Microwave assisted Synthesis and study of some chromium (III) complexes of L- Arabinose with TBC in Distilled water

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Abstract- This study reports the microwave-assisted synthesis and characterization of chromium (III) complexes derived from L-arabinose using tertiary butyl chromate (TBC) as the chromium source in distilled water as the reaction medium. The synthesis was performed under controlled conditions with varying molar ratios of L-arabinose to TBC (1:3, 1:2, 1:1, 2:1, and 3:1) to evaluate the influence of stoichiometry on complex formation and stability. Microwave irradiation was employed to enhance reaction kinetics, resulting in shorter reaction times and improved yields compared to conventional methods. The resulting complexes were characterized using UV-Visible spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, magnetic susceptibility, and molar conductivity measurements. FTIR analysis indicated coordination through hydroxyl groups of L-arabinose, suggesting chelation with the chromium center. Spectral data supported the formation of octahedral Cr (III) complexes. The variation in molar ratios demonstrated notable effects on the coordination environment and the stability of the complexes. These findings highlight the efficiency of microwave-assisted synthesis in preparing chromium (III) carbohydrate complexes and provide insight into the coordination behaviour of L-arabinose with chromium-based oxidants in aqueous media.

Keywords: L-Arabinose, Tertiary butyl chromate (TBC), Distilled Water (DW), FTIR, TGA-DTA.

INTRODUCTION

Microwave-Assisted Organic Synthesis [1-4] (MAOS) refers to the use of microwave irradiation to heat chemical reactions, significantly accelerating reaction times, improving yields, and often enhancing selectivity compared to conventional heating methods. Since its introduction in the 1980s, MAOS has become a powerful tool in both academic and industrial organic chemistry due to its efficiency and potential to support green chemistry [5] principles.

L-Arabinose [6-8] is a naturally occurring five-carbon sugar (a pentose) that belongs to the class of aldopentoses, meaning it contains an aldehyde group at the first carbon. It has the molecular formula $C_5H_{10}O_5$ and exists predominantly in its furanose (five-membered ring) and pyranose (six-membered ring) forms in solution. L-Arabinose [9] can exist in linear form or as cyclic hemiacetals (furanose and pyranose), with interconversion between forms occurring in aqueous solutions. L-Arabinose is used as a chiral building block in the synthesis of pharmaceuticals, agrochemicals, and complex natural products[10]. It is a component of biopolymers such as hemicellulose [11] and pectin. It is highly soluble in water.

In light of the increasing use of microwave irradiation as a clean[12] and energy-efficient method, in alignment with the twelve Principles of Green Chemistry[13], the authors have carried out the oxidation of L-arabinose using ditertiary butyl chromate[14] (DTBC) under microwave conditions in an aqueous medium. Among the various chromium (VI)-based oxidizing agents—such as Collins' reagent[15], pyridinium chlorochromate[16] (PCC), pyridinium fluorochromate[17] (PFC), tetramethyl ammonium fluorochromate[18] (TMAFC), and quinolinium chlorochromate[19] (QCC)—DTBC was chosen due to its mild reactivity and broad applicability to organic substrates. Additionally, its synthesis is relatively straightforward, making it a more convenient choice compared to some of the other chromium (VI) oxidants. The oxidation products obtained from this reaction are of particular interest because they can act as ligands, potentially forming adducts or coordination complexes with chromium in different oxidation states [20-21]. Investigating these products may provide deeper insights into the reaction mechanism and contribute to broader generalizations about chromium-mediated oxidation processes.

APPLICATION OF MAOS

1. MAOS enables the quick construction of various heterocycles (e.g., pyridines, triazoles, indoles), often in minutes with high yields [22].
2. Microwave irradiation significantly reduces coupling times in peptide bond formation and improves purity [23].
3. MAOS often allows for solvent-free conditions or the use of benign solvents (like water), reducing environmental impact [24].
4. MAOS has been extended to the synthesis of polymers and nanomaterials, offering better control over size and morphology [25].

MATERIAL AND METHODS

Chemical used: - In the present work the chemicals used were L-Arabinose, DW (Distilled water), TBA (Tertiary butyl alcohol), acetone, CrO_3 (VI), silver nitrate, potassium persulphate, ammonium iron (II) sulphate (Mohr's salt), potassium dichromate, barium diphenylamine-4-sulphonate.

Experimental Process: - The chemicals (AR grade obtained from commercial sources) used in this research. The solutions used was freshly prepared. The resultant products obtained in this work were also tested in water. In this research the methods (experimental) used consist of following steps: -

a) Preparation of oxidant TBC: - The calculated quantity of pure and dry powdered CrO_3 was dissolving with TBA, oxidant has been prepared i.e. TBC at room temperature. The bigger pieces of CrO_3 were avoided, due to its corrosive, toxic, and potentially carcinogenic properties.
b) Preparation of substrate solutions: - In the laboratory the L- Arabinose (1.5g) was successfully dissolved in the solvent (10ml) i.e. DW (Distilled water). A clean and dry beaker was used as the container for this procedure and stirring the mixture with a glass rod.
c) Oxidation of substrate and oxidant: - The synthesis was carried out by mixing the substrate and oxidant solutions under constant stirring, followed by microwave irradiation. Five different substrate-to-oxidant (S:O) ratios were used: 1:3, 1:2, 1:1, 2:1, and 3:1. This resulted in five distinct solid products, each with unique colours and compositions. The products were thoroughly washed several times with acetone to remove soluble impurities, unreacted chromium trioxide (CrO_3), and any remaining substrate. The purified solids were then collected and stored in clean, airtight glass containers.
d) Estimation and characterisation: - The percentage composition of carbon (C), hydrogen (H), and oxygen (O) in the synthesized products was determined using an elemental analyzer (Heraeus Vario EL III / Carlo Erba 1108). Chromium (Cr) content was estimated volumetrically by titration. Fourier-transform infrared (FTIR) spectroscopy was performed using a Shimadzu 8201 PC spectrophotometer, while thermogravimetric analysis (TGA) was conducted with a Perkin Elmer Diamond TG/DTA thermal analysis system.

Characateristics of the products of L – Arabinose with TBC

Table -1 (Reactant)

Product code	Substrate	Solvent for the substrate	Oxidant	S:O ratio	Heating condition	Time	Yield
ADW13 (A.6)	L-Arabinose	DW	TBC	1:3	160W	4 min. 10 sec.	3.26g
ADW12 (A.4)	L-Arabinose	DW	TBC	1:2	160W	5 min. 30 sec	2.20g
ADW11 (A.1)	L-Arabinose	DW	TBC	1:1	160W	6 min.	1.76g
ADW21 (A.2)	L-Arabinose	DW	TBC	2:1	160W	7 min. 20 sec.	1.44g
ADW31 (A.3)	L-Arabinose	DW	TBC	3:1	160W	9 min. 40 sec.	0.78g

Table -2 (Product)

Product code	Colour	Solubility in water	Empirical formula	Proposed formulation of the product
ADW13	Dull Brown	Sparingly soluble	$Cr_2C_4H_8O_{13}$	Cr_2O_3. $(HCOOH)_2$ $(C_3H_2O_5)$ (H_2O)
ADW12	Dull green	Insoluble	$Cr_2C_4H_{10}O_{12}$	Cr_2O_3. $(HCOOH)(C_3H_4O_5)$ $(H_2O)_2$
ADW11	Ash blue	Insoluble	$CrC_5H_{10}O_{12}$	CrO. $(C_2H_2O_4)$ $(C_3H_2O_4)$ $(H_2O)_3$
ADW21	Dark blue	Insoluble	$Cr_2C_5H_8O_{13}$	2CrO. $(C_2H_2O_4)$ $(C_3H_2O_5)$ $(H_2O)_2$
ADW31	Light blue	Insoluble	$Cr_2C_7H_{14}O_{13}$	2CrO. $(C_2H_2O_2)_2$ $(C_3H_4O_4)$ $(H_2O)_3$

RESULT AND DISCUSSION

1. Microwave heating significantly reduces reaction time compared to conventional methods, shifting from minutes and hours to mere seconds for completion.
2. The degradative fragments are found in the synthesised products such as formic acid, Oxalic acid, Tartronic acid, 2- Oxopropanedioic acid etc.
3. The colour of the products ranges from light shade to dark shade which indicates the presence of chromium in different oxidation states in the product depending on the conditions of the reaction.
4. All the resultant products formed by oxidation of substrate with Tert-Butyl Chromate (TBC) are mostly insoluble soluble in water.
5. The five complexes derived from the oxidation of L- Arabinose with TBC in DW (Distilled water) solvents exhibited distinct physical characteristics, including variations in color and solubility.
6. The reaction performed in DW were endothermic. Comparing the reaction time and corresponding yield of different substrate: oxidant molar ratio of products, it can be concluded that the sample ADW13 was most efficiently prepared sample of L- Arabinose with low time of formation and good yield.
7. The substrate oxidant ratio also affects the nature and characteristics of the products formed. With increase in molar concentration of the oxidant for each reaction set intensification of the colour of the products was performed and this may be indicative of the increase percentage of chromium in the sample. This was confirmed from the elemental analysis of the sample as evident from the empirical formula of the compound. It may be due to different oxidation states of chromium in different products.
8. The colours observed in the products obtained through the oxidation of L-Arabinose by TBC suggest the formation of complexes in different oxidation states.
9. The higher the ratio of the oxidant, the more pronounced the oxidation of the substrate, and conversely, a decrease in the oxidant ratio corresponds to a reduction in the extent of substrate oxidation.
10. When we increase the proportion of oxidant, it will take less time to form product and the yield of the product will be high and it will be shown in the sample no. is ADW13.
11. When we decrease, the proportion of oxidant, it will take more time to form product and the yield of the product will be less and it will be shown in the sample no. is ADW31.
12. For sample ADW13, ADW12 where the oxidant ratio is at its maximum, the most stable oxidation state observed is III, represented by the formation of Cr_2O_3. In contrast, the other compound shows oxidation state of chromium is II, in the form of CrO.
13. In most of the cases, the different colour of the product is due to various factors, including the nature of the chemical bonds involved, the presence of impurities, or environmental conditions.
14. In some cases, excessive concentrations of oxidants resulted in charring of the substrate. This indicates the importance of carefully controlling the oxidant-to-substrate ratio to optimize reaction conditions and product yields.

CONCLUSION

The microwave-assisted synthesis of chromium (III) complexes using L-arabinose and tertiary butyl chromate (TBC) in distilled water was successfully achieved. The method proved to be efficient, offering faster reaction times and higher yields compared to conventional techniques. The use of different molar ratios influenced the coordination environment and stability of the resulting complexes. Spectroscopic and analytical studies confirmed the formation of Cr (III) complexes, likely involving coordination through the hydroxyl groups of L-arabinose. Overall, this work demonstrates that microwave irradiation in aqueous media is a green, effective approach for synthesizing chromium (III) carbohydrate complexes with potential applications in coordination chemistry and related fields.

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