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MICROWAVE ACCELERATED OXIDATION OF ETHYLCYCLOHEXANECABOXYLATE BY DITERTIARY BUTYL CHROMATE IN ORGANIC MEDIA

Shubhankar Aich[1], Anil Kumar Delta[2]

[1]Assistant Professor, Department of Chemistry, Marwari College Ranchi
[2]Associate Professor, University Department of Chemistry, Ranchi University, Ranchi

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Abstract: *Microwave irradiation has significantly affected the field of organic synthesis and has emerged as a valuable method for facilitating rapid and efficient chemical transformations. In this study, we investigated the oxidation of ethylcyclohexanecarboxylate using di-tertiary-butyl chromate (TBC) under microwave irradiation in various organic solvents, including tetrahydrofuran (THF), 1,4-dioxane, and dichloromethane (DCM). The reaction mixtures were prepared by combining the substrate solution with TBC in appropriate ratios, followed by stirring and microwave irradiation for specific durations. The resulting products were characterized using a combination of chemical and instrumental techniques, including elemental analysis, Fourier transform infrared (FTIR) spectroscopy, differential thermal analysis (DTA), thermogravimetric analysis (TGA), and mass loss patterns. Our findings demonstrate that this microwave-assisted approach aligns with the principles of green chemistry and offers a sustainable and efficient route for the oxidation of ethyl cyclohexane carboxylate.*

Keywords: **Di-tertiary-butyl chromate (TBC), Ethylcyclohexanecarboxylate, Tetrahydrofuran (THF), Dichloro-methane (DCM), and Microwave heating.**

1. INTRODUCTION

Microwave-assisted organic synthesis (MAOS)[1-2] and microwave-induced organic reactions (MIOR)[3] have revolutionized organic chemistry by offering sustainable and efficient synthetic approaches. These techniques align with green chemistry[4-5] principles, reduce reaction times, improve yields, and minimize waste generation. The concept of microwave dielectric heating, introduced by Spencer[6] in 1947, was applied to organic synthesis in the pioneering work of Gedye et.al.[7-9] in 1986. Since then, the field has flourished, with over 2000 research articles demonstrating the versatility of microwave-assisted techniques. A comprehensive review by P. Lindstrom et al [10]. highlighted the advantages of MAOS and MIOR, including significantly reduced reaction times, improved product yields, and minimal waste generation. These techniques are attractive alternatives[11] to the conventional heating methods.

In this study, we explored the oxidation of ethylcyclohexanecarboxylate[12] using di-tertiary-butyl chromate[13] (TBC) under microwave irradiation. TBC, a robust and versatile oxidant, has been extensively studied since its introduction by Oppenaur and H. Oberrauch[14] in 1949. The products of ethylcyclohexanecarboxylate have the potential to serve as ligands for the formation of Cr complexes in various oxidation states.

Ethylcyclohexanecarboxylate, an alicyclic ester, is a colourless liquid with a characteristic odour. It is used as a flavouring agent[15-16] and an intermediate or scaffold for the synthesis of bioactive molecules[17-20] in pharmaceutical chemistry. By oxidizing ethyl cyclohexane carboxylate with TBC under microwave irradiation, we synthesized and characterized chromium complexes[21-23] in lower oxidation states. This approach expands the scope of ethyl cyclohexane carboxylate chemistry and demonstrates the versatility of TBC as oxidizing agent[24-25].

2. MATERIALS AND METHODS

All chemicals used in this study were of analytical reagent (A.R.) grade and were procured from commercial sources and used as received. Ethyl cyclohexane carboxylate, chromium (VI) oxide, tertiary butyl alcohol, tetrahydrofuran (THF), 1,4-dioxane, dichloromethane (DCM), acetone, silver nitrate, potassium persulfate, ammonium iron (II) sulfate (Mohr's salt), potassium dichromate, and barium diphenylamine-1-sulfonate were used.

The oxidant di-tertiary-butyl chromate (TBC) was synthesised in situ through the dissolution of a precisely weighted quantity of chromium (VI) oxide in 10 ml of tertiary butyl alcohol. Ethylcyclohexanecarboxylate (2 ml.) was dissolved in 10 ml of tetrahydrofuran (THF), 1,4-dioxanloromethane (DCM) in a rigorously cleaned and desiccated beaker under continuous magnetic stirring at room temperature. The substrate-to-oxidant molar ratios were 1:1, 2:1, and 3:1, respectively. The reaction mixture was irradiated in a Samsung household microwave oven G-273V (20 L, 2450 MHz, and

150 W) for various oxidation times. Thermometric measurements were conducted to assess the exothermic and endothermic natures of the reaction by recording the initial and final temperatures of the reaction mixture. The isolated products were subsequently washed with acetone, meticulously dried.

labelled A11ECHC, A21ECHC, A31ECHC, B11ECHC, B21ECHC, B31ECHC, C11ECHC, C21ECHC, C31ECHC, and stored for further analytical and spectroscopic characterization. The percentage compositions of carbon and hydrogen were determined using a EUROVECTOR E-3000 elemental analyser. The chromium content was subsequently quantified by volumetric titration using potassium persulfate, potassium dichromate, and Mohr's salt solutions. The oxygen content was calculated by subtracting the percentages of carbon, hydrogen, and chromium from 100. The empirical formulae for the complexes were deduced from the elemental analysis data. Fourier transform infrared (FTIR) spectra of the products were recorded on a PerkinElmer Fourier transform infrared spectrometer (FTIR4000-450 cm^{-1}). Thermogravimetric and differential thermal analyses (TG-DTA) of the compounds were performed using a Perkin Elmer Diamond TG-DTA system. The samples underwent a controlled heating process at a constant heating rate of 10°C /min, progressing from ambient temperature to a final temperature of 700°C. The characterization data for all synthesized products, including FTIR spectra, TG-DTA thermographs and corresponding analytical data in Tables 1-3 are summarised.

3. ETHICAL COMPLIANCE

This research project involved human participants and was conducted in accordance with the approval granted by the Ethics Committee of the University Department of Chemistry, Ranchi University.

4. RESULTS AND DISCUSSION

The exhaustive analytical data presented in Tables 1, 2, and 3, and FTIR, TG-DTA graphs encompassing physical parameters, elemental analysis, and proposed chemical formulations, respectively, coupled with the FTIR, TGA-DTA graphical representations, facilitate the derivation of several pertinent technical conclusions pertaining to the synthesis of chromium-ethylcyclohexanecarboxylate (ECHC) complexes. A meticulous examination of these datasets enables a comprehensive understanding of the complexation process, thereby permitting inferences to be drawn regarding the structural and compositional attributes of the resultant chromium-ECHC complexes.

Table 1: Preliminary product characterisation (Ethylcyclohexanecarboxylate-TBC)

Serial no.	Sample label	Solvent	Substate/Oxidant Ratio	Microwave Irad. Time (in sec.)	Yield (in g)	Colour	Solubility (in water)
1.	A11 ECHC	THF	(1:1) 2ml/2g	54	2.64	Greenish Brown	Sparingly Soluble
2.	A21 ECHC	THF	(2:1) 2ml/1g	58	2.05	Greenish Brown	Insoluble
3.	A31 ECHC	THF	(3:1) 2ml/0.67g	64	1.83	Dark Green	Insoluble
4.	B11 ECHC	1,4 Dioxane	(1:1) 2ml/2g	72	1.72	Greenish Brown	Insoluble
5.	B21 ECHC	1,4 Dioxane	(2:1) 2ml/1g	80	1.27	Dark Green	Insoluble
6.	B31 ECHC	1,4 Dioxane	(3:1) 2ml/0.67g	85	0.89	Dark Green	Insoluble

7.	C11 ECHC	DCM	(1:1) 2ml/2g	40	2.86	Dark Brown	Sparingly Soluble
8.	C21 ECHC	DCM	(2:1) 2ml/1g	45	2.48	Greyish Green	Sparingly Soluble
9.	C31 ECHC	DCM	(3:1) 2ml/0.67g	52	1.72	Light Green	Insoluble

Table 2: Product formulation– I

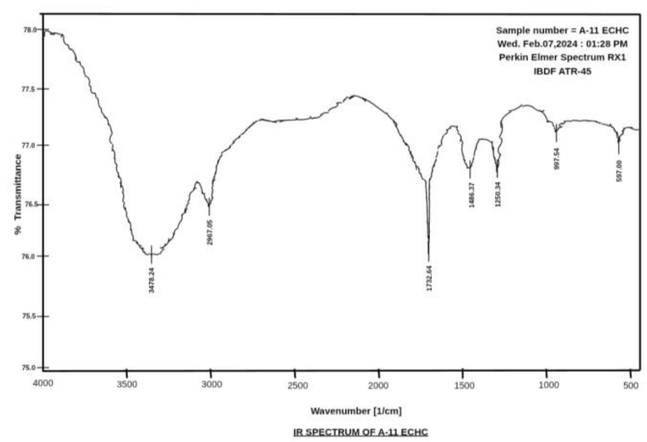
Serial No.	Sample No.	Cr%	C%	H%	O%	Empirical Formula
1.	A11 ECHC	20.07	20.85	3.47	55.61	$Cr_2C_9H_{18}O_{18}$
2.	A21 ECHC	21.22	22.04	4.49	52.25	$Cr_2C_9H_{22}O_{16}$
3.	A31 ECHC	22.03	22.88	4.23	50.86	$Cr_2C_9H_{20}O_{15}$
4.	B11 ECHC	20.53	21.34	4.34	53.79	$Cr_2C_9H_{22}O_{17}$
5.	B21 ECHC	21.31	22.13	4.09	52.47	$Cr_2C_9H_{20}O_{16}$
6.	B31 ECHC	22.70	23.58	4.80	48.92	$Cr_2C_9H_{22}O_{14}$
7.	C11 ECHC	18.31	19.01	3.52	59.16	$Cr_2C_9H_{20}O_{21}$
8.	C21 ECHC	19.33	20.07	4.09	56.53	$Cr_2C_9H_{22}O_{19}$
9.	C31 ECHC	20.55	21.34	4.34	53.77	$Cr_2C_9H_{22}O_{17}$

Table 3: Product formulation– II

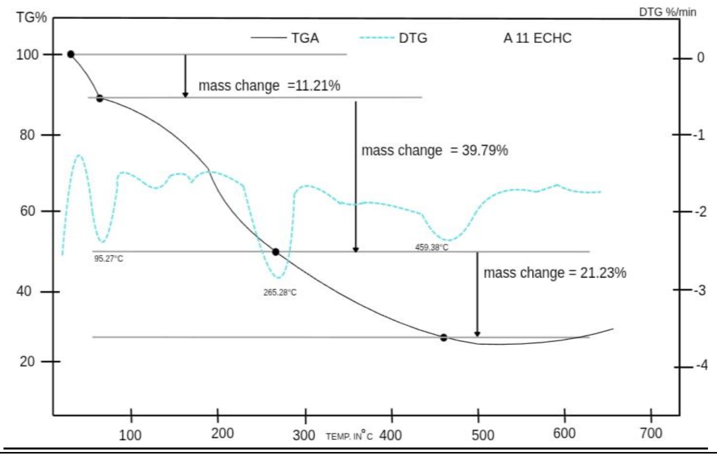
Sl. No.	Sample No.	Empirical Formula	Formulation
1.	A11 ECHC	$Cr_2C_9H_{18}O_{18}$	$Cr_2O_3\ 2(CH_3COOH)\ (HOOC\ CH_2\ COOH)\ 2CO_2\ (H_2O)_3$
2.	A21 ECHC	$Cr_2C_9H_{22}O_{16}$	$Cr_2O_3\ 2(CH_3COOH)\ (HOOC\ (CH_2)_2\ COOH)\ HCOOH\ (H_2O)_3$
3.	A31 ECHC	$Cr_2C_9H_{20}O_{15}$	$Cr_2O_3\ (CH_3COOH)\ (HOOC\ (CH_2)_3\ COOH)\ 2HCOOH\ (H_2O)_2$
4.	B11 ECHC	$Cr_2C_9H_{22}O_{17}$	$Cr_2O_3\ 2(CH_3COOH)\ (HOOC(CH_2)_2COOH)\ CO_2\ (H_2O)_4$
5.	B21 ECHC	$Cr_2C_9H_{20}O_{16}$	$Cr_2O_3\ (CH_3COOH)\ (HOOC\ (CH_2)_3\ COOH)\ HCOOH\ CO_2\ (H_2O)_3$
6.	B31 ECHC	$Cr_2C_9H_{22}O_{14}$	$Cr_2O_3\ (CH_3COOH)\ (HOOC\ (CH_2)_4\ COOH)\ (HCOOH)\ (H_2O)_3$
7.	C11	$Cr_2C_9H_{20}O_{21}$	$Cr_2O_3\ 2(CH_3COOH)\ 2(HOOC\ COOH)\ CO_2\ (H_2O)_4$

	ECHC		
8.	C21 ECHC	$Cr_2C_9H_{22}O_{19}$	Cr_2O_3 2(CH_3COOH) (HOOC CH_2 COOH) (HOOC COOH) (H_2O)$_4$
9.	C31 ECHC	$Cr_2C_9H_{22}O_{17}$	Cr_2O_3 2(CH_3COOH) (HOOC (CH_2)$_2$ COOH) (CO_2) (H_2O)$_4$

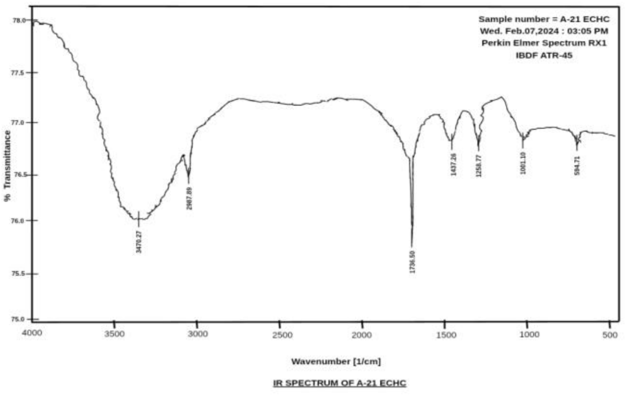
FTIR, TG-DTG THERMOGRAPHS

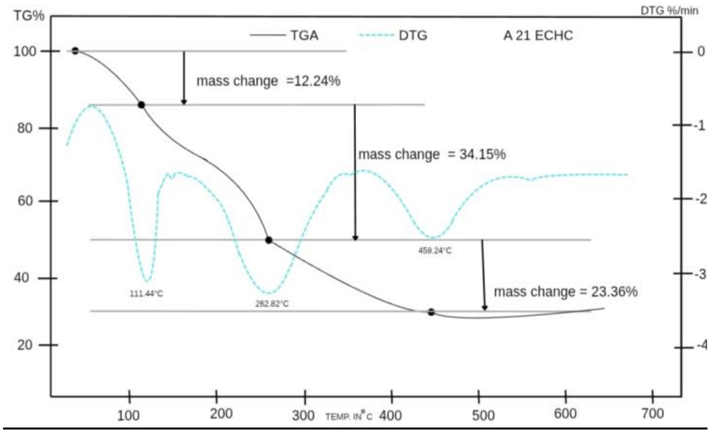


(i)FTIR Spectrum of A11 ECHC



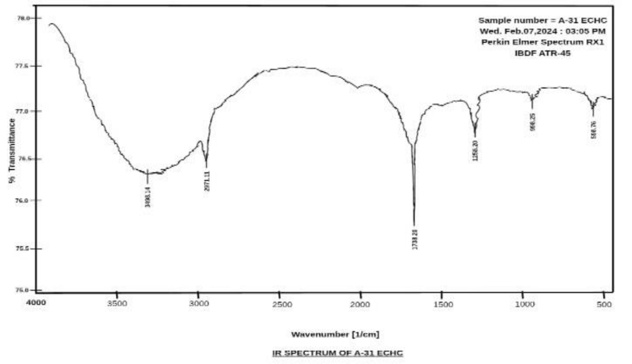
(ii) TG-DTG Thermograph of A11 ECHC



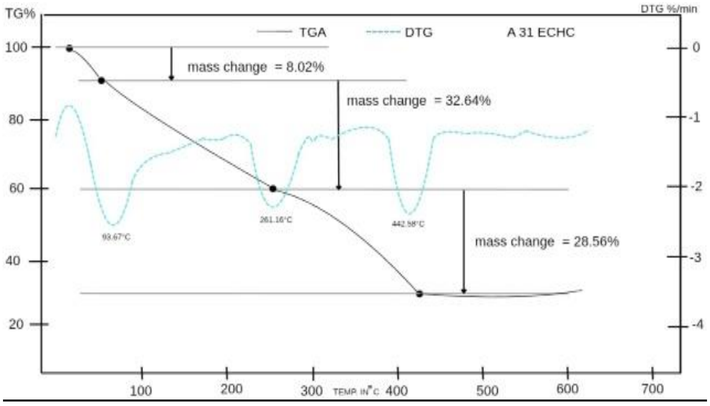


(iii)FTIR Spectrum of A21 ECHC

(iv) TG-DTG Thermograph of A21 ECHC



(iii)FTIR Spectrum of A31 ECHC



(vi) TG-DTG Thermograph of A31 ECHC

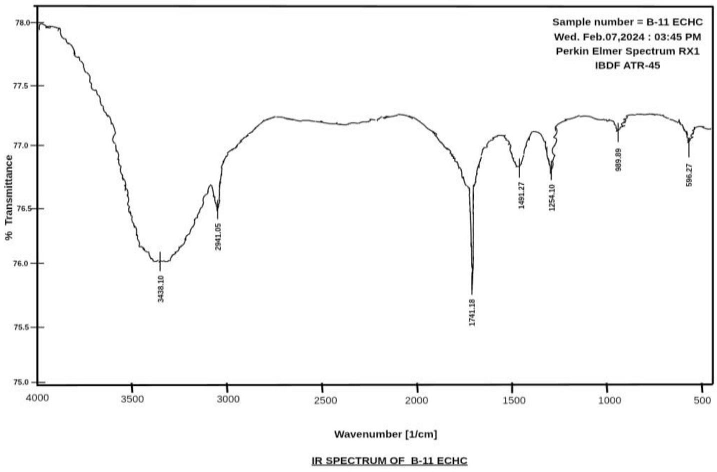


Fig (vii) FTIR Spectrum of B11ECHC

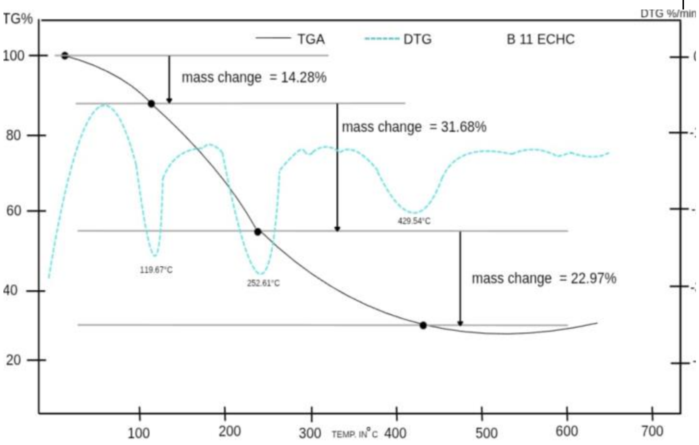
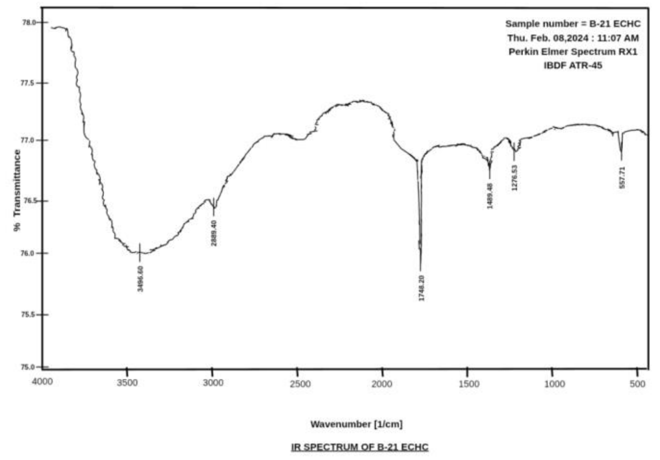


Fig (viii) TG-DTG Thermograph of B11ECHC



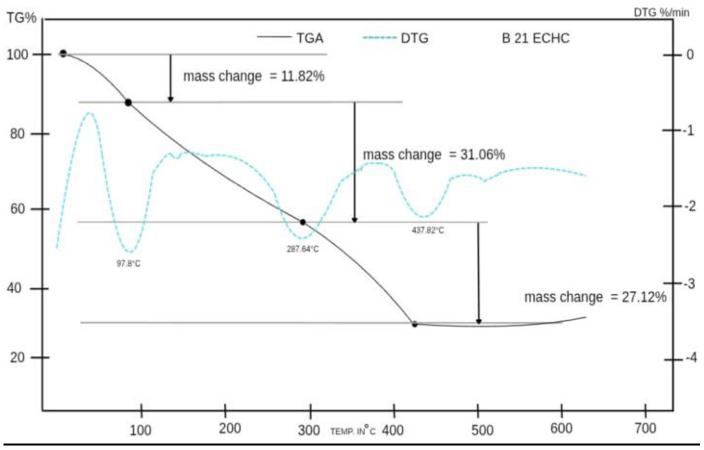
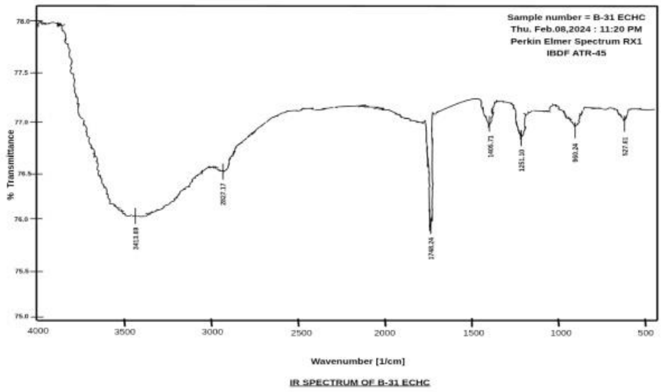


Fig (ix) FTIR Spectrum of B21ECHC

Fig (x) TG-DTG Thermograph of B21ECHC



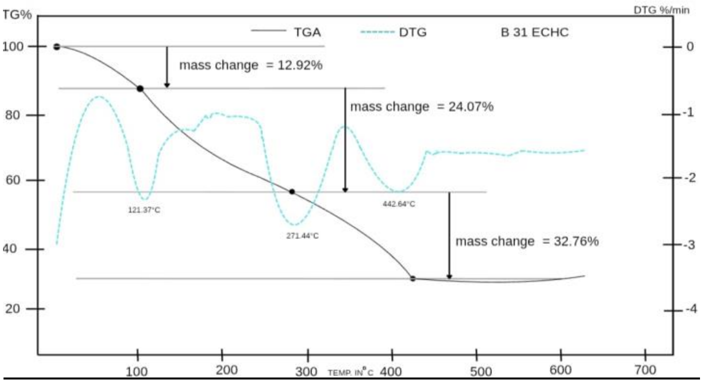


Fig (xi) FTIR Spectrum of B31ECHC

Fig (xii) TG-DTG Thermograph of B31ECHC

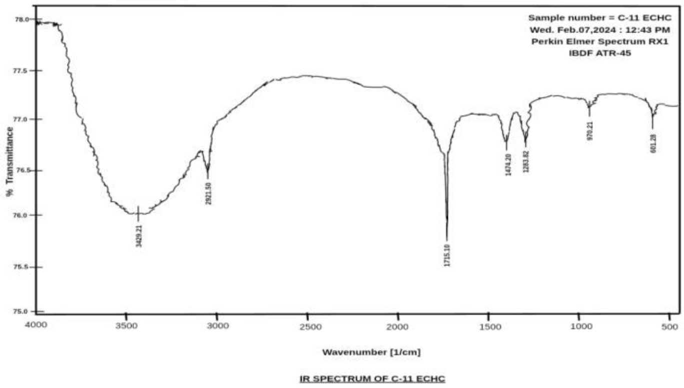


Fig (xiii) FTIR Spectrum of C11ECHC

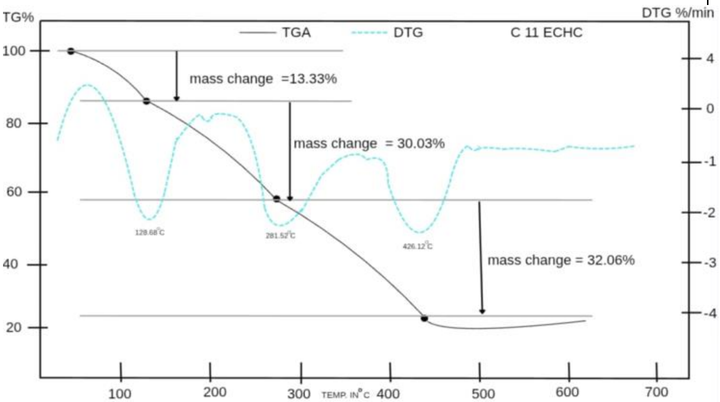


Fig (xiv) TG-DTG Thermograph of C11ECHC

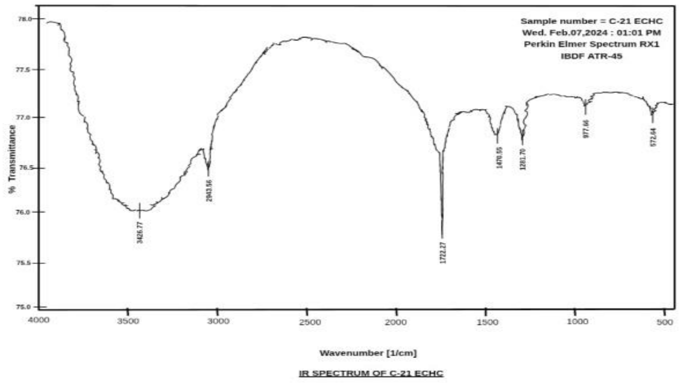


Fig (xv) FTIR Spectrum of C21ECHC

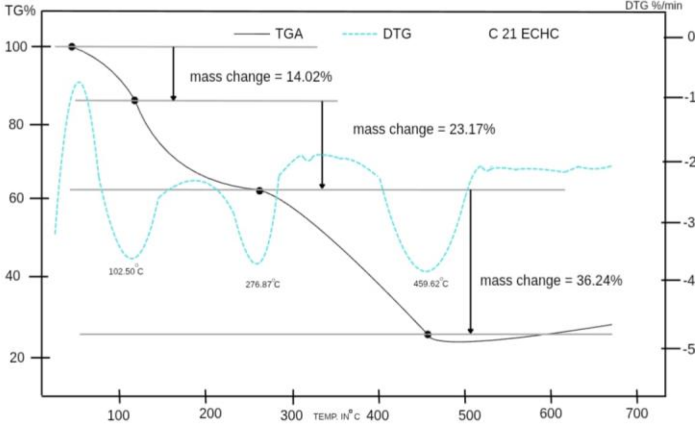
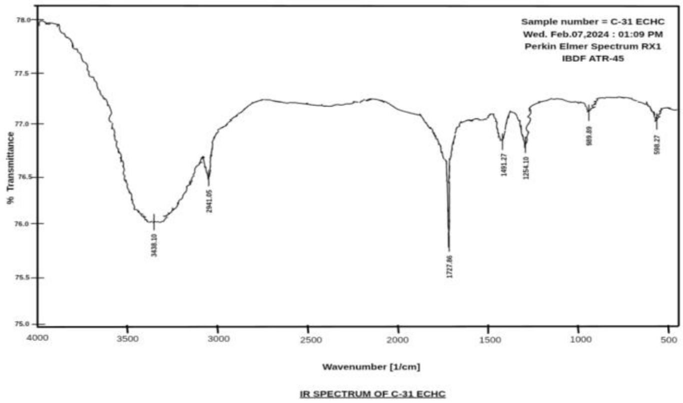


Fig (xvi) TG-DTG Thermograph of C21ECHC



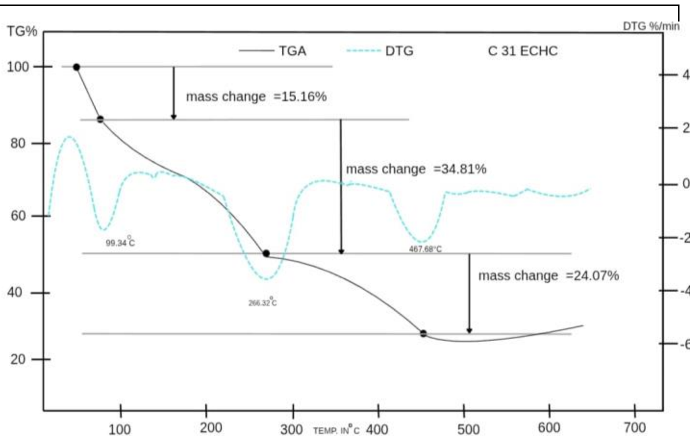


Fig (xvii) FTIR Spectrum of C31ECHC

Fig (xviii) TG-DTG Thermograph of C31EC

- ine complexes exhibiting distinct physical properties, including colour and solubility, were obtained after the oxidation of ethyl cyclohexane carboxylate with TBC in different solvents.
- As shown in Table 3, the common oxidation products formed during the process included formic acid, acetic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, carbon dioxide, and water.
- A comparative study of the reaction kinetics revealed notable discrepancies in the thermodynamic behaviour. Specifically, reactions conducted in 1,4-dioxane exhibited endothermic characteristics, whereas analogous reactions performed in alternative solvents demonstrated exothermic properties.
- Dichloromethane (DCM) was the most efficient solvent for mass production. It yielded the highest product weight (up to 2.86 g) with the shortest microwave exposure time (40–52 s).
- Among the solvents tested 1,4-Dioxane was the least efficient medium, requiring the longest irradiation times (72–85 s) and producing the lowest yields (as low as 0.89 g). This suggests that the coordination process is significantly more favourable in chlorinated or ether-based solvents with lower boiling points under microwave conditions.
- The ratio of the ECHC substrate to chromium oxidant dictates both the yield and final metal density.
- In every solvent system (THF, Dioxane, DCM), the 1:1 ratio consistently produced the highest yield. Increasing the ratio to 3:1 led to a significant decrease in product recovery. This indicates an inverse yield relationship.
- Interestingly, although higher ratios (3:1) produced less total mass, they generally resulted in a higher Cr percentage (Cr%) in the final complex (peaking at 22.70% for Sample B31ECHC). This implies that a higher relative concentration of the oxidant leads to a more metal-concentrated coordination environment.
- Table 3 presents a fascinating look at the proposed chemical structures. The formulations suggest that these are not simple binary salts but complex polynuclear chromium (III) species:
- Most formulations are centred around a Cr_2O_3 or hydroxy-bridged framework.
- The products appeared to incorporate a variety of ligands, including acetic acid (CH_3COOH), carbon dioxide (CO_2), and water molecules (H_2O). The presence of CO_2 in the formulations (e.g., in A11ECHC and B11ECHC) suggests that some atmospheric fixation or decarboxylation of intermediates may occur during the microwave process.
- Almost all stable products are hydrates (containing H_2O or $(H_2O)_n$, which correlates with the high oxygen percentages (often exceeding 50%) observed in Table 2.
- The colours range from light green to dark brown. Generally, the " green " variants (A31ECHC, B21ECHC, B31ECHC, C31ECHC) are correlated with higher chromium concentrations and specific coordination geometries.
- Most products are insoluble in water. Only the 1:1ratios in THF and DCM (A11ECHC, C11ECHC, C21ECHC) showed "sparing" solubility. This suggests that as the metal-to-ligand ratio shifts or the reaction time increases, the complexes become more polymeric and hydrophobic.
- Future research may involve recrystallizing the products in a suitable solvent and examining the resulting crystals to gain further insight into their properties and structures.

5. CONCLUSION

The oxidation of ethylcyclohexanecarboxylate with di-tert-butyl chromate (TBC) in various solvents under various conditions yielded a diverse range of products and exhibited interesting trends. Overall, the oxidation of ethylcyclohexanecarboxylate with TBC is a complex reaction influenced by multiple factors, including the solvent, oxidant ratio, and reaction time. Understanding these factors is crucial for optimizing the reaction to obtain specific products and minimize unwanted by-products.

6. DATA AVAILABILITY STATEMENT

The data presented herein were generated using only the experimental procedures.

7. ACKNOWLEDGMENTS

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Authors Contributions:

[Author 1]: Conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing (original draft presentation), and funding acquisition.

[Author 2]: Conceptualization, methodology, visualization, supervision, validation, formal analysis, investigation, resources, data curation, writing (review and editing), and project administration.

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Conflict of interest:

The authors declare that they have no conflicts of interest.

8. REFERENCES:

1. Kappe, C. O. "Microwave-Assisted Chemistry." In "Microwave-Assisted Organic Synthesis," pp. 1-19. Springer, 2013.
2. De la Hoz, A., et al. (2011). Microwave-Assisted Organic Synthesis: A Critical Review. Tetrahedron, 67(2), 283-303.
3. Singh, M. S., & Singh, A. K. (2019). Microwave-Induced Organic Reactions: A Review. Journal of Chemical Research, 43(10), 557-562.
4. The twelve principles of Green Chemistry' United States Environmental Protection Agency. 2006 Retrieved
5. Lahoz, Antonio De, Diaz-Ortiz, Angel and Prieto, Pilar, Microwave assisted green organic synthesis in alternative energy sources for green chemistry, 2016 pp. 1-33.
6. Spencer, P., "Method of Treating Foodstuffs," US Patent 2,495,429, 1950.
7. Gedye, R., Smith, F., Westaway, K., Ali, H., Baldisera, L., Laberge, L., & Rousell, J. (1986). The use of microwave ovens for rapid organic synthesis. Tetrahedron Letters, 27(3), 279-282.
8. Gedye, R. N., & Wei, J. B. (1998). Microwave-assisted organic synthesis: A review. Canadian Journal of Chemistry, 76(5), 525-532.
9. Gedye, R. N., & Rank, W. (1999). Microwave-assisted organic synthesis in solvent-free conditions. Journal of Chemical Research, Synopses, (10), 542-543.
10. Lindstrom, P., Tierney, J., Wathey, B. and Westman, J. "Microwave Assisted Organic Synthesis-a Review," Tetrahedron, vol. 57, no. 45, pp. 9225-9283, 2001.
11. Katre, Sangita; Study of oxidation of chromic acid with chromium complexes by classical and green approach; Der Chemica Sinicia,2014, 5 (6) Pelagia Research Library, pp 48-50.
12. ethyl cyclohexanecarboxylate - Wikidatahttps://share.google/Qpb1WE3SYYKyFd04i
13. Wheeler, J.M., "Ditertiary Butyl Chromate: A Versatile Oxidant," Journal of Chemical Research, vol. 2001, no. 10, pp. 432-433, 2001.
14. Oppenaur, R.V. and Oberrauch, H. "Oxidation of Amines with Di-tert-butyl Chromate," Journal of the American Chemical Society, vol. 71, no. 10, pp. 3421-3424, 1949.
15. Adams, T. B.,et.al. (1996). "The FEMA GRAS assessment of alicyclic substances used as flavour ingredients." *Food and Chemical Toxicology*, *34*(8), 763–828. https://doi.org/10.1016/s0278-6915(96)00051-8.

16. Geithe, C., et al. (2016). "The Broadly Tuned Odorant Receptor OR1A1 is Highly Selective for Key Food Odorants." *Chemical Senses*, 42(3), 181–193.

17. Park, H. G., et al. (2018). "Stereoselective synthesis of functionalized cyclohexane carboxylates as precursors for GABA-receptor ligands." Journal of Organic Chemistry, 83(14), 7542–7551.

18. Kandemir, H., et al. (2024). "Synthesis and biological evaluation of novel cyclohexanecarboxamido hydrazones as potent antimicrobial agents." Medicinal Chemistry Research, 33, 112–125.

19. Bodor, N., & Buchwald, P. (2000). "Soft Drug Design: General Principles and Recent Applications." Medicinal Research Reviews, 20(1), 58–101.

20. "Synthesis and biological evaluation of novel cyclohexanecarboxamido hydrazones as potent antimicrobial agents." *Medicinal Chemistry Research*, 33, 112–125.

21. Ling, L., Chen, C., Luo, M., & Zeng, X. (2019). "Chromium-Catalyzed Activation of Acyl C–O Bonds with Magnesium for Amidation of Esters with Nitroarenes." Organic Letters, 21(6), 1912–1916.

22. Steiman, T. J., & Uyeda, C. (2015). "Reagents for Reductive Transition Metal Catalysis." Chemical Science, 6, 2327–2337.

23. Zeng, X. (2013). "Recent Advances in Chromium-Catalyzed Carbon–Carbon Bond-Forming Reactions." Chemical Society Reviews, 42(13), 5658–5671.

24. Katre, Sangita and Pandey, H.O. A Green approach to oxidation of succinic acid by chromium (VI) based complexes functioning as oxidant in International Journal of green chemistry and Bioprocess 2013 3(3) pp.3032.

25. Katre, Sangita D. Recent Advances in the Oxidation Reactions of Organic Compounds using Chromium (VI) Reagents in Res.J.Chem.Environ. Vol. 24 (1) January (2020).