International Journal of Chemistry and Applications.
ISSN 0974-3111 Volume 6, Number 2 (2014), pp. 109-113

http://www.irphouse.com

Study of Redox Processes Involving Some Alcohols and Aldehyde with Non-Classical Oxidant

Ruchika Singh, Dr. D. N. Roy, Dr. Hari Om Pandey, Dr. Anita Gupta and RichaKumari

Research Scholar
Department of Chemistry, Ranchi University, Ranchi-834001, India
Email: ruchika.singh09@gmail.com

ABSTRACT

The present work deals with Physico-chemical studies of the products formed by the oxidation of organic compounds with Chromium/Manganese containing oxidants. Over recent years chromium (VI) based oxidizing agents have been extensively worked on, leading to the development of a good number of reagents some of which have become quite popular and performing well as oxidizing agents.
In the present work, we have used TBC & TAC for the oxidation of a few selected organic compounds of alcohol and aldehyde series. We have used different solvents like, tetrahydrofuran, dichloromethane, acetonitrile & dioxane, in order to study the effect of different oxidants on same substrate and also effect of solvents on the oxidation of organic compounds. For a better comparison we have taken different substrate: Oxidant ratios. The oxidation products obtained were found to differ in their color, composition, constitution and magnetic behavior.

Key words: Vanillin, Quinoline, TGA, FTIR and Element Analysis.

INTRODUCTION

Heating is applied to both organic and inorganic chemistry. Different amount of compound can be heated. This allows some parts of the object being heated to heat more quickly or more slowly than others. In reaction time enormous accelerations in reaction time can be achieved, if heating is performed in closed vessels, a reaction that takes several hours underconventionalconditions can be completed over the course of minutes chromium (VI) based reagents have been extensively used in organic synthesis. TBC is a versatile oxidizing agent. IN present work we have to use to

Paper Code:

oxidize vaniline and quinolone, using 1, 4 dioxane, THF, Acetonitrile as a solvent, in different oxidant: substrate molar ratio under heating. Thesolid product obtained i.e. v_1 and $v_3$were isolated in pure form and characterized by on the basis of elemental analysis, FTIR spectra studied and thermal analysis.

In this way, 17 samples of solid products were obtained which were analyzed by:

1. Various thermo gravimetric analysis including TGA, TG, DTA (IIT Bombay)
2. Titrimetry for the analysis of Cr.
3. Magnetic analysis using Gouy's balance.

MATERIALS AND METHODS:

A: - Heating assisted oxidation of vanillinebyTAA

1 Substrate: Oxidant ratio (1:1)

The oxidant was prepared by dissolving 1g of cro_3 in 10ml of TAA in a clean and dry beaker. In another beaker 1.5g of vanilline was accurately weighted and dissolved in 10ml of of THF. The two solution product are obtained are dark brown ppt. the product was washed several times with acetone to get the clear ppt. Dried and collected in air tight bottle as sample no v_3

2 Substrate: - oxidant ratio (2:1) `

The oxidant was prepared by dissolving 1g of cro_3 in 10ml of TAA in a clean and dry beaker. In another beaker 3gof vanilline was accurately weighted and dissolved in 10ml of acetonitrile. The two solution product are obtained are brown ppt. the product was washed several times with acetone to get the clear ppt. Dried and collected in air tight bottle as sample no v_1

B: - Heating assisted oxidation of quniline

1 Substrate: - oxidant ratio (1:2)

The oxidant was prepared by dissolving 1g of cro_3 in 10ml of TAA in a clean and dry beaker. In another beaker 3g of quniline was accurately weighted and dissolved in 10ml of of THF. The two solution product are obtained are greenish brown ppt. the product was washed several times with acetone to get the clear ppt. Dried and collected in air tight bottle as sample no V_{18} (refer Table 1).

Table 1

Product code	Solvent	Oxidation	S:O ratio	Heating Condition (normal heater)	Time	Color	Solubility	Empirical formula
V1	THF	TAA	1:1	2h	2h	Dark brown	Insoluble in water	$Cr_3C_9H_{12}O_9$
V2	THF	TAA	2:1	2h	2h	brown	Soluble in water	$Cr_2C_8H_{12}O_8$
V3	THF	TAA	1:2	2h	2h	Greenish brown	Slightly soluble in water	$Cr_2C_4H_8O_8$

Sample no:- V1
Proposed empirical formula:- $Cr_3C_9H_{12}O_9$
Proposed formulation of the complex: $Cr_2O_3CrO.OHC_6H_3$ $(OCH_3)CH_2OH.HCOOH$

On the basis of these analyses, different formulations of all the compounds were done.

It has been observed in the oxidation of Vanilline, that, in most of the cases, as the concentration of the oxidant is increased, the colour of the product formed is more towards the deeper shade. For example in the oxidation of Vanilline by TBC i.e. in V1 (S: O ratio 1:1) color of the product is brown, inV2 (ratio2:1) thecolour of the compound is light brown and in V3 (ratio1:2) the colour of the complex is brown.

IT was observed that the solid products were obtained on stirring the reaction mixture for 15-30 minutes, on an average, and in few cases after leaving the mixture overnight. In case of dioxane, as the solvent for the substrate, the product could be obtained only after stirring the reaction mixture with simultaneous heating. It was also noticed that in case of solvent, THF, yield is less as compared to others. When the higher ratios of the oxidants were used, the time taken for the completion of the reaction and the formation of the complexes were comparatively less than in cases when oxidant ratios was towards the lower side, though in some cases charring occurred due to higher concentration of oxidant.

From the study of the nature of the products by using various molar ratios of the oxidants, it is seen that during the oxidation of Vanillin TAA & TBC when the solvent. THF is used, the fragmentation is complete in almost all the S: O ratios i.e. degradation oxidation takes place even in lower ratio of oxidant leading to the formation of Vinyl ethyl ether C_4H_8O, and vinyl acetate $C_4H_6O_2$, Methylsalicylate$C_8H_8O_3$But in other solvents like dichloromethane acetonitrile and dioxane, it is observed that when the ratio of oxidant is high, the oxidation product is $C_{10}H_{12}O_6$showing the fragmentation is complete. When the ratio of oxidant is lower i.e. halfed or made one fourth, the oxidation products were found to contain Cinnamaldehyde C_9H_8O, vinyl alcohol, as the oxidation product indicating that the compound didn't undergo fragmentation, it got simply oxidized and might have complexed with chromium as ligand or adduct. The color of the complex shows the reduced state of chromium.

The compound Quinoline was found to undergo oxidation to form pyridine- 2-3-dicarboxylic acid.Pyridine-2, 3-dicarboxylic acid is not stable and undergo decarboxylation to give nicotinic acid. The colour of the complex in most of the cases was near to brown which might be due to charge transfer rather than electronic transition. It was noticed that the time taken for the completion of the reaction in different oxidant to substrate ratio is different. When the ratio of oxidant is more the complex was formed in lesser time in comparison to those when the ratio of the oxidant was less. It was also found that the yield of the product in all the ratios were more or less the same.

The pattern of fragmentation of Quinoline in all the cases of solvent is almost same i.e. the complexation of unoxidized or less oxidized products in case of lower ratio of oxidant and complexation or coordination of smaller fragments in case of higher ratio of oxidant. In case of neat, quinolone as such is evidence in the product when S: O ratio 1:1. In other cases like S:O 2:1 & 1:1 the smaller fragments like,$Cr2C_5H_9NO_5$,$Cr_2C_6H_{11}O_6$,$Cr_2C_{14}H_{16}N_2O_8$etc. are observed showing the greater extent of oxidation.

When Acetonitrile and dioxane are used as the solvent (during the oxidation of quinolone), the same pattern is observed quinolinic acid ($C_7H_5NO_4$) is observed in case of S: O: 4:1 ratio. Other fragments like $Cr_2C_5H_9NO_5$, are observed in cases of higher ratios of oxidants.

In other cases quinolone was oxidized to at least quinolinic acid, N-oxide, benzoic acid, Nicotinic acid even in lower oxidation ration.

All the complexes/compounds of vaniline, quinolone are paramagnetic i.e. feebly attracted by the magnetic field.

Various complexes formed with their properties, empirical formula and proposed formulations are summarized in table 2.

Table 2

Sl. No	Product Code	Solvent for the Substrate	Oxidant Used	S:O ratio	Color	Magnetic Property	Solubility in water	Empirical Formula	Proposed Formulation
1	V1	THF	TAA	1:1	Brown	Paramagnetic	Insoluble in water	$Cr_3C_9H_{12}O_9$	$Cr_2O_3.CrO.OHC_6H_3(OCH_3)CH_2OH.HCOOH$
2	V2	THF	TAA	2:1	Greenish Brown	Paramagnetic	Soluble in water	$Cr_2C_8H_{12}O_8$	$2CrO_3 (CH_3O)_2C_6H_3OH.H_2O$
3	V3	THF	TAA	1:2	Dark Brown	Paramagnetic	Soluble in water	$Cr_2C_4H_8O_8$	$Cr_2O_4CH_2CH (O_2CCH_3).H_2O$
4	V4	Dichloromethane	TBC	3:2	Greenish Brown	Paramagnetic	Partial Soluble in water	$Cr_2C_6H_{14}O_8$	$2CrO_2C_4H_8O.CH_3COOH.H_2O$
5	V5	Dichloromethane	TBC	1:4	Dark Brown	Paramagnetic	Soluble in water	$Cr_2C_8H_{12}O_{11}$	$2CrO_3.OH.C_6H_4COOCH_3.H_2O$
6	V6	Dichloromethane	TBC	1:2	Brown	Paramagnetic	Soluble in water	$Cr_3C_9H_{12}O_6$	$2CrO.CrO.C_6H_5CH=CHCHO.2H_2O$
7.	V7	THF	TAC	1:1	Light Brown	Paramagnetic	Partial Soluble in water	$Cr_3C_9H_{15}O_9$	$2CrO.CrO_2.C_6H_5=CHCOOH.3H_2O$
8.	V8	THF	TAC	1:2	Dark Brown	Paramagnetic	Insoluble in water	$Cr_2C_{10}H_{12}O_6$	$Cr_2O.OH.C_6H_3 (OCH_3)CH=CH.COOH.2H_2O$
9.	V9	THF	TAC	2:1	Deep Brown	Paramagnetic	Insoluble in water	$Cr_2C_{12}H_{18}O_9$	$Cr2O_3C_{10}H_7.CO.CH_3COOH.3H_2O$
10.	Q10	Dioxane	TAC	1:1	Deep Brown	Paramagnetic	Partial Soluble in water	$Cr_2C_{14}H_{16}N_2O_8$	$2CrO_2 (C_{10}H_{12}NO)_2NH.HCOOH$
11.	Q11	Dioxane	TAC	2:1	Yellowish Brown	Paramagnetic	Insoluble in water	$Cr_2C_8H_{11}NO_7$	$Cr_2O_2CH_3CHO.NO_2 (CH_2)_2 CH_3COOH$
12.	Q12	Dioxane	TAC	1:2	Greenish Brown	Paramagnetic	Soluble in water	$CrC_{10}H_{11}O_7N$	$CrO_2C_8H_6NO_3.CH_3COOH$
13.	Q13	Acetonitrile	TBC	2:1	Dark Brown	Paramagnetic	Soluble in water	$Cr_2C_6H_8O_5N$	$Cr_2OC_6H_5NO_2.2H_2O$
14.	Q14	Acetonitrile	TBC	1:1	Yellowish Brown	Paramagnetic	Partial Soluble in water	$Cr_2C_{12}H_{22}O_{10}N_2$	$2CrONHC_{10}H_9NO_2.CH_3COOH.4H_2O$
15.	Q15	Acetonitrile	TBC	4:1	Brown	Paramagnetic	Slightly soluble in water	$Cr_2C_6H_{11}O_6$	$Cr_2OC_6H_5NO_2.3H_2O$
16.	Q16	Dioxane	TBC	1:1	Greenish Brown	Paramagnetic	Slightly soluble in water	$Cr_2C_{14}H_{16}N_2O_8$	$Cr_2OC_7H_5NO_4.2CH_3CHOCH_2COOHCN$
17.	Q17	Dioxane	TBC	2:1	Dark Brown	Paramagnetic	Slightly soluble in water	$Cr_2C_5H_9NO_5$	$2CrOC_5H_5NO.2H_2O$

ACKNOWLEDGEMENT
The authors thanks the head, SAIF, Indian Institute of Technology, MUMBAI, for providing necessary Facilities.

References:

[1] Collins, J.C W. Frank, F.J. Dipyridine Chromium (V) Oxide. Oxidation of alcohol in Dichloromethane, Tetrahedron Lett. (1968), 3363.
[2] Corey, E.J. Schmidt G. Useful Procedures for the Oxidation of Alcohols Involving Pyridinium Dichromate in Aprolic Media, Tetrahedron Lett (1979), 399.
[3] Guizice, F.S. Luzzio, F.A. The Oxidation of alcohols using 2, 2'-Bipyridinium Chlorochromate, Synthesis (1980), 69.
[4] Bhattacharjee, M. M.: Choudhari. M. K: Purkayastha, S. Some Aspects stoichiometry of alcohols, Evidence for oxygen transfer and identity of reduced Chromium species. Tetrahedron (1987), 43, 5389.
[5] Bhattacharjee, M. M.: Choudhari, M. K.: Dasgupta, H. S.: Roy, N. PyridiniumFlourochromate, A New and Efficient Oxidant for organic substrate. Synthesis (1982). 588.
[6] Tajbakhsh, M: Hosseinadeh, R.: Yazdani-Niaki. M. Synthesis and application of 2, 6-Dicarboxy pyridiniumChloromate as a New oxidizing agent for alcohols, Silyl ethers and THP ethers under mild and non-aqueous conditions. J. Chem Research (S) 2002).2
[7] Hosseinadeh, R. :Tajbaksh, M: Yazdani-Nujaki M. 2-6-Dcarboxy pyridiniumChlorochromate: A Mild Efficient and Selective Reagent for oxidative Deprotection of oxime to Carbonyl Compound. Tetrahedron Lett. (2002), 43, 9413-9416.
[8] Tajbakhsh, M: Haravi M. M.: Mohanzadeh, F.: Sarabi S: Ginassemzadeh, M.. Methyl piperidiniumchlorochromate absorbed on Alumina: A New Deoximation Reagent. Montash Chem. (2001), 132, 1229-1231.
[9] Kassaie, M. K.: Mahjob, A. R.: Ghammami, S. Tetramethyl ammonium flurochromate (VI) a new and efficient oxidant for organic substrates. Tetrahedron Letters (2003), 44, 4555-4557.
[10] Kassaea, M. Z.: Sajjadi-Ghotbabadi, H: SayeedAlengi, S Z.N-Benzyl methyl ammonium flurochromate: A New Reagent for the oxidation of Organic Compounds. The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. Pittcon 2003, March 9-14 (2003, Oriando, Florida, Abstract 1200-7P.
[11] T. Massuura. T Suga and T. Sako, Bull Chem. Society. Japan 35 (1962).