

# Synthesis, Spectral Analysis and Synthetic Applications of a Few Hexavalent Chromium Complexes of Propanedioic Acid

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## Abstract

*Propanedioic or Malonic acid was treated with a versatile, non-aqueous oxidant Di-tertiary Butyl Chromate, by taking different molar ratios of substrate and oxidant. Various solid products formed were isolated, washed, purified and collected as samples. The formulae and structure of these oxidized products have been established with the help of elemental analysis, FTIR spectra and Thermogravimetric analysis (DTA-TGA). The products obtained by the oxidation of malonic acid with DTBC are complexes of chromium(VI) which are further used to catalyze various organic reactions.*

*The present study investigates the action of Di-tertiary Butyl Chromate, a chromium (VI) based oxidant, on malonic acid with the aim to investigate if chromium in reduced state enters into complexation with the oxidized fragments or with the unreacted substrate itself. It also attempts to find out if degradation occurs along with oxidation and whether the oxidation is selective in arresting the reaction at different stages (by taking different S:O molar ratios) to yield same product or not.*

**Keywords:** Chromium (VI) complexes, Malonic acid, Oxidation, Organic synthesis.

## Introduction

Oxidation has received considerable attention due to the wide range of biological processes in which metal ions participate. Selective oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry. The oxidation of organic molecules by chromium(VI) reagents is a well-known technique to organic chemists. Strong oxidants of chromium(VI) like  $\text{CrO}_3$ , chromates, dichromates etc. have long been used for the oxidation of several classes of organic compounds like alcohols, aldehydes, ketones, carboxylic acids etc. by different group of coworkers.<sup>1-5</sup>

The oxidizing characteristics of hexavalent chromium can be altered significantly by the types of ligands which surround the central metal atom. By changing the ligands, the activity of the oxidizing agent can be regulated and at the same time some degree of stereoselectivity may be imparted. The main concern of the current research work is the preparation of

hexavalent chromium species which are capable of producing high yields of a desired product in an oxidation reaction and are easily separable in the reacted and unreacted forms from the desired product. Such reagents are necessary and particularly beneficial to the pharmaceutical and chemical industry.

Hexavalent chromium complexes act as remarkably efficient catalysts in redox reactions and exhibit a broad scope of selectivity with a wide range of applications in synthetic organic chemistry. A number of new chromium (VI) containing compounds have been used to study the kinetics and mechanism of oxidation of various compounds.

Khare and Ansari<sup>6</sup> reported the kinetics of oxidation of a mixture of malonic acid and tartaric acid by chromic acid in presence of Hydrochloric acid and salts at 28°C. They proposed that the probable products of oxidation are  $\text{CO}_2$  and carbonyl dicarboxylic acid. The reaction follows first order kinetics with respect to each substrate, oxidant and hydrogen ion concentration. They concluded that oxidation of malonic acid should therefore take place on the methylene group of Malonic acid and it should involve two electron steps. Hence proton of Malonic acid will be eliminated when Chromic acid attacked on  $>\text{CH}_2$  and hence Carbonyl dicarboxylic acid i.e. Meso Oxalic acid is obtained which is not oxidized by Chromic acid.

The oxidation of Malonic acid by various metal ion oxidants has been reported with different results. Extensive studies on the oxidation of malonic acid by several oxidants have been reported.<sup>7,8</sup> Malik and co-workers<sup>9</sup> investigated the Chromic acid oxidation of malonic acid using a greener approach in aqueous media at 303K to yield glyoxylic acid as product. A hundred-fold rate enhancement of chromium (VI) oxidation of malonic acid has been done by combining Sodium Dodecyl sulphate and 2,2'-Bipyridine and the product was characterized by  $^{13}\text{C}$ -NMR and FTIR spectroscopy. Three representative N-heteroaromatic nitrogen base promoters (2-picolinic acid, 2,2'-bipyridine (bpy) and 1,10-phenanthroline) in combination with the anionic surfactant sodium dodecyl sulphate (SDS) enhanced the rate of the oxidation reaction compared to the unpromoted reaction.

The observed net enhancement of rate effects has been explained by considering the hydrophobic and electrostatic interaction between the surfactants and reactants.

Di tertiary Butyl Chromate has proven to be a potent and versatile oxidizing reagent. We particularly studied in this

research, the oxidation of malonic acid by DTBC as oxidant by taking different ratio of substrate and oxidant, in Tetrahydrofuran as a solvent. The various products formed were obtained, washed, purified and collected as samples. These Cr(VI) complexes formed are characterized by infrared spectroscopy, thermogravimetry, elemental analysis and physical properties.

### Material and Methods

All chemicals and reagents were purchased from Sigma-Aldrich (Munnich, Germany) and were used without further purification. Reactions were performed in oven-dried round bottom flasks. The flasks were fitted with rubber septa and the reactions were conducted under nitrogen atmosphere. Glass syringes were used to transfer the solvents and liquid reagents. Malonic acid (E Merck, Germany) was used as received. All the experimental reactions were monitored by analytical TLC performed on silica gel glass plate containing 60 GF-254 and visualization on TLC after elution achieved by UV light or iodine indicator or by exposure to methanolic acidic solution of *p*-anisaldehyde (anis) followed by heating (<1 min) on a hot plate (~250 °C). Column chromatography was performed with Merck 60-120 mesh silica gel.

Chromium was estimated iodometrically. In case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic peroxy disulphate ( $K_2S_2O_8$ ) solution.

Experiments i.e. oxidation of Malonic acid were carried in a microwave oven using 160 Watts and operating at 2.45 GHz. IR spectra were recorded by on 300Mz (Bruker) and 500 Mz (Varian) spectrometers in appropriate solvents using TMS as internal standard or the solvents as secondary standards and the chemical shifts are shown in  $\delta$  scales. Coupling constants "J" are expressed in Hertz. High resolution mass spectra were obtained by using ESI-QTOF mass spectrometry/BRUKER ESQUIRE HCT spectrometer. IR spectra were recorded on a FTIR-7600 Lambda Scientific Pvt. Ltd. using KBr disk for the range 4000-400  $cm^{-1}$ . Thermogravimetric (TGA) analysis has been carried on Universal V 4.5 A Thermal analysis system.

**General procedure for preparation of DTBC:** 2 g of Chromium trioxide was dissolved in 10 ml Tertiary butyl alcohol in a clean and dry beaker. The reaction mixture was stirred well for 15 minutes at room temperature to form the oxidant i.e. DTBC.

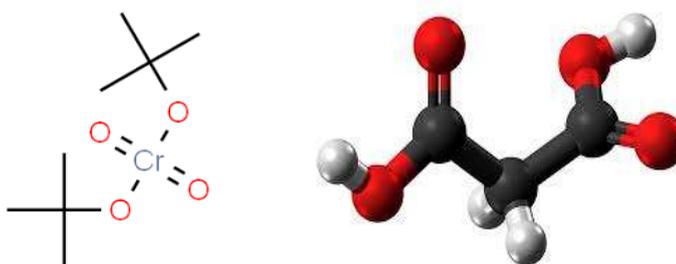


Figure 1: Structures of Ditertiary Butyl Chromate and Malonic acid



Figure 2: Microwave assisted Organic Synthesis

**General procedure for oxidation of Malonic acid by DTBC:** 2.08 g of malonic acid was weighed accurately and dissolved in 10 ml of Tetrahydrofuran in a clean flask. The oxidant i.e. DTBC was then added slowly dropwise to the above mixture over a period of 15 min and stirring was continued for 50 min. The mixture was then heated for 16 min. at 60°C when the desired product is formed. It was washed several times with acetone, dried over Na<sub>2</sub>SO<sub>4</sub> and purified by silica gel chromatography (5% ethyl acetate in hexane). The pure product was collected in an air- tight bottle as sample S<sub>1</sub>.

**General procedure for oxidation of Benzothiazoyl carbaimide by S<sub>1</sub>:** To a solution of 0.056 g Benzothiazoyl carbaimide (0.33 mmol) in dry N,N-Dimethyl formamide (5 ml) was added 0.013 g of catalyst S<sub>1</sub>. The reaction mixture was stirred for 4 hours at room temperature and then the temperature was raised to 70°C. Stirring was continued at this temperature for next 6 hours. The reaction mixture was quenched with water and extracted with ethyl acetate (3x25ml) and brine (25 ml). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The reaction was monitored by TLC. Product was purified by silica gel chromatography and collected as sample S<sub>2</sub>.

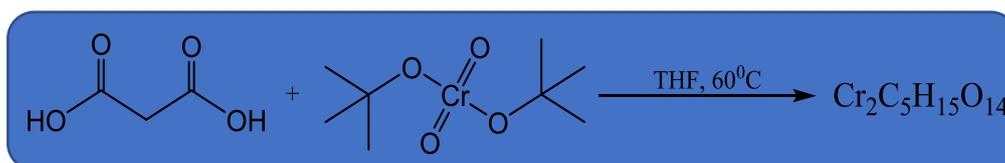
0.5 g N,N'-diphenyl thiourea (2.20 mmol) was dissolved in dry N,N-Dimethyl formamide (10 ml) and catalytic amount (0.1 g) of sample S<sub>1</sub> was added. This reaction mixture was stirred at 60-70°C for 6 to 8 hours. The mixture was poured into water and then extracted with ethyl acetate. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. It is collected as sample S<sub>3</sub>.

**General procedure for oxidation of N-phenyl thiourea by S<sub>1</sub>:** 0.5 g N-phenyl Thiourea was dissolved in 10 ml dry N,N-Dimethyl formamide (10 ml) and catalytic amount (0.1 g) of sample S<sub>1</sub> was added. The mixture was stirred at 60-70°C for 3 to 4 hours. The mixture was poured into water and then extracted with ethyl acetate. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. It is collected as sample S<sub>4</sub>.

## Results and Discussion

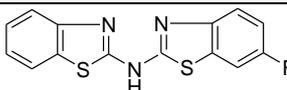
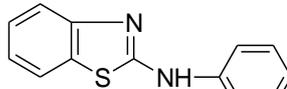
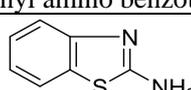
In our research on oxidation processes, we chose Di-tertiary Butyl Chromate (DTBC) as an oxidant because it has been proven to be useful oxidant in some reactions including the oxidation of Crotonic acid<sup>10</sup>, Crotonaldehyde<sup>11</sup>, Succinic acid<sup>12</sup>, N,N-Dimethylaniline<sup>13</sup>, Dimethylglyoxime<sup>14</sup> etc. DTBC as an oxidant was very well-suited reagent for microwave synthesis because as an ionic and magnetically retrievable material, it carries a benefit of efficient conversion of electromagnetic energy into heat according to the dielectric heating mechanism. The structure and properties of the obtained Chromium(VI) complex (Scheme 1) were characterized by FTIR and mass spectral analysis as well as elemental analysis.

The versatility of the procedure was further demonstrated by the oxidation of some natural products such as steroids<sup>15</sup>, terpenes<sup>16,17</sup>, fatty acids<sup>18-21</sup>, cellulose<sup>22,23</sup>, biosynthetic mechanism of cholesterol<sup>22</sup> respectively. Table 1 summarizes the reactants, products, expected structure and molecular weights of products, solvents used etc.



Scheme 1: Oxidation of malonic acid with chromium oxidant DTBC.

Table 1  
Summary of reactants and products

Sample code	Substrates	Solvent	expected mol. Wt. of the product	expected structure of the product
S <sub>1</sub>	Malonic acid + DTBC	THF	403	Cr <sub>2</sub> C <sub>5</sub> H <sub>15</sub> O <sub>14</sub>
S <sub>2</sub>	Benzothiazoyl carbaimide + S <sub>1</sub>	DMF	301 ( <i>m/z</i> 304 [M+H] <sup>+</sup> )	 N-Bis-benzothiazole
S <sub>3</sub>	N,N'-diphenyl thiourea + S <sub>1</sub>	DMF	226 ( <i>m/z</i> 229 [M+H] <sup>+</sup> )	 N-phenyl amino benzothiazole
S <sub>4</sub>	N- phenyl thiourea + S <sub>1</sub>	DMF	150	 Amino benzothiazole

The quantitative analysis of carbon and hydrogen was carried out by using instrumental method at SAIF, CDRI, Lucknow. In the present work, the chromium content was estimated volumetrically while the oxygen content was found out by subtraction of sum total of percent composition of C, H and Cr from 100. The structure of products formed was ascertained from the spectral data. The Infrared spectral data has been interpreted on the basis of reported literature data.

#### Characterization of sample S<sub>1</sub> (Cr<sub>2</sub>C<sub>5</sub>H<sub>15</sub>O<sub>14</sub>)

Colour: Dark greenish

Elemental composition:

Elements	Observed percentage	Calculated percentage
Carbon	15.73	14.93
Hydrogen	3.76	3.48
Oxygen	54.51	55.72
Chromium	26.00	25.87

Proposed empirical formula: Cr<sub>2</sub>C<sub>5</sub>H<sub>15</sub>O<sub>14</sub>

Proposed formulation of the complex: Cr<sub>2</sub>O<sub>3</sub>. HOOC-CH<sub>2</sub>-COOH. HOOC-CHO. 4H<sub>2</sub>O

FTIR Results:

Peaks	Nature of peaks	Group assignment
3753.6	Weak	O-H stretching (free)

3423.5 (2800-3500)	Very broad	O-H stretching (H-bonded); C-H stretching (aldehydes)
2370.6	Weak	C-H stretching
1578.0	Sharp	-COOH group
1429.4	Sharp	C-O-H bending
1281.3	Medium	O-C (carboxylic acids)
1177.7	Weak	C-O stretching
1061.2	Weak	C-C-C bending
953.8	Medium	C-O stretching
814.0	Medium	O-H stretching (due to water)
745.4	Medium	O-H stretching (due to water)
609.7	Weak	M-O stretching
549.8	Weak	M-O stretching
478.8	Weak	M-O stretching

The FTIR spectrum of product S<sub>1</sub> shows a very broad band at 2800-3500 cm<sup>-1</sup> due to O-H stretching<sup>25</sup> indicating the presence of -COOH group as well as due to C-H stretching showing the presence of aldehydes<sup>26,27</sup>. The presence of -COOH group<sup>28</sup> is also indicated by characteristic peaks at 1578.0 and 1429.4 cm<sup>-1</sup>. The presence of coordinated water<sup>29-32</sup> in the complex is indicated by the two medium peaks at 814.0 and 745.4 cm<sup>-1</sup>. The complex exhibits weak bands at 609.7, 549.8 and 478.8 cm<sup>-1</sup> which indicates the presence of metal-oxygen bond<sup>30</sup>.

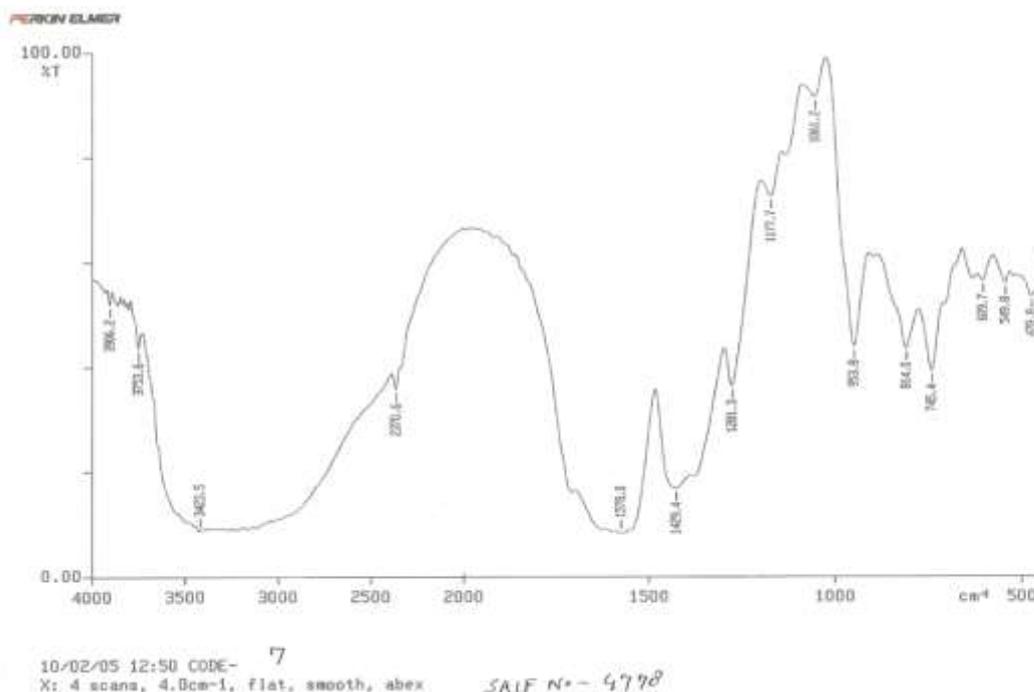
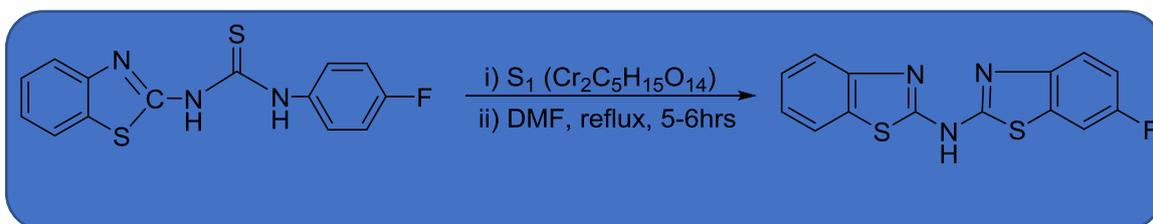


Figure 3: FTIR spectrum of complex S<sub>1</sub>

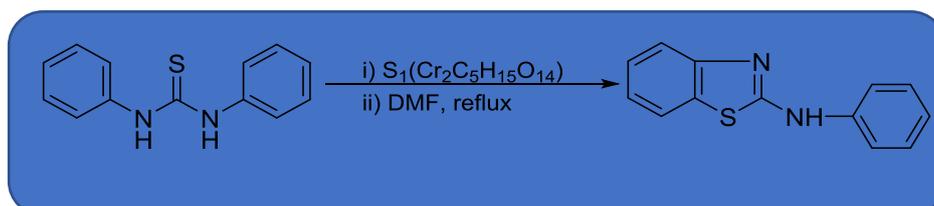
Subsequently, reaction of compound S<sub>1</sub> with Benzothiazoyl carbimide using DMF as a solvent, first by stirring at ambient temperature and then refluxing at about 70°C for 5-6 hours (Scheme 2) have afforded N-Bis-benzothiazole in 86% yield. The structure of product S<sub>2</sub> was determined on the basis of <sup>1</sup>H NMR spectrum. It shows only two doublets and two triplets with same coupling constant (*J* = 7.5 Hz) consistent with the structure of S<sub>2</sub>. It is interesting to mention that the oxidative cyclization of benzothiazoyl

carbimide is chemoselective, resulting into the formation of N-Bis-benzothiazole.

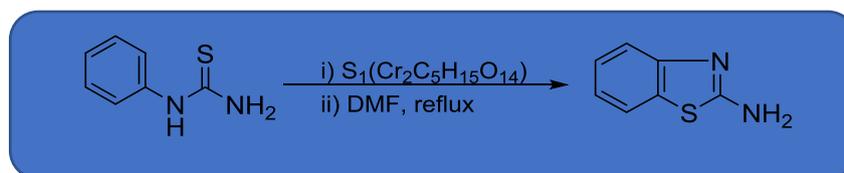
N-phenyl amino benzothiazole was synthesized from N,N'-diphenyl thiourea by reacting with a catalytic amount of compound S<sub>1</sub> at 60-70°C using DMF as a solvent (Scheme 3). 2-amino benzothiazole was obtained by the reaction of Compound S<sub>1</sub> with N-phenyl thiourea using DMF as a solvent which involves oxidative cyclization and intramolecular cyclization (Scheme 4).



Scheme 2: Oxidation of Benzothiazoyl carbimide with chromium complex S<sub>1</sub>.



Scheme 3: Oxidation of N, N-diphenyl thiourea with chromium complex S<sub>1</sub>.



Scheme 4: Oxidation of N-phenyl thiourea with chromium complex S<sub>1</sub>.

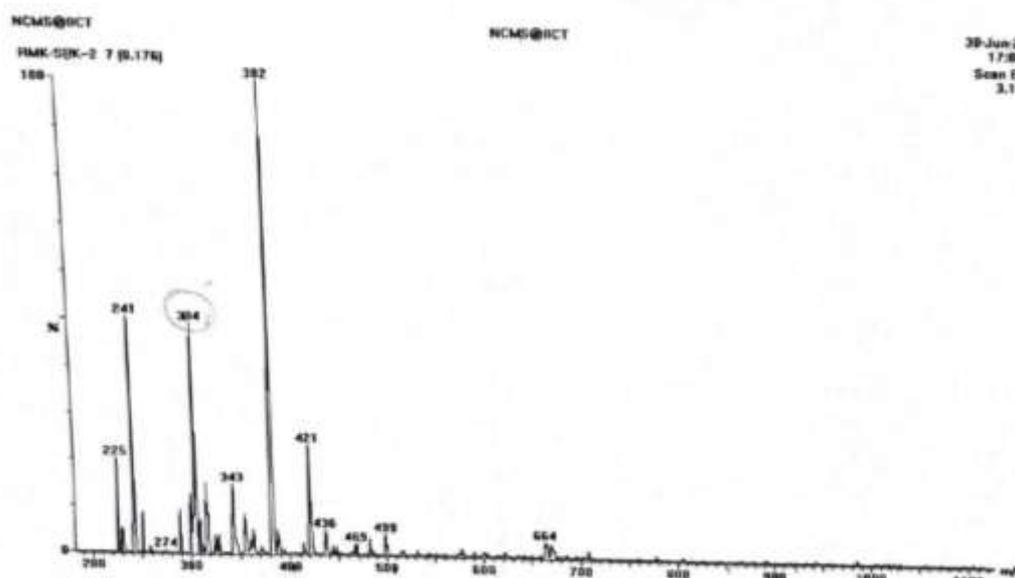


Figure 4: Mass spectrum of sample S<sub>2</sub>

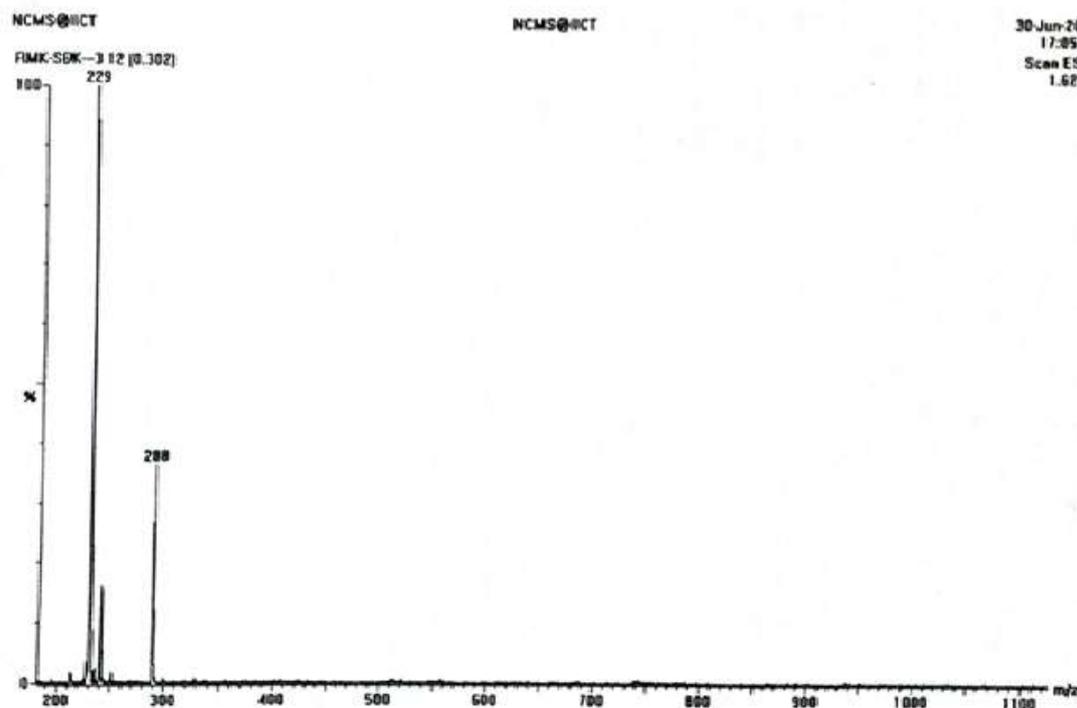


Figure 5: Mass spectrum of S<sub>3</sub>

## Conclusion

In conclusion, we have described a simple procedure in which DTBC was used for the oxidation of Malonic acid under microwave irradiation using Tetrahydrofuran as solvent. The chromium complex so formed was used for further oxidation of organic compounds. This work examines a Chromium(VI) oxidation of various organic substrates under different synthetic conditions. This method offers some advantages in terms of simplicity of performance, simple operation condition, no side-product formation, very less reaction time and a wide range of substrates can be converted to their corresponding oxidation products. The oxidation and degradative oxidation products of malonic acid include Acetic acid, Formic acid, Oxalic acid, Glyoxalic acid etc.

In this study, we have synthesized and characterized some new Chromium(VI) complexes with Malonic acid core in good yields, followed by using them for further oxidation of Benzothiozoyl carbaimide, N,N'-diphenyl thiourea and N-phenyl thiourea to form N-Bis-benzothiazole, N-phenyl amino benzothiazole and Amino benzothiazole respectively. The structure of all the products was confirmed through spectral analysis.

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