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Comparative Study of Products Formed by the Interaction of Acetyl-Acetone with CrO_3 or TBC i.e. [Cr(VI)] in different Solvents with different Molar Ratios

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Abstract—*Oxidation of Acetyl-Acetone was carried out by Cr VI based oxidant in different solvents like dim ethyl form amide (DMF) and dimethyl sulfoxide (DMSO) using suitable combination Viz. (DMF(alone)/with water/with TBA/DMSO (alone)/DMSO+Water/ DMSO+TBA) and by using different molar ratio of substrate : Oxidant. Solid products in the form of chromium complexes were obtained in each case & the structure of these complexes were studied & Analyzed after purification.*

1. INTRODUCTION

Cr VI based oxidant have been employed to carryout oxidation from a long period. Chromium containing compound like Cr-Oxide, Cr-trioxide, Chromates $(Cr0_4)^{-2}$,Tertiary butyl chromates are very important and versatile oxidant. Chromium is a transition metal possess complex forming tendency. When tertiary butyl Chromate and also Chromium trioxide was used as an oxidant with Acetyl-acetone gave the corresponding aldehyde, acid, ester, ketone and alcohol etc. in different molar ratio of the solvent. Key word - DMF, DMSO, FTIR, TGA, DTA etc.

2. OBJECTIVE

Despite being used extensively for oxidation of several organic compounds practically no attempts was made to study these oxidation processes with reference to a particular clas of compounds. In present work action of Cr (VI) oxidant on Acetyl-Acetone has been studied with the following objectives

a) Whether a parallelism exists or not?

b) Whether the oxidation is selective - does arresting the reaction up to different stages (by taking different molar ratios) result into same product or not?

c) Whether change of solvent affects the reaction or not?

3. EXPERIMENTAL & FORMULATION

1. 0.25, 0.5, 0.75 or 1gram of dry, pure and accurately weighed oxidant Cr (VI) was taken & dissolved in different solvents of DMF & DMSO in different medium.
2. 1ml of acetyl acetone was mixed with DMF/DMSO alone/with water/with alcohol etc.
3. These two solutions were mixed with vigorous shaking & then transferred to a round bottom flask and was deflexed using air condenser upon water bath, then after solid product of different colour was obtained.
4. Product obtained was washed successively till all the impurities were washed out and then the purity of the sample was tested using sharpness of M. P. and TLC method.
5. Thermo gravimetric analysis (TGA) measures the weight loss with respect to temperature.
6. IR spectra was carried out with the help of FTIR, for knowing he nature of functional group. IR result signify many peaks.

Solvent	Subs: CrO_3 (Molar Ratio)	Composition of the product	Structural Formula
DMF (Alone)	1 : 0.25	$C_{20}H_{30}O_9Cr$	$(CH_3COCHCOCH_3)_4\ H_2OCr^{+4}$
	1 : 0.5	$C_{20}H_{29}O_9Cr$	$(CH_3COCHCOCH_3)_4\ CrOH^{+5}$
DMF + TBA	1 : 0.25	$C_{35}H_{60}O_{17}Cr$	$(CH_3COCH_2COCH_3)_7\ 2H_2O\ CrO^{+2}$
	1 : 0.5	$C_{25}H_{38}O_{11}Cr$	$(CH_3COCH_2COCH_3)_3$ $(CH_3COCHCOCH_3)_2CrO^{+4}$
DMF + H_2O	1 : 0.25	$C_{25}H_{39}O_{12}Cr$	$(CH_3COCHCOCH_3)_5\ 2H_2O\ Cr^{+5}$
	1 : 0.5	$C_{25}H_{39}O_{12}Cr$	$(CH_3COCHCOCH_3)_5\ 2H_2O\ Cr^{+5}$
	1:1	$C_{25}H_{39}O_{12}Cr$	$(CH_3COCHCOCH_3)_5\ 2H_2O\ Cr^{+5}$

Solvent	Molar Ratio	Composition of the product	Structural Formula
Solvent → DMSO (Alone)	1 : 0.5	$C_{15}H_{21}O_7Cr$	$(CH_3COCHCOCH_3)_3\ CrO^{+5}$
DMSO+TBA	1 : 0.25	$C_{25}H_{40}O_{12}Cr$	$(CH_3COCHCOCH_3)_4$ $(CH_3COCH_2COCH_3)\ 2H_2O\ Cr^{+4}$
	1:0.5	$C_{25}H_{37}O_{11}Cr$	$(CH_3COCHCOCH_3)_5\ H_2O\ Cr^{+5}$
	1:0.75	$C_{25}H_{38}O_{12}Cr$	$(CH_3COCHCOCH_3)_5\ H_2O\ Cr^{+6}\ (OH)$
	1:1	$C_{20}H_{28}O_9Cr$	$(CH_3COCHCOCH_3)_4\ CrO^{+6}$
DMSO + H_2O	1 : 0.25	$C_{20}H_{30}O_9Cr$	$(CH_3COCHCOCH_3)_4\ H_2O\ Cr^{+4}$
	1:0.5	$C_{20}H_{30}O_9Cr$	$(CH_3COCHCOCH_3)_4\ H_2O\ Cr^{+4}$
	1:0.75	$C_{25}H_{41}O_{12}Cr$	$(CH_3COCH_2COCH_3)_2$ $(CH_3COCHCOCH_3)_3\ 2H_2O\ Cr^{+5}$
	1:1	$C_{20}H_{34}O_{10}Cr$	$(CH_3COCH_2COCH_3)_4\ H_2O\ CrO^{+6}$

Complexes such as $(CH_3COCHCOCH_3)_{2,\ 3,\ 4,\ 5,\ 7}\ nH_2O$

Cr/CrO/Cr(OH) etc. depending upon substrate : oxidant molar ratio..

In case of DMF (Alone) and DMF in alcoholic media, when higher concentration of oxidant is used, higher oxidation state of chromium is more common in the complex state. It follows therefore that when excess of Cr (VI) is taken as oxidant, the complex seems to have Cr (VI) as the central atom while lesser concentration of Cr (VI) to start with leads to complication involving lower oxidation state of chromium.

In case of DMSO and H_2O study, it is only 1:1 ratio of substrate: Oxidant that gives Cr (VI) in the complex compound, while in the case of DMSO and TBA both 1:1 and 0.75 ratio of substrate : oxidant give Cr (+VI) in the complex compound.

Substrate has been oxidized and the Cr has undergone complication with the substrate functioning as ligand. Chelating agent acetyl acetone invariably traps the resulting chromium ion in the mixture leading to some stable complexes.

4. DISCUSSION AND RESULTS

The sold products obtained were isolated and characterized a the basis of elemental analysis, IR-spectral studies & thermal analysis. The loss in mass observed in Thermograllimatic curve due to loss of acid & H_20 molecule as expected.

The change in solvent has produced changes in different aspects of the products including their colour composition & constitution.

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