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ORIGINAL ARTICLE

Oxidation of adipic acid using T.B.C. (non aq. oxidant) and analysis of products

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ABSTRACT
Ditertiary butyl chromate (T.B.C.), a versatile non aqueous oxidant was used to oxidise caproic acid. The various solid products were obtained by taking different molar ratio in substrate : oxidant as 1 : 0.75., 1 : 1.25 which were collected as AB2 and AB4 after washing, with water, acetone and benzene and purifying with TLC. The formulae and structures of oxidised products have been tried to explain in this research paper.
Keywords: *TBC = Ditertiary butyl chromate, IR = Infra red, NMR = Nuclear magnetic resonance , TLC = Thin layer chromatography.*

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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 coworkers[7-15], such as R.V. Oppenaur & H. Obberausch, T. Suga & N.K.Zassi, Y Watanabe & Zassi, G. D. Mishra and others to oxidise different class of compounds like alcohols, aldehydes, ketones, carboxylic acids etc.

I particularly studied the oxidation of adipic acid using T.B.C. as oxidant. Adipic acid when treated 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. Which were washed, purified and collected as samples. Following two complexes which are named as samples AB2 and AB4 have been analysed.

MATERIAL AND METHOD [16-20]

a)AB2 : (Molar ratio, substrate : oxidant = 1 : 0.75)

1g of adipic acid was mixed in 0.75 g T.B.C. which was obtained by mixing 0.75 g CrO_3 in 1.3 ml tertiary butyl alcohol and heated 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 AB2 for analysis.

b) AB4 (Molar ratio, substrate : oxidant = 1 : 1.25)

Adipic acid (1 g) when heated with T.B.C. (1.25 g for about 5 minutes an exothermic vigorous reaction occurred by releasing very hard and irritating brown fumes for about 1 minute after that Solid greenish brown coloured product was obtained. This was allowed to cool for 1 hour. The product was washed and filtered properly to get pure product. The product was insoluble in acetone 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 AB4 for analysis.

RESULTS AND DISCUSSION [1-6, 17-20]

a) AB2

i) **Physical characteristics**: It is green solid mass which is insoluble in water, ethanol, and benzene.

ii) **Elemental analysis:**

It is green solid having percentage composition: C = 34.432%, H = 5.432%, O = 25.782%, Cr = 33.951%

iii) **Empirical formula :**

Simplest ratio C : H : O : Cr = 9 : 14 : 5 : 2

On the basis of above percentage composition, the empirical formula of AB2 is $C_9H_{14}O_5Cr_2$ (Formula mass 306)

iv) **IR Analysis:**

FTIR Peaks (Wave no. cm^{-1})	**Group Assignments**
669.02	Cr-O (str.)
759.07	Cr- O (str.)
929.11	Cr- O (str.)
1215 .47	C-O (str.)
1397.21	C-OH bending or CH_2 bending
1617.97	α, β unsaturated C=O str. or $C=C_{COOH}$
2400	chelation
3019.59	C-H (str.)
3424.85	OH (str.)

Groups identified on the basis of IR Spectra are Cr-O, -COOH/$-COO^-$,$C=C_{COOH}$ -CH_3, -CH_2-, -OH, Chelation

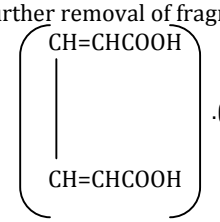
v) **NMR Spectra:**

δ in ppm	Proton count	Type of proton
0.827	0.08	Primary (CH_3 or CH_2CH_3)
0.880	0.03	Primary (CH_3 or CH_2CH_3)
1.225	0.10	Primary (CH_3 or CH_2CH_3)
1.54	1.0	Secondary or –CH2-CH2-
2.403	0.01	-OH
7.260	0.47	-CHO or -COOH

Groups identified on the basis of NMR Spectra are: -CH_3, -CH_2-, -OH, -CHO or COOH

vi) Mass spectra:

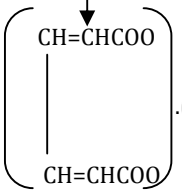
Formula mass of the compound $C_9H_{14}O_5Cr_2$ is 306 which on removal of 6H shows 100% peak in mass spectra at mass 300. Further removal of fragments in mass spectra can be as following:



.(CH_2=CHCHO).Cr_2.

mass 300 (100% peak)

CH_3(15)



.(CH_2CHO).Cr_2

Mass 285 (35 % peak)

C_3(24)

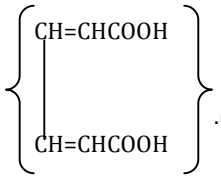
$(CHCOO)_2(CH_2CHO).Cr_2$

Mass 261 (10 % peak)

C_6H_5(77)

Cr_2O_5 (184) (10 % peak)

vii) **Possible structure of AB2 :** 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 AB2 may be :



$.(CH_2{=}CHCHO).Cr_2.$

b) AB4

i) Physical characteristics: It is brownish green solid mass which is insoluble in water, ethanol, and benzene.

ii) Elemental analysis:

It is green solid having percentage composition: C = 26.069 %, H = 3.769%, O = 19.623%, Cr = 50.539%

iii) Empirical formula :

Simplest ratio C : H : O : Cr = 6 : 12 : 4 : 3

On the basis of above percentage composition, the empirical formula of AB4 is $C_6H_{12}O_4Cr_3$ (Formula mass 304)

iv) IR Analysis:

FTIR Peaks (Wave no. cm^{-1})	**Group Assignments**
669	Cr-O (str.)
768.7	Cr- O (str.)
1068.67	Cr- O (str.)
1215 .64	C-O (str.)
1396.57	C-OH bending or CH_2 bending
1615.16	α, β unsaturated C=O str. or $C{=}C_{COOH}$
3019.59	C-H (str.)
3424.85	OH (str.)

Groups identified on the basis of IR Spectra are:

Cr-O, -COOH/$-COO^-$, $C{=}C_{COOH}$ $-CH_3$, $-CH_2-$, -OH, Chelation

v) NMR Spectra:

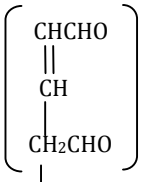
δ in ppm	Proton count	Type of proton
0.879	0.11	Primary (CH_3 or CH_2CH_3)
1.0	0.03	Primary (CH_3 or CH_2CH_3)
1.25	0.11	Primary (CH_3 or CH_2CH_3)
1.5	1.0	Secondary or –CH2-CH2-
2.0	0.02	-OH
2.4	0.02	-OH
7.2	0.39	-CHO or -COOH

Groups identified on the basis of NMR Spectra are: $-CH_3$, $-CH_2-$, -OH, -CHO or COOH

vi) Mass spectra:

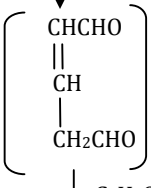
Formula mass of the compound $C_6H_{13}O_4Cr_3$ is 305 which on removal of 5H shows 100% peak in mass spectra.

Further removal of fragments in mass spectra can be as following:



$.HCOOH.Cr_3$ (300) (100% peak)

CH_2(14)



$.Cr_3O_2$ (286)

(38%peak at 285)

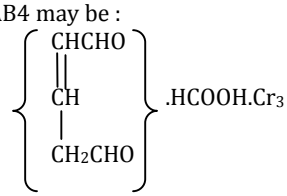
C_4H_4O (68)

$HCHO.Cr_3O_2$ (218) (10%peak at 215)

HCHO(30)

Cr_3O_2(188) (15%peak)

vii) Possible structure of AB4 : 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 AB4 may be :



Formula mass : 300

CONCLUSION

On the basis of this research work it is clear that when adipic acid is oxidized with TBC in different molar ratios the products obtained are complexes of chromium with unsaturated dicaboxylic acid or dialdehyde or smaller carboxylic acid ligands. These products are formed due to oxidative degradation of adipic acid.

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