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Microwave Accelerated Oxidation Of Cyclohexanamine By Ditertiary Butyl Chromate In Organic Media

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Abstract: Microwave irradiation has significantly affected the field of organic synthesis and has, emerged as a valuable methodology for facilitating rapid and efficient chemical transformations. In this study, we investigated the oxidation of cyclohexanamine by 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 cyclohexanamine oxidation.

***Key Words*:** Di-tertiary-butyl chromate (TBC), Cyclohexanamine, Tetrahydrofuran, Dichloro Methane (DCM), Microwave heating.

I. 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, reducing reaction times, improving yields, and minimizing waste generation.

The concept of microwave dielectric heating, introduced by Percy Spencer[6] in 1947, was applied in organic synthesis in the pioneering work of R. 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[10] et al. 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 cyclohexanamine[12] using di-tertiary-butyl chromate[13] (TBC) under microwave heating. TBC, a robust and versatile oxidant, has been extensively studied since its introduction by Oppenaur and H. Oberrauch[14] in 1949. The products of cyclohexanamine have the potential to serve as ligands for the formation of chromium complexes in various oxidation states.

Cyclohexanamine, an alicyclic amine, is a colourless liquid with a characteristic odour. It has applications as a corrosion inhibitor[15] and a key feedstock in herbicide[16] production. By oxidizing cyclohexanamine with TBC under microwave irradiation, we aimed to synthesize and characterize chromium complexes[17-19] in lower oxidation states. This approach expands the scope of cyclohexanamine chemistry and demonstrates the versatility of TBC as oxidizing agent[20-21].

II. MATERIALS AND METHODS

All chemicals used in this study were of analytical reagent (A.R.) grade, procured from commercial sources and used as received. Cyclohexanamine, 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. 2 ml of Cyclohexanamine was dissolved in 10 ml of tetrahydrofuran (THF), 1,4-dioxane, or dichloromethane (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 A11CHAMINE, A21CHAMINE, A31CHAMINE, B11CHAMINE, B21CHAMINE, B31CHAMINE, C11CHAMINE, C21CHAMINE, C31CHAMINE, and stored for further analytical and spectroscopic characterization. The percentage compositions of carbon, hydrogen, and nitrogen 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, nitrogen, and chromium from 100. The empirical formulae for the complexes were deduced from the elemental analysis data. Infrared (IR) spectra of the products were documented on a Perkin-Elmer Fourier transform infrared spectrometer (FTIR4000-450cm^{-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, with a constant heating rate of 10°C /min, progressing from ambient temperature to a final temperature of 700°C. The recorded data are summarized in Tables 1-3.

III. 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, Ranchi.

IV. RESULTS AND DISCUSSION

- Nine complexes exhibiting distinct physical properties, including colour and solubility, were obtained after oxidation of cyclohexanamine with TBC in different solvents.
- As shown in Table 3, the common oxidation products formed during the process include acetic acid, crotonic acid, acrylic acid, adipic acid, carbon dioxide, water, and nitrogen oxide.
- A comparative study of the reaction kinetics revealed a notable discrepancy in the thermodynamic behaviour. Specifically, reactions conducted in 1,4-dioxane exhibit endothermic characteristics, whereas analogous reactions performed in alternative solvents demonstrate exothermic properties.
- A positive correlation was observed between the extent of cyclohexanamine oxidation and di-tertiary-butyl chromate ratio, with increasing oxidation evident for A11CHAMINE, B11CHAMINE, and C11CHAMINE (Table-2).
- An inverse correlation was observed between the reaction time and rate of oxidation, with a concomitant increase in the oxidation ratio noted with increasing TBC ratios.
- The substrate-to-oxidant molar ratio was found to be a critical parameter influencing the properties and features of the resulting products. An increase in oxidant concentration resulted in progressive darkening of the product colour (Table-1).
- The formation of adipic acid in B31CHAMINE, as observed in Table 3 suggests that cyclohexananine undergoes minimal oxidation in 1,4-Dioxane, likely because of its limited solubility in this solvent.

- As shown in Table 3, Nitric oxide (NO) was the predominant product observed in three instances A31CHAMINE, B31CHAMINE and C31CHAMINE where the oxidant is present in sub-stoichiometric amounts. In contrast, nitrogen dioxide (NO_2) formation was observed in all other cases, characterised by an excess of oxidant.
- The most stable Cr oxidation state (III) was observed in the form of Cr_2O_3 in A11CHAMINE, A21CHAMINE, B11CHAMINE, B21CHAMINE, C11CHAMINE and C21CHAMINE as evident in Table 3.
- Based on the data presented in Table 1 and 2, THF emerges as the most promising solvent for this reaction. Table 1 demonstrates not only the highest yield but also the shortest reaction time with THF, while Table 2 indicates the enhanced oxygen atom abundance in THF solvent system. These combined observations strongly suggest that THF provides the most optimal conditions for a specific reaction compared to DCM and 1,4-Dioxane.
- Future research may involve recrystallization of the products in a suitable solvent, followed by an examination of the resulting crystals to gain further insight into their properties and structures.

V. CONCLUSION

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

Table 1: Preliminary product characterisation (Cyclohexanamine-TBC)

Sl. No.	Sample No.	Solvent	S/O ratio	MW (in sec)	Yields (in gm)	Colour	Solubility
1.	A11 CHAMINE	THF	1:1 2.0ml/2.0g	25	1.88	Dark Brown	Insoluble
2.	A21 CHAMINE	THF	2:1 2.0ml/1.0g	30	1.42	Dark Brown	Insoluble
3.	A31 CHAMINE	THF	3:1 2.0ml/0.67g	38	1.05	Light Brown	Partially soluble
4.	B11 CHAMINE	1,4-DIOXANE	1:1 2.0ml/2.0g	37	1.30	Dark Brown	Insoluble
5.	B21 CHAMINE	1,4-DIOXANE	2:1 2.0ml/1.0g	41	1.23	Light Brown	Insoluble
6.	B31 CHAMINE	1,4-DIOXANE	3:1 2.0ml/0.67g	47	0.80	Light Brown	Sparingly soluble
7.	C11 CHAMINE	DCM	1:1 2.0ml/2.0g	34	1.55	Dark Brown	Insoluble
8.	C21 CHAMINE	DCM	2:1 2.0ml/1.0g	37	1.28	Dark Brown	Insoluble
9.	C31 CHAMINE	DCM	3:1 2.0ml/0.67g	42	0.85	Light Brown	Sparingly soluble

Table 2: Product formulation– I

Sl. No.	Sample No.	Cr%	C%	H%	N%	O%	Empirical Formula
1.	A11 CHAMINE	24.30	16.82	3.27	3.27	54.82	$Cr_2C_6H_{14}NO_{14}$
2.	A21 CHAMINE	15.11	20.93	4.07	4.07	55.82	$CrC_6H_{14}NO_{12}$
3.	A31 CHAMINE	17.45	24.16	5.37	4.70	48.32	$CrC_6H_{16}NO_9$
4.	B11 CHAMINE	27.37	18.95	3.68	3.68	46.32	$Cr_2C_6H_{14}NO_{11}$

5.	B21 CHAMINE	17.57	24.32	4.73	4.73	48.65	$CrC_6H_{14}NO_9$
6.	B31 CHAMINE	18.57	25.71	5.00	5.00	45.72	$CrC_6H_{14}NO_8$
7.	C11 CHAMINE	24.30	16.82	3.27	3.27	52.34	$Cr_2C_6H_{14}NO_{14}$
8.	C21 CHAMINE	17.57	24.32	4.73	4.73	48.65	$CrC_6H_{14}NO_9$
9.	C31 CHAMINE	17.45	24.16	5.37	4.70	48.32	$CrC_6H_{16}NO_9$

Table 3: Product formulation– II

Sl. No.	Sample No.	Empirical Formula	Formulation
1.	A11 CHAMINE	$Cr_2C_6H_{14}NO_{14}$	Cr_2O_3 CH_3COOH CO_2 $CH_2{=}CHCOOH$ $(H_2O)_3NO_2$
2.	A21 CHAMINE	$CrC_6H_{14}NO_{12}$	CrO CH_3COOH CO_2 $CH_2{=}CHCOOH$ $(H_2O)_3$ NO_2
3.	A31 CHAMINE	$CrC_6H_{16}NO_9$	CrO CH_3COOH $CH_3CH{=}CHCOOH$ $(H_2O)_3$ NO
4.	B11 CHAMINE	$Cr_2C_6H_{14}NO_{11}$	Cr_2O_3 CH_3COOH $CH_3CH_2{=}CHCOOH$ $(H_2O)_2$ NO_2
5.	B21 CHAMINE	$CrC_6H_{14}NO_9$	CrO CH_3COOH $CH_3CH{=}CHCOOH$ $(H_2O)_2$ NO_2
6.	B31 CHAMINE	$CrC_6H_{14}NO_8$	CrO $COOH(CH_2)_4COOH$ $(H_2O)_2$ NO
7.	C11 CHAMINE	$Cr_2C_6H_{14}NO_{14}$	Cr_2O_3 CH_3COOH CO_2 $CH_2{=}CHCOOH$ $(H_2O)_3NO_2$
8.	C21 CHAMINE	$CrC_6H_{14}NO_9$	CrO CH_3COOH $CH_3CH{=}CHCOOH$ $(H_2O)_2$ NO_2
9.	C31 CHAMINE	$CrC_6H_{16}NO_9$	CrO CH_3COOH $CH_2CH_2{=}CHCOOH$ $(H_2O)_3$ NO

VI. DATA AVAILABILITY STATEMENT

The data presented herein were exclusively generated through experimental procedures.

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Authors Contributions:

[Author 1]: Conceptualisation, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing (original draft presentation), Funding Acquisition.

[Author 2]: Conceptualisation, Methodology, Visualisation, Supervision, Validation, Formal analysis, Investigation, Resources, Data curation, Writing (review and editing) Project Administration.

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Conflict of interest:

The authors declare no conflict of interest.

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