

Microwave assisted synthesis and IR spectral analysis of a few complexes of 4- Hydroxy-3-methoxybenzaldehyde with ditertiary butyl chromate

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Abstract - A few Cr (III) complexes of 4-Hydroxy-3-methoxybenzaldehyde (Vanillin) were synthesized by oxidizing it with ditertiary butylchromate (TBC) assisted by microwave heating technology. As compared to conventional heating techniques for chemical synthesis, microwave irradiation proves to be a better technique in terms of reaction efficiency, better yield, and enhanced specificity, less pollution and in achieving energy efficiency. The products were characterized by advanced chemical technological tools, namely, elemental analysis and FTIR spectroscopy. It has been found that the nature and characteristics of the products largely depends on the substrate/oxidant ratio and the solvent used during each set of reaction.

Key Words: Microwave, FTIR, spectroscopy, synthesis, technology, engineering, analysis, vanillin, TBC, research, oxidation

1. INTRODUCTION

4-Hydroxy-3-methoxybenzaldehyde, i.e., Vanillin (C₈H₈O₃) is the primary component of the extract of the vanilla bean [1]. Although there has been quite a lot of study on vanillin and its derivatives in the past decade, but the approach towards understanding the chemistry of its reaction with ditertiary butylchromate (TBC) as the oxidant has not been attempted in details. TBC [14, 15] is a versatile reagent used in the oxidation of many organic compounds and also in the synthesis of many metal complexes. But, there are only a few reports on the synthesis and physicochemical studies of chromium (III) complexes of Vanillin [7]. Microwave assisted synthesis [3] is a relatively new technique used by chemists all over the world [2]. The need for implementing Green technology [9, 10] in the field of Chemical science and research that involves a large use of chemicals for synthetic and analytical processes has shifted our perspective towards using this environment – friendly technique in our work. However there are limitations to the instrumentation process and there is a vast scope in improving the technology of microwave ovens [3,4] commonly used for scientific research so as to use it more efficiently. In view of the above context, we intend to report the microwave

assisted synthesis and Infrared (IR) spectroscopic studies of a few compounds obtained by the reaction of vanillin with TBC in different solvent, namely Tetrahydrofuran (THF), dichloromethane and 1,4 – dioxane and thereafter present a comparative overview of the characterization of the products using Fourier Transform Infrared (FTIR) Spectroscopy [6,8].

2. EXPERIMENTAL

2.1 Materials and methods

Chemicals used:

All the chemicals used in this research were of A.R. grade and obtained from commercial sources. The chemicals used were 4-hydroxy-3-methoxybenzaldehyde (Vanillin), Tetrahydrofuran (THF), Dichloromethane, 1, 4-Dioxane, Tert-Butyl alcohol, Acetone, Chromium (VI) oxide, Silver nitrate, Potassium persulphate, Ammonium iron(II) sulphate (Mohr's salt), Potassium dichromate, Barium diphenylamine-4-sulphonate..

Preparation of solutions:

Preparation of TBC

TBC, which has been used as the oxidant in the present work was prepared in situ by dissolving a weighed amount of Chromium (VI) oxide in 10 mL tert-butanol.

Preparation of reaction mixture

Substrate/ oxidant ratio 3:1 - 0.67 gm CrO₃ dissolved in 10 ml of tert butyl alcohol to prepare tert butyl chromate and 3.04 gm Vanillin dissolved in 10 ml THF

Substrate/ oxidant ratio 2:1 - 1.0 gm CrO₃ dissolved in 10 ml of tert butyl alcohol to prepare tert butyl chromate and 3.04 gm of Vanillin dissolved in 10 ml THF

Substrate/ oxidant ratio 1:1 - 2.0 gm CrO₃ dissolved in 10 ml of tert butyl alcohol to prepare tert butyl chromate and 3.04 gm of Vanillin dissolved in 10 ml THF

Other solutions were prepared by standard methods.

2.2 Procedure

Vanillin was found to be freely soluble in all the three selected solvents, namely, THF, dichloromethane and 1, 4-dioxane. Oxidation of this substrate with TBC was performed in three sets, each for the three solvents. In each of these reaction sets, a solution of the substrate was prepared in THF, dichloromethane and 1, 4-dioxane respectively. A solution of the oxidant, i.e., TBC was prepared separately in situ from Chromium trioxide and t-butanol, varying the substrate/oxidant molar ratio as 3:1, 2:1 and 1:1 for each set. The two solutions were then mixed together to prepare a homogeneous reaction mixture. This mixture was then stirred continuously for a considerable time and any change in consistency was noted. The mixture was then heated in an LG MG 3937C 20-Litre, 2450 MHz 700-Watt Solo Microwave Oven (MW irradiation 160 W, variable reaction time). Initial and final temperature of the reaction mixture was recorded to specify the exothermic/endothermic nature of the reaction under investigation. The reactions were found to be exothermic, in general. The nine products formed in each of these cases were washed with acetone, dried and weighed, bottled and labeled as V-131, V-121, V-111, V-231, V-221, V-211, V-331, V-321, V-311 and was used for further analysis and characterization.

2.3 Elemental analysis and preliminary physical characteristics:

All the nine compounds obtained after the oxidation of Vanillin with TBC in different solvents were found to differ in basic physical properties like colour, magnetic properties and melting points. However, each of these products was insoluble in cold water but soluble in hot water. Magnetic measurements show that the oxidation state of Cr in these compounds is +3. Percentage composition of C, H and O was determined using a Thermo Scientific Flash 2000 Organic Elemental Analyzer while the chromium content in these samples was estimated volumetrically using $K_2S_2O_8$ (excess), 0.1 N $K_2Cr_2O_7$ solution and 0.1 N Mohr's salt solution [5,11]. Empirical formula of these complexes was then deduced. The recorded details have been summarized in table.1

Sample Label	Solvent used	Substrate/oxidant ratio	Reaction time (in sec)	Yield (in gm)	Empirical Formula of products
V-131	THF	3.04g/0.67g; 3:1	60	3.1	$CrC_9H_{14}O_7$
V-121	THF	3.04g/1.0g; 2:1	30	3.7	$Cr_2C_{10}H_{11}O_{16}$

V-111	THF	3.04g/2.0g; 1:1	20	6.0	$Cr_2C_{13}H_{17}O_{12}$
V-231	CH_2Cl_2	3.04g/0.67g; 3:1	75	1.75	$CrC_{11}H_{14}O_9$
V-221	CH_2Cl_2	3.04g/1.0g; 2:1	40	3.0	$Cr_2C_9H_{15}O_{11}$
V-211	CH_2Cl_2	3.04g/2.0g; 1:1	20	4.85	$Cr_2C_9H_{19}O_{11}$
V-331	1,4-dioxane	3.04g/0.67; 3:1	40	3.0	$CrC_{12}H_{16}O_{10}$
V-321	1,4-dioxane	3.04g/1.0g; 2:1	30	5.3	$Cr_2C_{11}H_{14}O_9$
V-311	1,4-dioxane	3.04g/2.0g; 1:1	20	9.0	$Cr_2C_{12}H_{14}O_{13}$

3. INTERPRETATION OF IR SPECTRA OF THE COMPLEXES

Fourier Transform Infrared (FTIR) spectroscopy is an important analytical technique used in the field of Chemical Science and technology and for advanced research. Analysis of the FT IR spectrum of the complexes obtained from vanillin in the present work has revealed some interesting characteristics about their composition and bonding. The results were recorded in the form of an FT IR spectrum for each sample. A typical IR spectrum obtained for the sample labeled V-111 has been shown in fig. 1.

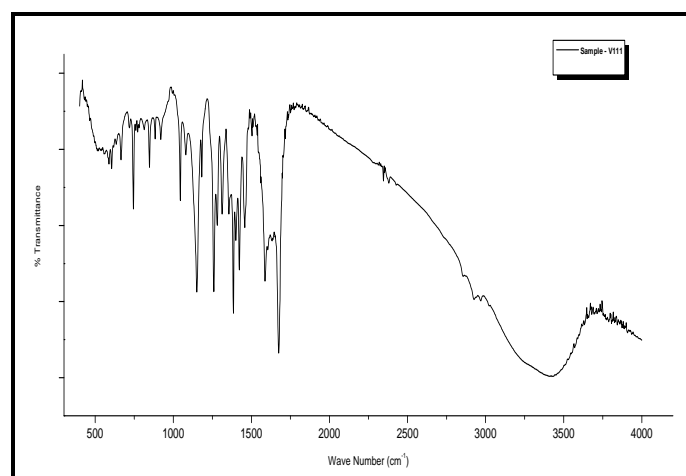


Fig. 1.A sample IR spectrum (Sample V-111)

Presence of Cr-O and Cr=O bonds in these complexes is indicated by the (Cr-O) stretching frequencies ranging from 536-665 cm^{-1} and ν (Cr=O) peaks near 846, 847 cm^{-1} . The broad and strong absorption bands appearing from 3200 - 3500 cm^{-1} show the presence of H-Bonded (O-H) group, intensity and peak broadening varying greatly with variation in substrate/ oxidant ratio. This indicates the difference in extent of coordination of the (O-H) oxygen atom with the Cr atom. The lowest (O-H) stretching frequency being centered at 3310 cm^{-1} in the compound labeled V-231 while the maximum value recorded is for V-331 at 3422 cm^{-1} . A strong (C=O) carbonyl absorption is visible near 1675 cm^{-1} . However, the absence of characteristic C-H stretching frequency for an aldehyde group suggests that the vanillin aldehyde group has been oxidized to a carboxylic group. This is further confirmed by the appearance of relevant peaks near 910 cm^{-1} for (C-O) bending vibrations and one near 2969~2970 cm^{-1} for (C-O) stretching vibrations of a carboxylic group. The characteristic peaks for aromatic (C-H) stretching, aromatic (C-C) and (C=C) in-ring stretching vibrations near 3021~3022 cm^{-1} , 1422~1423 cm^{-1} and 1586~1588 cm^{-1} respectively indicates that the aromatic ring in Vanillin is intact and has not undergone any decomposition/ cleavage during the course of oxidation. The presence of (C-O) stretching vibrations for the methoxy group near 1259 cm^{-1} in the IR spectrum of these complexes is indicative of the oxygen atom of the ether group of Vanillin being uncoordinated. This is also supported by the weak alkyl (C-H) stretching vibrations appearing near 2924~2945 cm^{-1} for each of these compounds. Other weak absorption bands for bending and rocking vibrations of (C-H) group were recorded near 744 cm^{-1} and 1355~1357 cm^{-1} respectively. A comparative spectral analysis for the nine oxidation products of vanillin (Chart -1 and chart -2) shows considerable shift in the relative intensities and peak positions of these vibrational frequencies which may be attributed to a difference in the percentage composition of Cr metal and variable extent of its coordination with the ligand. The strong peaks at 1385 cm^{-1} and 1633 cm^{-1} might be due to the impurities present in the KBr. A very weak peak near 2400 cm^{-1} is characteristic of CO_2 absorption.

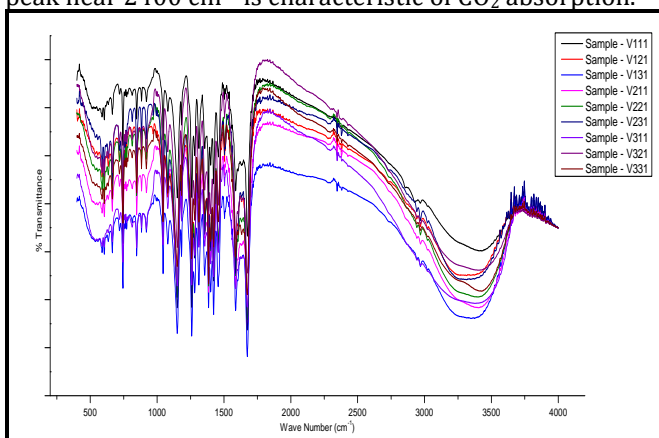


Chart -1: Comparison of relative intensities of the characteristic peaks in the IR spectrum of oxidation products of Vanillin (Plotted using OriginPro 8.5 software)

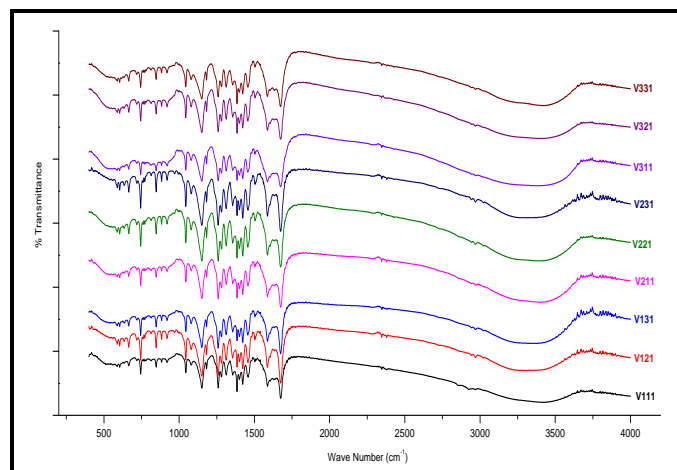


Chart -2: Comparison of relative positions of the characteristic peaks in the IR spectrum of oxidation products of Vanillin (Plotted using OriginPro 8.5 software)

4. CONCLUSIONS

Substrate/ oxidant ratio has greatly affected the course of reaction, nature and characteristics of the compounds formed during the oxidation of 4-Hydroxy-3-methoxybenzaldehyde with TBC. It was also observed that the efficiency of these oxidation reactions depends upon the choice of solvent. The most efficiently synthesized product was the sample labeled V-311 in 1, 4-dioxane. Most microwave assisted organic synthesis has been performed in domestic household microwave ovens using solvent-free technique, that is, carrying out the reactions on solid supports like- clays, alumina, silica, etc. Since this technology deals with high temperature and high pressure conditions, safety will always be a main concern. Besides, domestic household microwave ovens, which are readily available and inexpensive, reflux systems, pressurized systems and continuous flow systems have also been used. On the basis of applied research in close collaboration with the standard national laboratories, the reaction summary, FT IR data and analysis presented in this research paper can contribute significantly to optimize the operating conditions of the various instruments used for synthesis and analysis, thereby increasing the efficiency of the microwave assisted oxidation of organic compounds and the quality of oxidation products obtained from them. The use of a graphical tool (OriginPro 8.5) for data interpretation was found to be very helpful and this increases its scope in advanced and extensive research works. Furthermore, the obtained data may be implemented in the organic compounds databases and can be used for the simulation of oxidation processes.

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