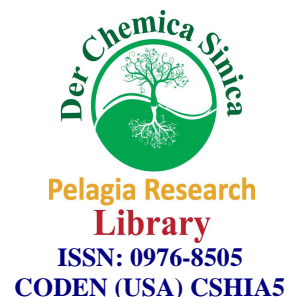




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### Study of oxidation of crotonic acid with chromium complexes by classical and green approach

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#### ABSTRACT

*The application of microwave irradiation to organic reactions has shown to enhance significantly the rate of many organic processes. Microwave assisted organic synthesis (MAOS) is a simple, efficient, rapid & green method for the synthesis of organic compounds/complexes. In the present paper, we have discussed the oxidation of crotonic acid by both conventional as well as MAOS methods. In the comparative study, the MAOS method was found more efficient over conventional method.*

**Keywords:** Crotonic acid, microwaves, chromium complexes, dioxane, tetrahydrofuran, oxidation.

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#### INTRODUCTION

Microwave irradiated organic reaction proceeds much faster and with higher yields as compared to conventional heating. Many reactions usually require several hours under conventional heating conditions but with the use of a microwave oven, can be done within some minutes or even seconds, at comparable temperatures. In many cases, microwave assisted organic techniques have proved to be more efficient than classical heating methods [1-4]. Tertiary butyl chromate (TBC) has proven to be a potent and versatile oxidizing agent. The use of TBC as an oxidant in organic synthesis is substantiated by a vast work carried out after its first use by R. V. Oppenauer and H. Oberrauch [5-9]. Crotonic acid and its derivatives are used in a wide variety of applications such as cosmetic polymers intermediates, pesticides & pharmaceuticals. The expected degradative oxidation products of crotonic acid are acetaldehyde, acetic acid, formic acid, glyoxalic acid, oxalic acid, glyoxal etc. Several different methods for the oxidation of crotonic acid are reported in the literature. Melikoff [10] oxidized it with hypochlorous acid and prepared a dihydroxy butyric acid. Fittig & Kochs [11] used barium permanganate, Glattfeld & Woodruff [12] potassium chlorate; in both cases, the identical dihydroxy butyric acid was obtained. Oxidation of crotonic and isocrotonic acids with hypochlorous and perbenzoic acids was reported by Geza Braun [13,14]. Kinetics of mechanism of the osmium(VIII) catalysed oxidation of crotonic acid by  $\text{KBrO}_3$  and N-chloro-p-toluenesulphonamide have been investigated by B. Singh & coworkers [15,16]. G. D. Mishra [17] oxidised crotonic acid by conventional heating method in different molar ratios with tertiary butyl chromate and have reported that the increase in the ratio of the oxidant leads to change in the nature of oxidation products. In the lower molar ratios of the oxidant, the oxidation product mainly contains aldehydes but in the higher molar ratio, the products mainly contain carboxylic acids. Very recently, R. Shukla, S. Rani & I. C. Tewari [18] reported the kinetics and mechanism of the reaction between crotonic acid and ceric perchlorates.

In the present work, we have oxidized crotonic acid with tertiary butyl chromate & tertiary amyl chromate using different substrate: oxidant ratio for a better comparative study. Also, different solvents i.e. dioxane & tetrahydrofuran, were used for dissolving the substrate. The oxidation of crotonic acid was done by conventional heating – stirring method as well as by microwave dielectric heating[19,20].

### MATERIALS AND METHODS

The chemicals used were all A. R. grade. The oxidant TBC was prepared by dissolving calculated quantity of pure and dry  $\text{CrO}_3$  in Tertiary butyl alcohol. The solution was stirred to ensure the completion of reaction. The clear brown coloured solution of TBC obtained by filtration and decantation was used as oxidant. The same procedure was applied with calculated quantities of  $\text{CrO}_3$  in tertiary amyl alcohol for the preparation of TAC. Six samples of crotonic acid in two solvents i.e. dioxane and THF were prepared as per details given in table-1. The samples namely CA-1, CA-2 & CA-3 were prepared by mixing, stirring and heating the solutions in substrate : oxidant molar ratio 1:1, 1:2 and 2:1 respectively, all in solvent dioxane. Samples CA-4, CA-5 & CA-6 were prepared by microwave irradiation in an LG household microwave oven MG-3937C (Microwave frequency 2450 MHz) in S:O molar ratio 2:1, 1:1 & 1:2 respectively. THF was used as a solvent for CA-4 and CA-6 whereas dioxane was used for the preparation of CA-5. The products formed were washed thoroughly with acetone until colourless washing and dried before collecting.

The samples were analyzed by different experimental methods. Chromium content in the samples was estimated volumetrically whereas carbon and hydrogen were estimated instrumentally by Elemental Analyser-Heraeus Vario EL III Carlo Erba1108. The IR spectra of the samples were recorded on a Fourier Transform Infra Red spectrophotometer Shimadzu 8201PC ( $4000\text{--}400\text{ cm}^{-1}$ ). The TG/DT analysis of the products was carried on thermal analysis system- Perkin Elmer. The samples were heated at a rate of  $10^0\text{ C/min}$ . in the temperature range of  $25^0\text{ C}$  to  $700^0\text{ C}$ .

Table – 1(Reactants)

Product code	Solvent for substrate	Oxidant	Molar ratio (S:O)	Reaction condition
CA-1	Dioxane	TBC	1:1	Stirring & heating at $75^0\text{C}$ for 18 min. and left overnight.
CA-2	Dioxane	TBC	1:2	Stirring & heating at $75^0\text{C}$ for 16 min. and left overnight.
CA-3	Dioxane	TBC	2:1	Stirring for 40 min. & heating at $75^0\text{C}$ for 10 min
CA-4	THF	TBC	2:1	Microwave heating (160W) for 14 min.
CA-5	Dioxane	TAC	1:1	Microwave heating (160W) for 9.5 min.
CA-6	THF	TAC	1:2	Microwave heating (160W) for 7 min.

Table – 2 (Products)

Product code	Colour	Solubility in water	Empirical formula	Formulation
CA-1	Dark brown	Insoluble	$\text{Cr}_2\text{C}_6\text{H}_{12}\text{O}_7$	$2\text{CrO} \cdot \text{CH}_3\text{COOH} \cdot \text{CH}_3\text{CH}=\text{CHCOOH} \cdot \text{H}_2\text{O}$
CA-2	Dark brown	Insoluble	$\text{Cr}_2\text{C}_6\text{H}_{14}\text{O}_{10}$	$\text{Cr}_2\text{O}_3 \cdot \text{CH}_3\text{COOH} \cdot \text{CH}_3\text{CHO} \cdot \text{HOC} - \text{COOH} \cdot \text{H}_2\text{O}$
CA-3	Dark grey	Insoluble	$\text{Cr}_2\text{C}_8\text{H}_{14}\text{O}_6$	$2\text{CrO} \cdot 2\text{CH}_3\text{CHO} \cdot \text{CH}_3\text{CH}=\text{CHCOOH}$
CA-4	Dull green	Insoluble	$\text{Cr}_2\text{C}_{10}\text{H}_{17}\text{O}_7$	$2\text{CrO} \cdot \text{CH}_3\text{CHO} \cdot 2\text{CH}_3\text{CH}=\text{CHCOOH}$
CA-5	greenish brown	Insoluble	$\text{Cr}_2\text{C}_6\text{H}_{13}\text{O}_7$	$\text{Cr}_2\text{O}_3 \cdot \text{CH}_3\text{CHO} \cdot \text{CH}_3\text{CH} = \text{CHCOOH} \cdot \text{H}_2\text{O}$
CA-6	Dark brown	Insoluble	$\text{Cr}_2\text{C}_4\text{H}_{11}\text{O}_7$	$\text{Cr}_2\text{O}_3 \cdot \text{CH}_3\text{COOH} \cdot \text{CH}_3\text{CHO} \cdot \text{H}_2\text{O}$

### RESULTS AND DISCUSSION

- Table-2 shows that the common oxidation products i.e. acetaldehyde & acetic acid are formed during the process along with water.
- The extent of oxidation is less when the proportion of oxidant is less, as substantiated by the observation that crotonic acid as such is present in CA-3 & CA-4 when substrate:oxidation ratio is 2:1 along with acetaldehyde and water.
- The extent of oxidation increases as the ratio of oxidant increases. In case of higher proportion of oxidant (S:O ratio 1:2), the highly oxidized fragments like acetic acid, glyoxalic acid are formed (as in CA-2 & CA-6) along with acetaldehyde and water, which are the common constituents in almost all the cases.
- The colourful products thus obtained by oxidation of crotonic acid by TBC & TAC may be the complexes of chromium in different oxidation states.

- In most of the cases, the colour of the products was found to be brown, which may be due to charge transfer rather than electronic transition.
- Products CA-1, CA-2, CA-5 & CA-6 have the water molecules associated in the formulations. The water molecules are not associated in the products CA-3 & CA-4, when the ratio of oxidant is less. So, the number of water in the formulations decreases as the ratio of oxidant decreases.
- The oxidation of crotonic acid can be carried out in much less time by the application of microwave irradiation as compared to classical method of heating.
- The oxidation state of chromium is II in CA-1, CA-3 & CA-4 while it is III in CA-2, CA-5 & CA-6.
- In case of CA-2 & CA-6, when the ratio of oxidant is maximum, the most stable oxidation state III is observed in the form of Cr<sub>2</sub>O<sub>3</sub>. In other cases, the oxidation states of chromium are less than III.
- It is observed that all the products formed are insoluble in water.
- As per the proposed formulations, the reaction does not result in any coupling of the rings.
- Recrystallization of the products in suitable solvent and the study of the crystals formed may be the further course of investigation.
- The proper selection of solvent for the products and subsequent studies of magnetic, photometric, cryoscopic & other properties may lead to valuable information.

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