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STUDY OF OXIDATION OF 1,2-PROPANEDIOL BY CHROMIUM (VI) COMPLEXES USING DIFFERENT SOLVENTS

Chemistry

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ABSTRACT

In the present communication, we have explored the oxidation of 1,2-Propanediol by Chromium (VI) complexes such as Ditertiary butyl chromate (TBC) and Ditertiary amyl chromate (TAC). The proposed study looked at the effects of different substrate:oxidant ratio and of various solvents on the oxidation of 1,2-Propanediol. The products formed have been characterised with the help of instrumental elemental analysis, Fourier Transform Infrared spectroscopy, DTA-TGA mass loss pattern and estimation of chromium by volumetric analysis.

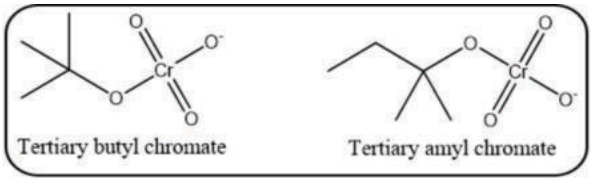
KEYWORDS

Oxidation, Chromium complexes, 1,2-Propanediol, Propylene glycol, Tertiary butyl chromate, Tertiary amyl chromate

INTRODUCTION

Propylene glycol, also known as 1,2-Propanediol is a clear, odourless, viscous liquid having molecular formula $C_3H_8O_2$. It has melting and boiling point -59°C and 188.2°C respectively and its density is 1.036gm/cm^3. It is miscible with solvents like acetone, chloroform and water. 1,2-Propanediol exists in two forms (stereo-isomers) as it contains asymmetrical carbon atom. The commercial product is a racemic mixture. 1,2-Propanediol is used as a solvent in many pharmaceuticals. It is also used as a moisturizer in a wide range of products. It gives normal reactions of primary and secondary alcohols. It gets oxidised to aldehyde by CrO_3. Propylene glycol is traditionally produced from propylene oxide but can also be generated from glycerol, a low-cost by-product in trans-esterification of triglycerides for biodiesel production [1]. It is among the products of biomass conversion[2] that can be oxidized into a variety of useful products[3-5]. A number of valuable products, such as hydroxyl acetone/acetol, methylglyoxal, lactic acid and pyruvic acid which find application in the production of fine chemicals and pharmaceuticals, can be obtained through oxidation of propylene glycol.

Cr(VI) compounds are known to organic chemists for decades as versatile and powerful oxidising agents[6].In recent years Chromium (VI) is considered as an important reagent in organic synthesis and has been used in aqueous and non-aqueous medium for the oxidation of organic compounds[7-9]. Many of the new reagents of chromium(VI) are mild as compared to chromium trioxide and can be handled easily and the reaction products may also be controlled. Some of them are highly selective oxidants and some other are highly regioselective in nature. Currently, the development of newer chromium (VI) reagents [10-19] for the oxidation of organic substrates continues to be of interest. Tertiary Butyl Chromate(TBC) has proven to be a potent and versatile oxidizing reagent, suitable for the direct introduction of a carbonyl group in an allylic position[20]. The compound was prepared for the first time by Wienhaus [21] but Oppenauer [22] introduced it as a new oxidizing reagent. In the last two decades, Tertiary Butyl Chromate and Tertiary Amyl Chromate(TAC) have gained considerable interest due to their use as oxidising agents. Many authors[23-30] have reported the oxidation of different organic compounds like Crotonic acid, Crotonaldehyde, Malonic acid, Diethyl malonate, Succinic acid, Dimethyl glyoxime, N,N-Dimethyl aniline, Glutamine etc by tertiary butyl chromate and tertiary amyl chromate.



Scheme-1 Structures of Chromium complexes used as oxidants

The present study aims to explore the potential of TBC and TAC for the selective oxidation of Propylene Glycol using different substrate: oxidant ratio for a better comparative study. Also, different solvents such as acetonitrile, dichloromethane, dioxane & tetrahydrofuran were used to determine their effect on the oxidation of propylene glycol. It deals with the investigation of the effects of oxidant nature and reaction conditions (temperature, concentrations of reagents, solvent nature etc.) on the product selectivity and yield.

Experimental

The chemicals used were all analytical grade. Freshly prepared solutions were used. The solubility of the products was also tested in water. Experimental methods used in the present work consist of -

i) *Preparation of TBC & TAC*

The oxidants i.e. TBC & TAC, have been prepared by dissolving weighed quantity of pure, dry & powdered chromium trioxide in calculated volumes of tertiary butyl alcohol and tertiary amyl alcohol respectively at room temperature. Care was taken to avoid bigger pieces of CrO_3 as this may lead to catching fire.

ii) *Preparation of the solutions of 1,2-Propanediol in different solvents*

Calculated amount of 1,2-Propanediol was dissolved in 10 ml of the solvents i.e. Dichloroethane, acetonitrile, THF and 1,4-dioxane etc. in a clean & dry beaker with constant stirring.

iii) *Oxidation of 1,2-Propanediol with TBC & TAC*

The solution of oxidant and that of substrate, prepared as above were mixed with constant stirring and gently heated. The reaction mixture, after having enough stirring and warming, as the case might be, was left for few hours for its completion. The solid products thus obtained were washed repeatedly with acetone, till the unreacted CrO_3/ unreacted substrates were washed off. The substrate: oxidant ratios (S:O ratios) used were 4:1, 2:1 and 1:1. Precautions were taken to avoid any violent reaction at the time of mixing. The solid products obtained were washed several times with acetone to remove the soluble impurities, unreacted CrO_3 or the substrate, if any, before collecting in clean, airtight glass bottles.

iv) *Estimation and Characterization*

The estimation of chromium in the products was done volumetrically using Potassium persulphate (in excess), 0.1 N Potassium dichromate and 0.1 N Mohr's salt solution. Percentage of carbon & hydrogen were estimated using "Elemental Analyser – Heraeus Vario EL III Carlo Erba 1108". The oxygen content was found out by subtraction of sum of total of percentage composition of C, H & Cr from 100. The Fourier Transform Infrared spectra were recorded on Shimadzu 8201PC (4000-400 cm^{-1}). The Thermogravimetric and differential thermal analysis (TG-DTA) of the compounds were carried out on "Thermal Analysis System-Perkin Elmer Diamond TG/DTA." The samples were heated at a rate of 100°C/min. in the temperature range of room temperature to 7000°C. Table-1 and Table-2 contains the reaction conditions under ordinary heating conditions.

RESULTS AND DISCUSSION

From the study of the nature of the products obtained by using various molar ratios of the oxidant, it seems that in higher ratio of the oxidant acetic acid and formic acid is formed as the oxidation product, that is, fragmentation is complete. So, the oxidation product did not undergo further oxidation and, hence, is available for the complexation with chromium in its reduced state. When the ratio of the oxidant was lower i.e. halved or made one-fourth, the oxidation products were found to contain CH_3-CH(OH)-CHO, and CH_3CO-COOH as the oxidation product indicating that the compound didn't undergo fragmentation, it

got simply oxidized & might have complexed with chromium as ligand or adduct. It is also noticed that when the oxidant is in higher ratio, colour of the complex formed is deeper in shade.

The oxidation products formed by the interaction of 1,2-Propanediol with TAC are almost same as in case of interaction with TBC. All the fragments observed in different complexes/compounds were as per the expectation on the basis of degradative oxidation products like $CH_3CH(OH)CHO$, CH_3-$CH(OH)$-$COOH$, $CH_3(CO)CHO$, $CH_3(CO)COOH$, CH_3CHO, CH_3COOH, HCOOH, HCHO etc.

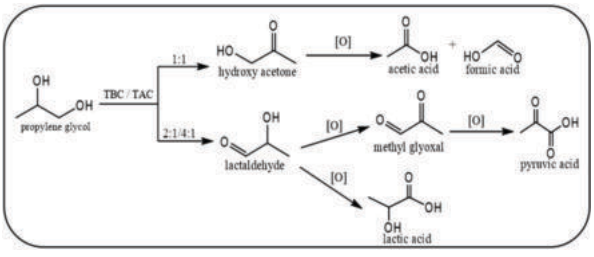
In case of THF as solvent, the degradative oxidation takes place even in lower ratio of oxidant leading to the formation of CH_3COOH, HCOOH and HCHO as in case of S:O ratio 4:1. All these fragments might have complexed with reduced state of chromium along with H_2O. In other ratios also, more or less same fragments like CH_3COOH etc are present in the product along with water. It is to be noted that the colour of the complexes in all the cases was green indicating the lower oxidation state of chromium.

Similarly, in case of acetonitrile as solvent, the extent of oxidation increases as the ratio of oxidant increases. For example, in S:O ratio 4:1 & 2:1 the fragment of three carbon atoms are there i.e. $CH_3COCOOH$. But when the ratio of oxidant increases to 1:1, the degradation takes place marked by the absence of three carbon ligands. The greenish colour of the complex in two cases indicates the reduction of chromium in lower state.

A very regular pattern is observed when dioxane is used as solvent. In lower ratio of oxidants S:O::4:1, less oxidized ligand, like $CH_3CH(OH)CHO$, is observed, whereas, a little bit more oxidized form CH_3COCHO is observed to be complexed with reduced form of Cr in 2:1 ratio. As expected, in the higher ratio of oxidant is 1:1, fragmented products like CH_3COOH, CH_3CHO etc are complexed with Cr. The colour of the complex shows the reduced state of Cr.

Table-1 Reaction Parameters For Oxidation Of 1,2-propanediol With Tbc

Product code	Solvent used	S:O ratio	Colour	Empirical formula	Formulation
T 1	THF	4:1	Light green	Cr2C5H20O12	Cr2O3·CH3COOH·CH3CHO·HCOOH·4H2O
T 2	THF	2:1	Green	CrC2H10O6	CrO.CH3COOH.3H2O
T 3	THF	1:1	Dark green	Cr2C3H12O7	Cr2O·CH3-CHO.HCOOH·3H2O
D 1	Dichloro methane	4:1	Light green	Cr2C6H21O11	Cr2O·CH3-CH(OH)-CHO.CH3-CO-COOH. 5H2O
D 2	Dichloro methane	2:1	Green	Cr2C5H15O8	Cr2O3·CH3CH(OH)-CHO.CH3CHO.2H2O
D 3	Dichloro methane	1:1	Grey	Cr2C3H12O7	Cr2O·CH3COOH·HCHO·3H2O
A 1	Aceto nitrile	4:1	Light grey	Cr2C5H19O11	Cr2O3.2CH3COOH.HCOOH.2H2O
A 2	Aceto nitrile	2:1	Dark green	Cr2C5H17O8	Cr2O.CH3CH(OH)-COOH.CH3CHO.3H2O
A 3	Aceto nitrile	1:1	Green	Cr2C3H14O7	Cr2O.CH3CH(OH)CHO.4H2O



Scheme-2 Oxidation of Propylene glycol by tertiary butyl chromate / tertiary amyl chromate

Table-2 Reaction Parameters For Oxidation Of 1,2-propanediol With Tac

Product code	Solvent used	S:O ratio	Colour	Empirical formula	Formulation
TT 1	THF	4:1	Light green	Cr2C7H16O14	2CrO2·2CH3COOH·2HCHO·HCOOH·2H2O
TT 2	THF	2:1	Bottle Green	Cr2C4H14O7	Cr2O·2CH3COOH ·2H2O
TT 3	THF	1:1	Dark green	Cr2C4H12O8	Cr2O·CH3COOH ·2HCOOH ·H2O
DT 1	Dioxane	4:1	Light green	Cr2C6H12O9	Cr2O3·2CH3-CH(OH)CHO·2H2O
DT 2	Dioxane	2:1	Light green	Cr2C5H14O7	Cr2O·CH3CO-CHO·CH3COOH ·2H2O
DT 3	Dioxane	1:1	Green	Cr2C4H12O6	Cr2O·CH3CHO·CH3COOH·2H2O
AT 1	Acetonitrile	4:1	Light green	CrC4H11O9	CrO2·CH3CO–COOH·HCHO·3H2O
AT 2	Acetonitrile	2:1	Greyish green	CrC4H8O8	CrO2·CH3CO–COOH·HCHO·2H2O
AT 3	Acetonitrile	1:1	Yellow brown	Cr2C3H10O10	Cr2O3·CH3COOH·HCOOH ·3H2O

CONCLUSION

I) It can be concluded from the study of oxidation of 1,2-Propanediol by TBC that it is oxidized to several products such as CH_3COOH, HCOOH, CH_3-$CH(OH)$-CHO, CH_3-CO-COOH and CH_3CHO. These oxidation products along with water, which is formed during the process of oxidation or may be absorbed from the atmosphere, are complexed with chromium to give complexes of different colour & composition. On the basis of study of formula given in Table-1, many generalisations could be made -

A) in THF as a solvent

a. In lower ratio of oxidant (S:O::4:1), the fragmentation has taken place but less oxidised CH_3CHO moiety is also there in the formulation.

b. In (S:O::2:1) only CH_3COOH moiety is there, whereas

c. In (S:O::1:1) the most degraded oxidation product HCOOH is formed i.e. the extent of oxidation increases as the proportion of oxidant increases.

B) in dichloromethane as solvent

Almost same generalisation with regard to extent of oxidation is concerned, but as compared to THF, the appearance of less oxidised moiety like $CH_3CH(OH)CHO$ in (S:O::4:1) and (S:O::2:1) shows that the oxidation is more efficient in THF.

C) However, no such conclusion could be drawn in case of acetonitrile as solvent for the substrate.

II) Study of the products formed by the oxidation of 1,2-Propanediol with TAC in the three solvents, leads to the conclusion that THF is more suitable for greater extent of oxidation as substantiated by the absence of three carbon ligands in all the three cases of different molar ratio.

The extent of oxidation is more in acetonitrile than in dioxane as supported by the fact that in S:O::4:1 ratio, the product is $CH_3COCOOH$ in case of acetonitrile as solvent whereas it is $CH_3CH(OH)CHO$ in case of dioxane. In case of S:O::2:1 also the products are $CH_3COCOOH$ and CH_3COCHO which leads to the same conclusion.

i. The extent of oxidation increases in the order of solvent as- Dioxane < acetonitrile < THF
ii. Green colour of the complexes shows the reduced state of Cr. The deepening of the colour, as the ratio of oxidant increases, may be due to increased proportion of Cr in reduced state.
iii. Dioxane is suitable solvent for slow controlled oxidation of organic substrate.

iv. DMSO is not a suitable solvent as the oxidation of substrate leads to viscous unidentifiable mass.

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