

Mechanism of oxidation of caproic acid by T.B.C.

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Abstract - Caproic acid ($CH_3(CH_2)_4COOH$) i.e Hexanoic acid was treated with a versatile non-aqueous oxidant, ditertiary butyl chromate (T.B.C.) by taking different molar ratio of substrate and oxidant. The various solid products were obtained which were isolated, washed, purified and collected as samples. The formulae and structures of oxidised products have been established on the basis of elemental analysis, N.M.R. spectra, I.R. spectra and mass spectra studies.

The products obtained by oxidation of caproic acid by TBC are complexes of chromium with small chain carboxylic acid, small chain aldehydes or dicarboxylic acid. Mechanism of formation of these complexes are explained in this research paper.

(Keywords: TBC = Ditertiary butyl chromate, IR = Infra red, NMR = Nuclear magnetic resonance, TLC = Thin layer chromatography.)

1.INTRODUCTION

Strong oxidants of chromium(vi) like CrO_3 , chromates, dichromates etc. have been used to oxidise several organic as well as inorganic compounds for the very long period. Such chromium(vi) containing oxidants have been used in both media- aqueous medium and non aqueous medium. T.B.C. is the most effective non aqueous oxidant which has been used to oxidize several classes of organic compounds by different groups of coworkers⁸⁻¹⁸ to oxidise different class of compounds like alcohols, aldehydes, ketones, carboxylic acids etc.

We particularly studied the oxidation of caproic acid using T.B.C. as oxidant. They treated caproic acid with a versatile non aqueous oxidant, ditertiary butyl chromate (T.B.C.) by taking different ratio of substrate and oxidant. The various products were obtained, washed, purified and collected as samples. They reported many complexes and suggested formulation of the following two complexes which are named as samples CB2 and CB4

1.1 Experiment:

a)CB2 : (Molar ratio, substrate : oxidant = 1 : 0.75)

1.16 g (one centimole) of caproic acid was mixed in 0.75 g T.B.C.(0.75 centimole) which was prepared by mixing 0.75g CrO_3 in 1.3 ml tertiary butyl alcohol and heated for about 5 minutes. An exothermic vigorous reaction occurred by releasing very hard and irritating white/brownish fumes for about 1 minute after that Solid green coloured product was obtained. This was allowed to cool for 1 hour. The product

was washed with water, hot water, acetone and benzene and each time the substance was filtered properly to get pure product. The product was partially soluble in acetone and insoluble in benzene. The product was then dried and tested for its purity in T.L.C.. The pure product was collected in tiny glass container as the sample CB2 for analysis.

b) CB4 (Molar ratio, substrate : oxidant = 1 : 1.25)

1.16 g (one centimole) of caproic acid was mixed in 1.0 g T.B.C. which was prepared by mixing 1.25 g CrO_3 in 1.75 ml tertiary butyl alcohol and heated for about 5 minutes. An exothermic vigorous reaction occurred by releasing very hard and irritating white/brownish fumes for about 1 minute after that Solid green coloured product was obtained. This was allowed to cool for 1 hour. The product was washed with water, hot water, acetone and benzene and each time the substance was filtered properly to get pure product. The product was soluble in acetone and insoluble in benzene. The product was then dried and tested for its purity in T.L.C. The pure product was collected in tiny glass container as the sample CB4 for analysis.

1.2 Results and discussion

(i) CB2 :

It is green solid having percentage composition: C = 34.736%, H = 6.46%, O = 18.686%, Cr = 40.118%

Empirical formula : $C_{12}H_{26}O_5Cr_3$

FTIR peaks(cm^{-1}) assign following groups:¹⁻²

FTIR Peaks (Wave no. cm^{-1})	Group Assignments
771.78	Cr-O (str.)
1069.05	Cr- O (str.)
1155.4	C-O (str.)
1402.94	OH bending or CH_2 bending
1631.5	C=O str. -CHO or -COOH
2920.11	C-H (str.) due to -CHO or -COOH
3397.38	OH (str.)

Groups assigned on the basis of I R Spectra are:- $-CH_3$, $-CH_2$, -CHO, -Cr-O,-OH

H NMR spectra assign following groups and position of protons:

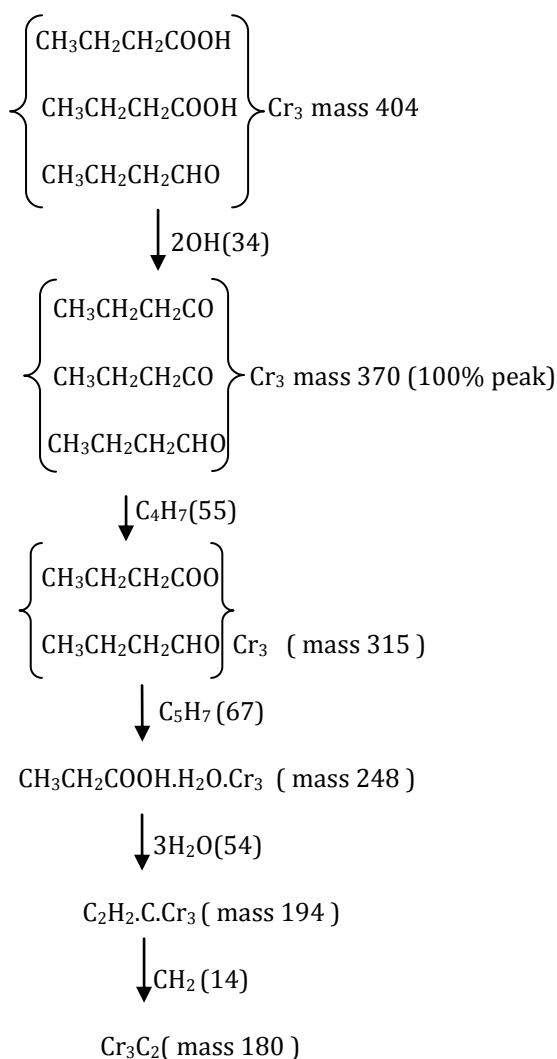
δ in ppm	Type of proton
0.9	Primary (CH_3 or CH_2CH_3)
1.1	Primary (CH_3 or CH_2CH_3)
1.3	Secondary ($-\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2-$)
2.4	-OH
7.2	-CHO or -COOH

Groups assigned on the basis of NMR Spectra are:

$-\text{CH}_3$, $-\text{CH}_2-$, $-\text{OH}$, $-\text{CHO}$

Mass spectra :

Formula mass of the compound $\text{C}_{12}\text{H}_{26}\text{O}_5\text{Cr}_3$ is 406 which gives 100% base peak on 369.08 in mass spectra which show removal of fragments H_2 and $(\text{OH})_2$ to form stable complex $\text{C}_{12}\text{H}_{22}\text{O}_3\text{Cr}_3$. Removal of fragments may be explained as:



Possible structure of CB2 : On the basis of empirical formula, functional groups assigned by IR spectra, position of protons assigned by NMR spectra, loss of fragments by mass spectra the possible structure of compound CB2 may be :-

Form 1 : $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO})_3 \cdot 2\text{OH} \cdot \text{Cr}_3$
(Formula mass 406)

Form 2:

$(\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH})_2 \cdot (\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}) \cdot \text{Cr}_3$
(Formula mass 404)

(ii) CB4:

It is green solid having percentage composition: C = 32.052%, H = 6.434%, O = 22.718%, Cr = 38.796%

Empirical formula : $\text{C}_{12}\text{H}_{26}\text{O}_8\text{Cr}_3$

FTIR peaks(cm^{-1}) assign following groups:

FTIR Peaks (Wave no. cm^{-1})	Group Assignments
669.1, 770.46, 929.7	Cr-O (str.)
1070, 1156.65, 1215.68	C-O (str.)
1416.95	OH bending or CH_2 bending
1631.5	C=O str. -CHO or -COOH
2400.2	Chelation due to H bonding
2928.39, 3019.62	C-H (str.) due to -CHO or COOH
3410.03	OH (str.)

Groups assigned on the basis of IR Spectra are:

$-\text{CH}_3$, $-\text{CH}_2-$, $-\text{COOH}$, $-\text{Cr-O}$, $-\text{OH}$

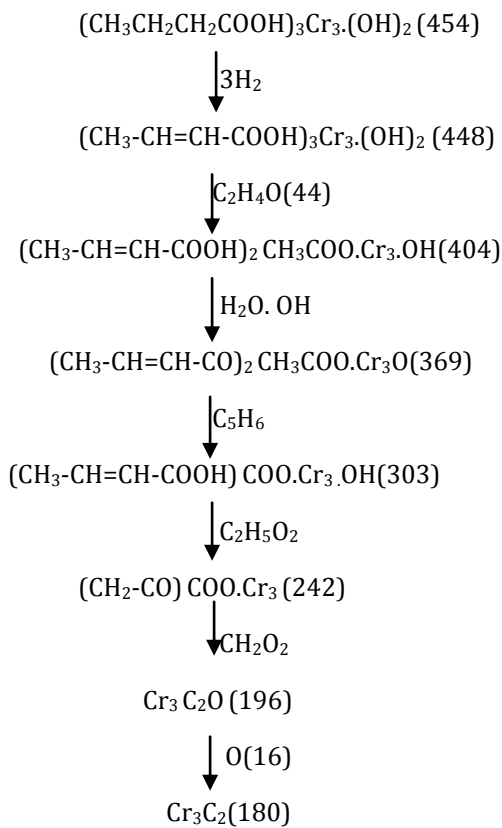
H NMR spectra assign following groups and position of protons:

δ in ppm	Type of proton
0.9	Primary (CH_3 or CH_2CH_3)
1.2	Primary (CH_3 or CH_2CH_3)
1.5	Secondary ($-\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2-$)
2.1, 2.3, 2.6	-OH
7.26	-CHO or -COOH

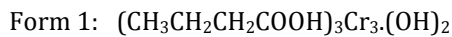
Groups assigned on the basis of NMR Spectra are:- $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{OH}$, $-\text{CHO}$ or $-\text{COOH}$

Mass spectra :

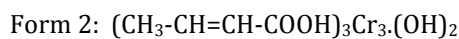
Formula mass of the compound $\text{C}_{12}\text{H}_{26}\text{O}_8\text{Cr}_3$ is 454 which gives peak at 448, 404, and 100% base peak on 368.84 in mass spectra which show removal of fragments 3H_2 , $\text{C}_2\text{H}_4\text{O}$, H_2O and OH to form stable complex $\text{C}_{10}\text{H}_{13}\text{O}_5\text{Cr}_3$.



Possible structure of CB4 : On the basis of empirical formula, functional groups assigned by IR spectra, position of protons assigned by NMR spectra, loss of fragments by mass spectra the possible structure of compound CB4 may be :-



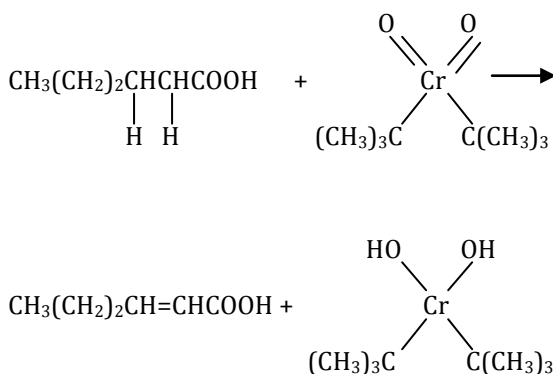
(Formula mass 454)



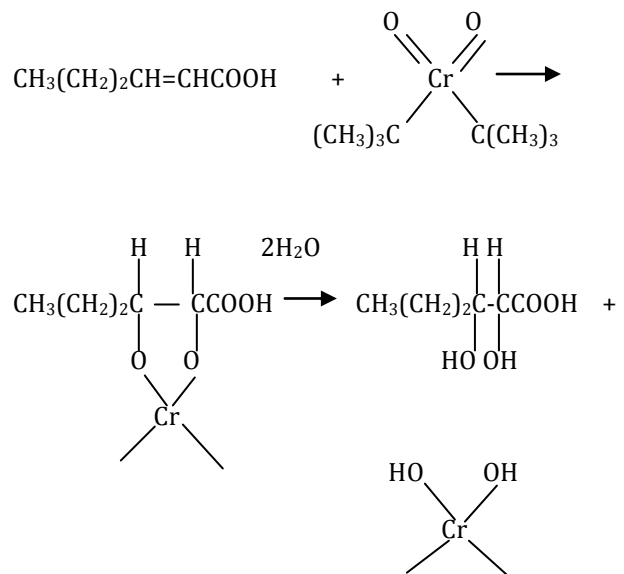
(Formula mass 448)

2. Possible mechanism of oxidation of caproic acid by TBC:^{3-7,18}

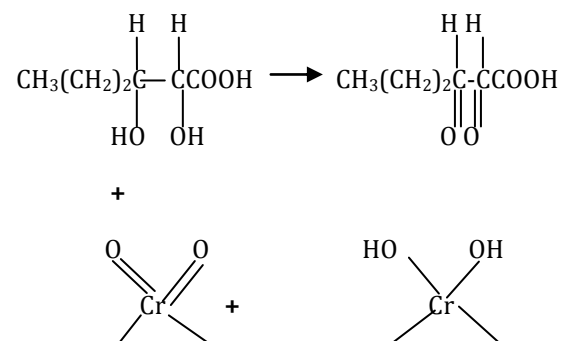
Step 1 Reagent (TBC) approaches on adjacent H atoms of the acid to form unsaturated intermediate



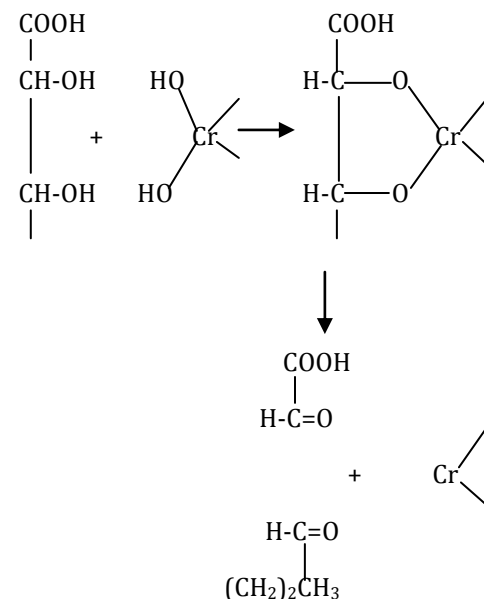
Step 2 TBC approaches on unsaturated carbon atoms to form dihydroxy acid



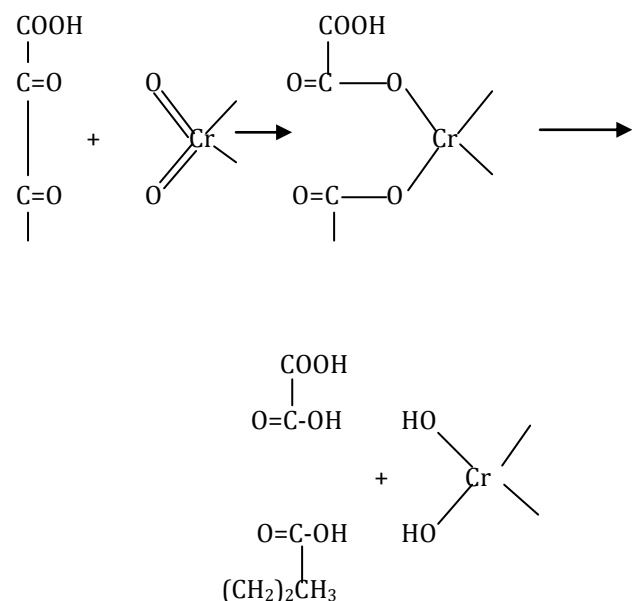
Step 3 Further the dihydroxy acid is oxidized to dioxo acid



Step 4 The dihydroxy acid may be oxidized as



Step 5 The dioxo acid obtained in step 3 may be oxidized as



12. T. Kuraoka & N. K. Zassi, J. Sc. Hiroshima Univ. 82 (1962), 50
13. G. Dupont, R. Dolor & O. Mondou, Bull. Soc. Chem. France, 60 (1953)
14. G. Mishra, N. Dwivedi, N. N. Mishra and H. O. Pandey, J. Inst. (Ind), 62, 57-58, (1991)
15. G. Misha, M. Alam, R. Thakur and N. N. Mishra, J. Inst. Chem. (Ind.) 63, 166 (1991)
16. G. D. Mishra, S. N. Tiwari and N. N. Mishra, J. Inst. Chem (Ind), 63 (6) 217 (1991)
17. G. D. Mishra and N. K. Tiwari, J. Chemtracks, 7,1 & 2, 163-168, (2005)
18. G. D. Mishra and N. K. Tiwari J. Chemtracks 13 (1), 287-292, (2011)

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References:

1. M. Silverstein & Francis X. Webster, Spectrometric Identification of organic compounds, Robert 26-66, 84-125,178-196, 200 (2009)
2. Dr. H. Kaur, Spectroscopy, 174-176, 333-335 (2009)
3. I. L. Finar, Organic Chemistry, Vol. 1, Fifth edition (2008)
4. R. T. Morrison and R. N. Boyd, Organic Chemistry, Indian reprint, 775-806 (2005)
5. Jerry March, Advance Organic Chemistry, McGraw Hill, 2nd ed. 1098-99 (1977)
6. Wiberg and Richardson, JACS 84, 2800 (1962)
7. Westheimer, Chem.Rev.45, 419-451(1949)
8. R. V. Oppenauer and H. Oberrauch, Univ. Innsbruck, Austria, 37, 246-62 (1949)
9. Watanabe Y. and N. K. Zassi, J. Sc. Hiroshima Univ. 80, 310 (1959)
10. T. Suga (Hiroshima univ.) Bull. Chem. Soc. Japan, 31, 569-77(1958)
11. Suga, T. Kihara, K. and Matsuura, T. Bull. Soc. Japan 35,38 (1962)