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The Study of Ligating Ability of Products of Degradative Oxidation of Crotonaldehyde by Ditertiary Butyl Chromate and Ditertiary Amyl Chromate

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Abstract

Ditertiary butyl chromate (TBC) and ditertiary amyl chromate (TAC) are the two important chromium (VI) based oxidants used, of late, for variety of synthetic works in organic chemistry. The study of products formed by the interaction of organic substrates like crotonaldehyde in different molar ratio and in different solvents with TBC and TAC may give valuable clue in regards to the mechanism of reaction and the structure of the compounds/complexes formed. The thermal loss pattern may be helpful in assessing the strength of the bonds and thus ligating ability of the degraded and undegraded organic fragments. In the present work, we have carried out the oxidation of crotonaldehyde neat and in different solvents like tetrahydrofuran, acetonitrile and dioxane with TBC and TAC under ordinary heating as well in microwave irradiation conditions. The products were analysed chemically, spectroscopically as well as thermogravimetrically to find some generalizations.

Keywords: Ditertiary amyl chromate (TAC), Dioxane, Crotonaldehyde, Chromium trioxide, tert. amyl alcohol (TAA), tert. Butyl alcohol (TBA).

Introduction

Of late, a large number of organic variants of chromium (VI) base oxidants like dipyridine chromium oxide[1], Chromium trioxide-3,5-dimethyl pyrazole complex[2] , 2,2'-Bipyridinium chlorochromate(BIPCC)[3] , Pyridinium flourochromate(PFC)[4], 2,6-Dicarboxy pyridinium chlorochromate[5,6] , N-Methyl pyridinium chlorochromate[7], Tetramethyl ammonium flourochromate[8], N-Methyl benzyl ammonium flourochromate[9], TBC ,TAC etc have been developed. TBC has been in use since it was reported by Oppenaeur[10]. TAC[11,12] has also been proved to be a potent oxidant for organic substrates. The development of new oxidants as well as the increasing use of microwave in place of ordinary heating is necessitated in view of the 12 pinciples[13] of green chemistry which demands the use of efficient and less polluting reagents. TBC and TAC are better than others in the respect that they are less hazardous, more efficient, easy to prepare and storage longevity .The substrate, crotonaldehyde, is an easily oxidisable organic compound. The expected oxidation products of crotonaldehyde are acetic acid, oxalic acid , glyoxalic acid, glyoxal, formic acid etc. in addition to undegraded oxidized products like 2,3dihydroxy butanal, 2,3-diketobutanal , 2,3-diketobutanoic acid etc. which have the ability to function as monodentate and bidentate ligands. The ligating ability of these fragments with chromium can be studied by analyzing the products obtained by the interaction of crotonaldehyde with TBC and TAC in different conditions of molar ratio and solvents under ordinary heating as well as microwave irradiation. The products were analysed thermogravimetrically and spectroscopically to find out the compositions and formulation.

Material and Methods

2 gm, 1 gm and 0.5 gm of pure and dry A.R. grade chromium trioxide (CrO_3) were dissolved in 10 ml of tertiary butyl alcohol. The solution is stirred and filtered to ensure the completion of reaction leading to the formation of clear brown solution of TBC. The same procedure is applied with calculated quantities of CrO_3 in tertiary amyl alcohol for the preparation of TAC.

The substrate solutions were prepared by dissolving 1.65 ml of pure A.R. grade crotonaldehyde in 10 ml of selected solvent (except in case of neat crotonaldehyde). The two solutions were mixed as per molar ratio in the given solvent and stirred continuously on a magnetic stirrer with heating. In case of microwave irradiation, the mixture solutions were kept in microwave oven for the periods as mentioned in table-2. Solid products of different colour and composition were obtained in all the cases which were washed with acetone until clear washing, dried and collected in labeled bottles.

Table 1: Reactants –Ordinary heating and stirring.

Product code	Solvent for the substrate	Oxidant used	S:O ratio	Duration of heating and stirring
CT-11	Neat	TBC	1 : 1	1 hour
CT-12	Neat	,,	2 : 1	50 min
CT-14	Neat	,,	4 : 1	1.2 hour
CTT-11	THF	,,	1 : 1	45min
CTT-12	THF	,,	2 : 1	50 min
CTT-14	THF	,,	4 : 1	55 min
CTA-11	Acetonitrile	,,	1 : 1	30 min
CTA-12	Acetonitrile	,,	2 : 1	25 min
CTA-14	Acetonitrile	,,	4 : 1	20 min
CTD-11	Dioxane	,,	1 : 1	15 min
CTD-12	Dioxane	,,	2 : 1	20 min
CTD-14	Dioxane	,,	4 : 1	30 min

Table 2: Reactants –Microwave Irradiation.

Product code	Solvent for the substrate	Oxidant used	S:O ratio	Duration of microwave irradiation (160 W)
MD-01	Dioxane	TBC	2 : 1	90 sec
MD-02	,,	TBC	1 : 2	80 sec
MD-03	,,	TAC	1 : 1	20 sec
MD-04	,,	TAC	2 : 1	26 sec

Results and Discussion

On the basis of the elemental analysis, FTIR peaks and thermogravimetric loss pattern, the empirical formulae and possible formulation of the products have been proposed as given in table-3 and table-4.

Table 3: Products – Ordinary heating.

Product code	Colour	Empirical formula	Proposed formulation of the products
CT-11	Dark brown	$Cr_2C_6H_{20}O_{16}$	$2CrO_2$ .3CH_3COOH.4H_2O
CT-12	Brown	$Cr_2C_4H_{13}O_6$	Cr_2O. HOOC-CHO.CH_3CHO.H_2O
CT-14	Black	$Cr_2C_8H_{24}O_{12}$	Cr2O3.2HOOC-CHO.CH3CH=CHCHO.2H2O
CTT-11	Brown	$Cr_2C_4H_{13}O_{14}$	2CrO. HOOC-CHO.2HCOOH. 3H_2O.
CTT-12	Reddish brown	$Cr_2C_3H_9O_6$	Cr_2O.CH_3COOH.HCOOH. H_2O
CTT-14	Greyish black	$Cr_2C_5H_{11}O_8$	Cr_2O. CH_3CH=CHCOOH HCOOH.3 H_2O.
CTA-11	Carbon black	$Cr_2C_3H_7O_8$	Cr_2O.HOOC-CHO. HCOOH.2H_2O.
CTA-12	Black	$Cr_2C_3H_8O_6$	Cr_2O.CH_3COOH. HCOOH..H_2O
CTA-14	Coffee colour	$Cr_2C_6H_{12}O_{10}$	$2CrO_2$ 2HOOC-$CHOCH_3CHO$.2H_2O
CTD-11	Dark brown	$Cr_2C_3H_8O_6$	Cr_2O. CH_3COOH.HCOOH. H_2O
CTD-12	Brown	$Cr_2C_4H_8O_9$	2CrO. HOOC-CHO. CH_3COOH.2H_2O
CTD-14	Brown	$Cr_2C_5H_{14}O_{11}$	Cr_2O_3. HCOOH. CH_3CH=CHCOOH.4H_2O

Table 4: Products –Microwave Irradiation.

Product code	Colour	Empirical formula	Proposed formulation of the products
MD -01	Light brown	$Cr_2C_4H_{18}O_{14}$	Cr_2O_3 .CH_3COOH.(COOH)$_2$.5H_2O
MD -02	Light brown	$Cr_2C_2H_{12}O_{11}$	Cr_2O_3.(COOH)$_2$.4H_2O
MD -03	Maroon	$Cr_2C_3H_{13}O_9$	Cr_2O_3. CH_3COOH.HCOOH.2H_2O
MD -04	Dark brown	$Cr_2C_4H_{12}O_7$	2CrO.HOOC-CHO.CH_3CHO.H_2O

The formulations of the products on the basis of spectroscopic and thermogravimetric analysis leads to many generalizations such as :

- ✓ Almost all the degradative fragments like acetic acid, oxalic acid , glyoxalic acid, glyoxal, formic acid etc in addition to undegraded oxidized products like 2,3-dihydroxy butanal, 2,3-diketobutanal , 2,3-diketobutanoic acid etc were found to be present in the products.
- ✓ The extent of oxidation increases as the ratio of oxidant increases. This is substantiated by the appearance of undegraded product CH_3CH=CHCOOH and the substrate as such in CT-14,CTT-14 andCTD-14 when the ratios of oxidant are lowest
- ✓ The extent of oxidation in acetonitrile is more as no undegraded product is obtained even in case of lowest oxidant ratio i.e. CTA-14.
- ✓ Chromium undergoes maximum change in oxidation state from VI to I in case of acetonitrile and THF as solvent.
- ✓ The oxidation is more efficient in solvents rather than in neat because in the former case, HCOOH is one of the products in almost all the solvents but it is not formed in neat crotonaldehyde even if the molar ratio is 1:1.
- ✓ The reaction is more controlled and efficient in case of dioxane as solvent. Moreover the most stable lower oxidation state of Cr i.e. III (Cr_2O_3) is observed only in case of dioxane as solvent or in case of neat crotonaldehyde.
- ✓ The large difference in the duration of reactions leading to products when dioxane and TAA are used as solvents for the substrate emphasizes the role of solvent during the process.
- ✓ The reactions are more efficient and take much less time (in seconds) for completion in microwave oven than in case of ordinary heating.
- ✓ In almost all the cases of microwave irradiation, chromium is reduced to most stable oxide i.e. Cr_2O_3
- ✓ The oxidation takes less time i.e. 20-25 sec with TAC as compared to TBC which takes 80 to 90 seconds in microwave irradiation.
- ✓ In microwave irradiation also the extent of oxidation is more when the the ratio of oxidant is more as supported by the formation of HCOOH in MD-03 as compared to the formation of HOOC-CHO and CH_3CHO in MD-04.

Thus it can be concluded that TAC is more effective as oxidant than TBC and microwave irradiation is by far the less energy consuming, time saving and less polluting means of carrying out the oxidation of organic substrates. The organic fragments like HCOOH, CH_3COOH, $(COOH)_{2,}$ HOOC-CHO etc have appreciable ligating ability with chromium in different oxidation states.

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