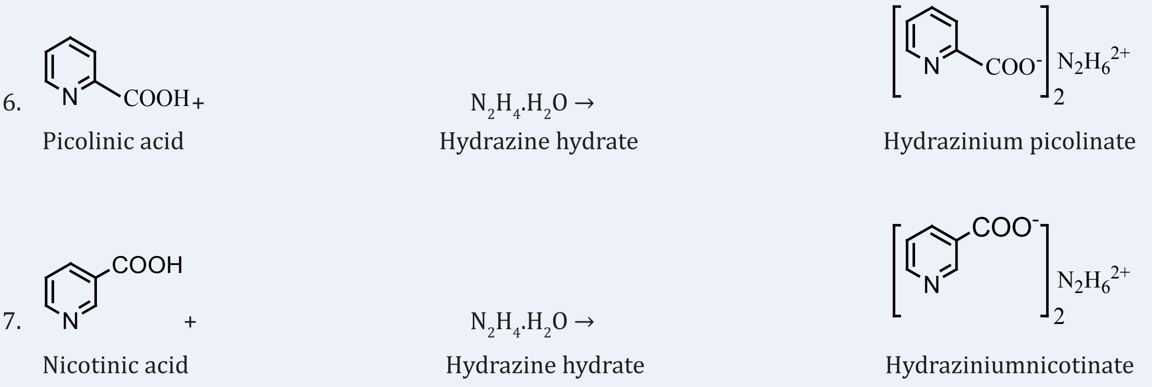


Abstract

Hydrazinium salts of aromatic carboxylic acids were prepared by neutralization of acid with hydrazine hydrate and characterized by analytical, IR spectral and TG-DTA analysis. All the compounds undergo decomposition yielding carbon residue as the end product. The *in vitro* antibacterial study of 2,4-dichlorophenoxyacetic acid and its hydrazinium salt against *Escherichia Coli* have been investigated and the results show that the as-prepared hydrazinium salts have better antibacterial activity than the free acid.

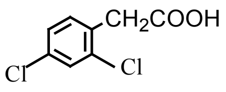
Keywords: 2,4-dichlorophenoxyacetic Acid, Antibacterial Activity, Aromatic Carboxylic Acids, Hydrazinium Salt, IR spectral, TG – DTA

1. Introduction

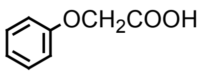
The simplest diamine is Hydrazine which forms salts with mineral and carboxylic acids [1], [2]. These hydrazinium salts are used as additives in propellants and as explosives [1]. It used as a drug for the treatment of Hodgkin's diseases and cancer [1]. In the synthesis of metal hydrazinium/hydrazine complexes, it used as ligand [3], [5]. It also used as flame retardant [6], only few of these salts show antibacterial activity [7]. Hence recently there is an interest towards the preparation of hydrazinium salts. Sizable work has been done in the synthesis of hydrazinium salts from aliphatic acids [8], [9] and aromatic carboxylic acids [10], [11]. However, there are no reports on the preparation of hydrazinium salt of aromatic substituted acetic acids, aromatic unsaturated acids and hetero acids. Therefore, we report the preparation of hydrazinium salts of aromatic substituted acetic acids (2,4-dichlorophenylacetic acid, phenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, and diphenylacetic acid), aromatic unsaturated acid (cinnamic acid) and hetero acids (picolinic acid and nicotinic acid).

Generally all phenolic derivatives show antibacterial property. Particularly 2,4-dichlorophenoxyacetic acid altered envelope properties of the bacteria *Escherichia coli*, such as hydrophobic index [12]. Unsubstituted phenoxyacetic acid is also a phenolic derivative. But, it has no potent substituents to have antibacterial property.

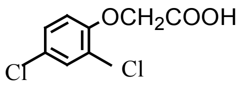
2,4-dichlorophenoxyacetic acid contains two potent chloro substituents. These influence it to have antibacterial property like chloroxylenol (4-chloro-2,5-Xylenol) which acts as antiseptic as well as disinfectant. This prompted us to make antibacterial study of hydrazinium salt of 2,4-dichlorophenoxyacetic acid against *Escherichia coli*. For clarity the structures of acids with their names are given;



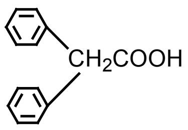
2,4-dichlorophenylacetic acid



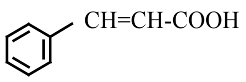
phenoxyacetic acid



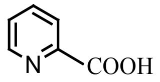
2,4-dichlorophenoxyacetic acid



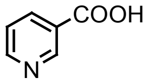
Diphenylacetic acid



cinnamic acid



picolinic acid



nicotinic acid

2. Experimental

2.1 Preparation

2.1.1 Hydrazinium 2,4-dichlorophenylacetate Hydrate

In this preparation, hydrazine hydrate was mixed with 2,4-dichlorophenylacetic acid in a molar ratio of 2:3. Turbid solution was obtained which was heated in a water bath and concentrated nearly to 20 ml. This was subjected to crystallization at room temperature for 24 hours. Light yellow colored hydrazinium salt crystallized out were washed with benzene and air dried.

2.1.2 Hydraziniumphenoxyacetate Hydrate

This was prepared by the same procedure as above by mixing phenoxy acetic acid with Hydrazine hydrate (2:3). Spongy white colored salt was crystallized within 20 minutes, which was washed with benzene and allowed to dry.

2.1.3 Hydrazinium 2,4-dichlorophenoxyacetate Hydrate

This salt was prepared by the same procedure by mixing hydrazine hydrate and 2,4-dichlorophenoxyacetic acid (1:1). White coloured salt crystallized out was immediately washed with alcohol and allowed to dry.

2.1.4 Hydraziniumdiphenylacetate Hydrate and Hydraziniumcinnamate Hydrate

For the preparation of hydraziniumdiphenylacetate hydrate, hydrazine hydrate was mixed with diphenylacetic acid (1:1). The mixture was heated and concentrated to 20 ml on extended heating. Light yellow coloured monohydrated hydrazinium (+1) salt of diphenylacetic acid separated out when subjected to crystallization for 48 hours. The crystals were washed by alcohol and air dried.

The above procedure has been followed for the preparation of hydraziniumcinnamate hydrate, where hydrazine hydrate was mixed with cinnamic acid. White colored crystal of monohydrated hydrazinium(+1) salt of cinnamic acid was separated out when subjected to crystallization for about 48 hours.

2.1.5 Hydraziniumpicolinate and Hydraziniumnicotinate

For hydraziniumpicolinate, hydrazine hydrate was mixed with picolinic acid (1:1). The mixture was concentrated to 20 ml by heating on a water bath. Then this solution was allowed to crystallization for 24 hours, Pale yellow coloured hydrazinium(+2) salt of picolinic acid was separated out, washed with alcohol and dried.

In a similar procedure, hydraziniumnicotinate salt, was prepared by mixing nicotinic acid with hydrazinium hydrate. Colorless hydrazinium(+2) salt of nicotinic acid was crystallized, washed with ether and dried.

3. Results and Discussion

The proposed formulae of hydrazinium salts are reliable with their analytical data (Table 1).

3.1 Infrared Spectra

All hydrated hydrazinium salts show the presence of water molecule by the appeared stretching frequency found in the range 3346 – 3330 cm^{-1}. However, for hydraziniumphenoxy acetate and 2,4-dichlorophenoxyacetate hydrate the O-H stretching frequency was overlapped with N-H stretching frequency. For all salts the bands found in the range 1390-1323 cm^{-1} and1598-1521 cm^{-1}were attributed to the symmetric and asymmetric stretching frequencies of the carboxylate ions. The bands found in the region 963–951 cm^{-1} [11][12][13] and 1043–1029 cm^{-1}were responsible for N-N stretching frequencies of $N_2H_5^+$ ion and $N_2H_6^{2+}$ respectively.

3.2 Thermal Studies

TGA and DTA results of some hydrazinium salts are shown in Figure 1–3.

3.2.1 Hydrazinium 2,4-dichlorophenylacetate Hydrate

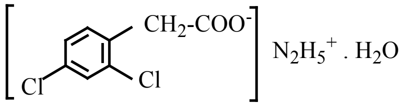
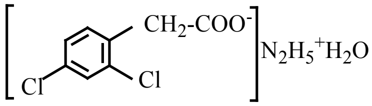
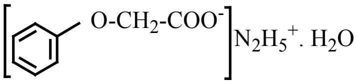
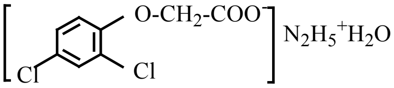
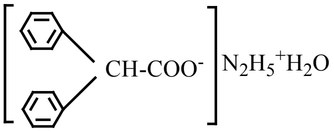
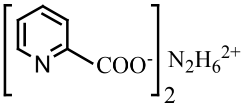
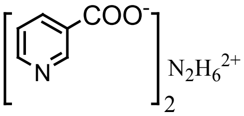


Table 1. Analytical data

S.No	Compound	Colour	Found (calculated) %			
			Hydrazine	Carbon	Hydrogen	Nitrogen
1		pale yellow	11.90(12.95)	37.40(37.93)	4.50(4.70)	9.98(10.97)
2		White	16.00(16.34)	47.20(47.47)	7.11(6.92)	13.00(13.84)
3		White	11.21(12.14)	47.10(47.04)	4.10(4.41)	8.80(8.82)
4		pale yellow	12.00(12.55)	63.20(63.80)	6.20(6.83)	10.59(10.63)
5		White	17.40(17.19)	51.00(51.19)	7.04(7.02)	14.85(14.05)
6		pale yellow	12.71(12.10)	51.29(51.38)	2.89(2.85)	9.96(9.99)
7		White	12.83(12.10)	51.20(51.38)	2.80(2.85)	9.95(9.99)

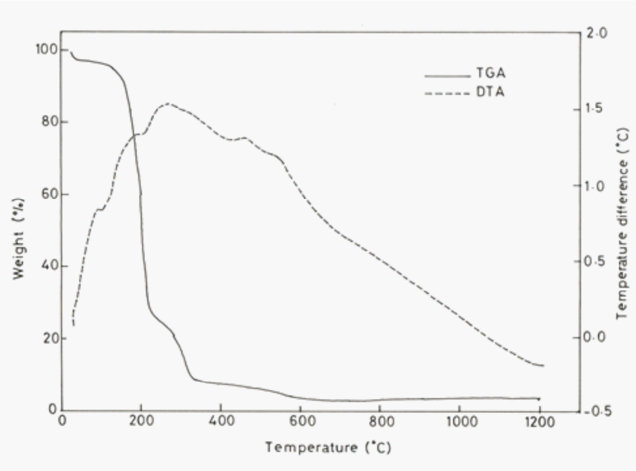


Figure 1. TG – DTA of Hydrazinium 2,4 dichlorophenoxyacetate hydrate.

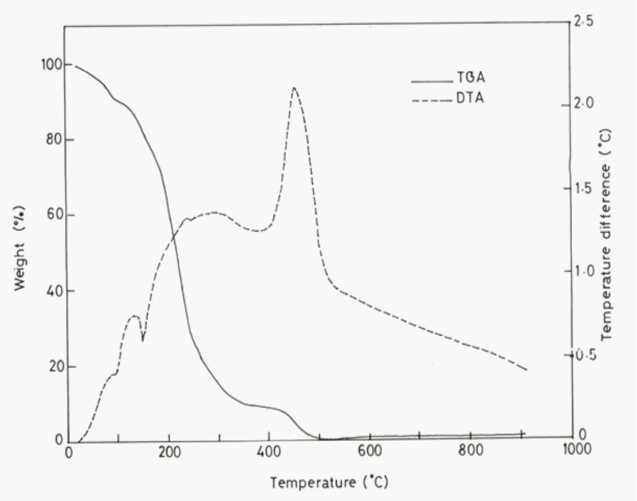


Figure 2. TG – DTA of Hydrazinium cinnamate hydrate.

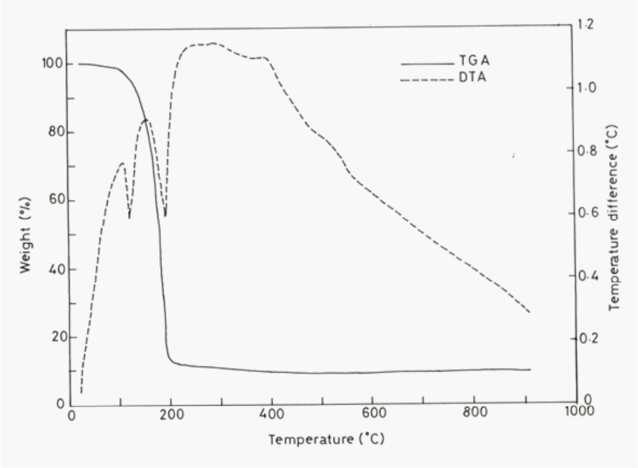
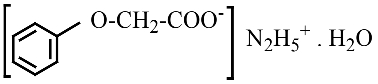


Figure 3. TG – DTA of Hydrazinim picolinate.

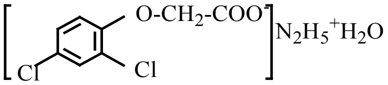
The thermal studies result of this salt clearly depict that, the decomposition of the salt has taken place by three steps. Initially, dehydration occurs with an endothermic peak found at 99°C. The decomposition of carboxylate intermediate into formic acid is the second step. This was confirmed by an endothermic peak as well as an exothermic peak found at 211°C and 269 °C respectively. In third step, further decomposition has taken place leading to carbon residue at 305°C.

3.2.2 *Hydraziniumphenoxyacetate Hydrate*



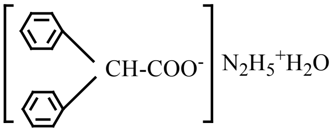
By three steps, the salt hydraziniumphenoxyacetate hydrate undergoes decomposition. An endothermic peak found at 99°C depicts melting of this salt. The second step implies the decomposition of salt leading to phenol with exothermic peaks found at 149 °C and 265 °C. In third step, it undergoes decomposition to carbon residue at 327 °C.

3.2.3 *Hydrazinium 2,4-dichlorophenoxyacetate Hydrate*



Thermal study data implies that initially both dehydration and dehydrazination occur by observing peak found at 170°C. Decomposition of acid intermediate into carbon residue occurred as the second step by an exothermic peak found at 285°C and 488 °C, respectively.

3.2.4 *Hydraziniumdiphenylacetate Hydrate*

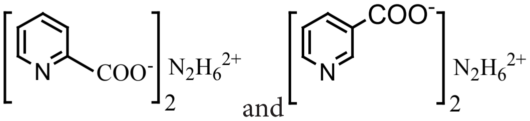


Decomposition of the compound hydraziniumdiphenylacetate hydrate occurred via three steps. An endothermic peak found at 106 °C attributed to exclusion of moisture. This was the first step. Followed by both dehydration and dehydrazination taking place leading to formic acid which was confirmed by the observed peaks at 186 °C and 233 °C. Decomposition into carbon residue is the third step.

3.2.5 *Hydraziniumcinnamate Hydrate*

Initially, an endothermic peak found at 92 °C corresponds to water abolition. Elimination of a molecule of hydrazine was occurred as second step by observing an endothermic peak found at 150 °C. Formation of carbon residue by the complete decomposition of the compound was occurred as third step.

3.2.6 *Hydraziniumpicolinate and Nicotinate*



For both the salts removal of moisture is the first step by the observed endothermic peaks at 121 °C and 117 °C. In the subsequent steps these compounds undergo decomposition leading to carbon residue.

3.3 Antibacterial Activity

The antibacterial activity of the 2,4-dichlorophenoxyacetic acid and its salt against *Escherchia Coli* are determined by disc diffusion method. From the result it has been observed that hydrazinium salt of 2,4-dichlorophenoxyacetic acid shows more activity than the free acid (Figure 4).

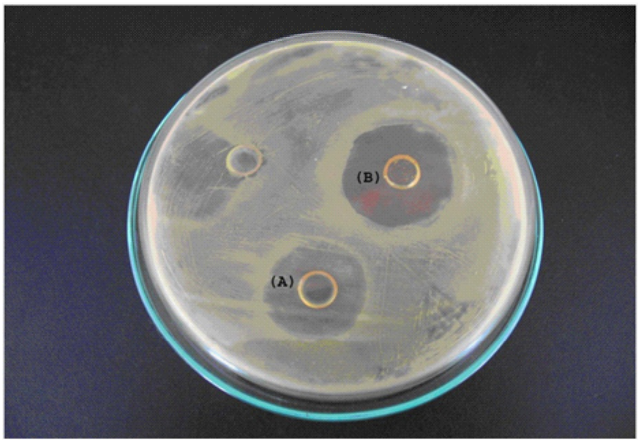


Figure 4. Antibacterial activity of 2,4-dichlorophenylacetic acid and hydrazinium 2,4 dichlorophenoxyacetate hydrate; A – 2,4-dichloro phenoxyacetic acid; B – Hydrazinium 2,4-dichlorophenoxyacetate hydrate.

4. Conclusion

Aromatic substituted acetic acids and aromatic unsaturated acids form hyrazinium (+1) salts, whereas aromatic hetero acids form hydrazinium(+2) salts.

All the hydrazinium salts undergo decomposition through various intermediate and finally lead to carbon residue.

The antibacterial activity of 2,4-dichlorophenoxyacetic acid and its hydrazinium salt against *Escherichia coli* has been studied. The hydrazinium salts show more promising activity than the free acid.

5. References

1. Schmidt E. W., Hydrazine and its Derivatives-Preparation, Properties and Applications, New York: Wiley Interscience; 1984.
2. Patil K. C., Soundararajan R., Paiverneker V. R., *Inorg Chem,* Vol. 18 pp. 1969, 1979.
3. Govindarajan S., Patil K. C., Poojary M. D., Monohar H., *Inorg Chim Acta,* Vol. 120, pp. 103, 1986.
4. Govindarajan S., Patil K .C., Manohar H., Werner P. E., *J Chem Soc Dalton Trans,* pp. 119, 1986.
5. Yasodhai S., Sivakumar T., Govindarajan S., *Thermochim Acta*, Vol. 338, pp. 57, 1999.
6. Patil K. C., Vittal J. P., Patel C. C., *Thermochim Acta,* Vol. 43, pp. 213, 1981.
7. Premkumar T., Govindarajan S., *World J Microbiol Biotechnol,* Vol. 22, pp. 1105, 2006.
8. Yasodhai S., Govindarajan S., *Thermochim Acta,* Vol. 338, pp. 113, 1999.
9. Yasodhai S., Govindarajan S., *J Therm Anal Cal,* Vol. 62, pp. 737, 2000.
10. Kuppusamy K., Sivashankar B. N., Govindarajan S., *Thermochim Acta*,Vol. 259, pp. 251, 1995.
11. Vairam S., Govindarajan S., *Thermochim Acta*, Vol. 414, pp. 263, 2004.
12. Balague C., Sturtz N., Duffard R., Evangelista de Duffard A. M., *Environ Toxicol.* Vol. 16, pp. 43, 2001.