Asian J. Exp. Sci., Vol. 26, No. 1, 2012; 1-4

Microwave Assisted Oxidation of Malonic Acid in Dioxane and Tetrahydrofuran by Ditertiary Butyl Chromate and Ditertiary Amyl Chromate

Sangita Katre[1], Anita Kumari Gupta[2] and H. O. Pandey[3]
[1]Research Scholar, Department of Chemistry, R.U. Ranchi, [2]Deptt. of Chemistry, S. S. Memorial College, Ranchi, Jharkhand, and [3] Department of Chemistry, R.U. Ranchi, Jharkhand

Abstract : Microwaves are being used as an alternative heat source in organic synthesis. Microwave Assisted Organic Synthesis (MAOS) is being adopted in almost all the industrial, pharmaceutical and academic laboratories to carry out a variety of organic reactions. In recent years, researchers have applied microwaves as tool in order to minimise reaction time, avoid side products, increase yield and simplify the course of reactions for combinatorial chemistry. In this paper, we report the microwave assisted oxidation of malonic acid in dioxane and tetrahydrofuran (THF) as solvents by ditertiary butyl chromate (TBC) and ditertiary amyl chromate (TAC) which have proven to be potent and versatile oxidising agents.

Key words: Microwave, Malonic acid, Dioxane, Tetrahydrofuran, Ditertiary butyl chromate, Ditertiary amyl chromate

Introduction

The conventional method of organic synthesis carried out by heating with an external heat source is quite slow and a time consuming process. Further, it is an insufficient method for transferring energy to the reactants, as it results in the increase in temperature of the reaction vessel comparatively more than the reaction mixture (Neeraj *et al*., 2009; Singh & Pandey, 2010). In contrast, microwave dielectric heating results into fast and homogeneous internal heating of the reactants due to the direct coupling of microwave energy with the molecules of the reactants and solvents as the reaction vessels are made up of microwave transparent materials. The spectacular decrease in reaction time and hence quicker synthesis, clean product formation, improved conversions and a wide scope for development of new reaction conditions are some of the merits that make MAOS an energy and time efficient process (Hayes, 2002; Tierney and Lidstrom, 2004; United states Environmental protection Agency Retrieved, 2006).The redox processes involving malonic acid is known for a long time especially in its use in oscillatory chemical reactions (Belousov, 1959; Zhabotinsky, 1964). In addition, Mn (IV), Mn (VI) (Drummond and Water, 1954), Ce (IV) (Neumann *et al*., 1997), Cr (VI) (Senapati *et al*., 1985; Rao *et al.,* 1992) etc. are the other oxidants, which have been used by different workers, who have obtained formic acid and oxalic acid as the major oxidation products. The other expected products like tartonic acid, ketomalonic acid, glyoxalic acid and glycolic acid could not be obtained in detectable amount in most of the cases probably due to their instability (https://Jscholarship). In the present work, we have carried out the oxidation of malonic acid in different solvents, viz. dioxane and tetrahydrofuran by chromium (VI) based oxidising agents i.e. TBC and TAC under microwave irradiation in order to find out if any of expected products are formed. The solid products obtained are expected to be the complexes of these oxidation products with chromium in different oxidation states. The analysis of the products obtained in different molar ratios of substrate and the oxidants was done with the help of determination of elemental composition, FTIR peaks and thermogravimetric loss patterns

Materials and Methods

One gram of pure A.R. grade chromium trioxide (CrO_3) was dissolved in 10 ml of tert.butyl alcohol to get a clear brown solution of ditertiary butyl chromate (TBC) and the same process was repeated with tert.amyl alcohol to get ditertiary amyl chromate (TAC). These two oxidants were used separately to oxidise malonic acid in solvents, dioxane and tetrahydrofuran. For better comparison we have used different substrate: oxidant ratios (S:O ratio) namely 2:1, 1:1 and 1:2. The solution of the substrate (in stoichiometric amount) in a particular solvent was mixed carefully with the solution of oxidants (TBC and

---

1. **Corresponding author:**

TAC) and the resulting mixture was stirred vigorously before irradiating in microwave reactor at 160 W for the time as mentioned in Table 1 (Reactants). The solid products obtained thus, in different cases, were washed several times with acetone to remove the traces of substrate or oxidant left unreacted. The purity of the products was tested by TLC method before collecting them as samples M-1 to M-9.

The samples were analysed by different experimental methods namely, estimation of Cr by volumetric method, estimation of C, H and O by instrumental method, FTIR spectral analysis and thermogravimetric mass loss pattern analysis. The results leading to the formulations of the samples are tabulated in Table 2 (Products).

Results and Discussion

The formulations of the compounds/complexes have been done on the basis of FTIR peaks, thermogravimetric loss pattern etc. Many generalizations can be made on the basis of observations as in Tables 1 & 2:

- The reaction time is comparatively less when tetrahydrofuran is used as solvent for the substrate as compared to dioxane as solvent.
- In case of dioxane as solvent, the reaction time is less in case of TAC as oxidant as compared to TBC as oxidant.
- The colour of the products changes from greenish to brownish on increasing the proportion of oxidant which shows that Cr is mainly reduced to Cr (III) states. The brown colour when the proportion of oxidant is more may be due to the fact that oxidant is not consumed completely and a portion of oxidant is left as Cr (VI). Moreover, the possibility of brown colour due to charge transfer effect in presence of highly polarizable ligands can also not be ruled out.
- The products are mostly insoluble or sparingly soluble in water except M-4.
- The extent of oxidation is less when the proportion of oxidant is less as substantiated by the observation that malonic acid as such is present in M-1, M-4 and M-7 when S:O ratio is 2:1 alongwith acetic acid and water.
- Malonic acid is present in S:O ratio 1:1 also, except in case of M-5 where tetrahydrofuran is the solvent for the substrate. This shows that oxidation reaction is more efficient in THF as solvent. In this case oxidised moiety, oxalic acid along with acetic acid and water is there in place of malonic acid as such.
- In case of higher proportion of oxidant i.e. S:O ratio 1:2, the highly oxidised fragments like oxalic acid as in M-3, and formic acid as in M-9 are observed along with acetic acid and water which are the common constituents in all the cases.
- The colourful products obtained thus by oxidation of malonic acid by TBC and TAC may be the complexes of Cr in different oxidation states.
- The most striking observation in the experiment is the formation of acetic acid in addition to the common products, oxalic and formic acid in almost all the ratio in both the

Table-1 : Showing various reactants

Product code	Substrate	Solvent	Oxidant	S:O ratio	Irradiation time(in sec)
M-1	Malonic acid	Dioxane	TBC	2:1	100
M-2	,,	,,	,,	1:1	190
M-3	,,	,,	,,	1:2	210
M-4	,,	THF	,,	2:1	24
M-5	,,	,,	,,	1:1	40
M-6	,,	,,	,,	1:2	50
M-7	,,	Dioxane	TAC	2:1	100
M-8	,,	,,	,,	1:1	90
M-9	,,	,,	,,	1:2	130

solvents. Malonic acid is a fit case of β-decarboxylation which is observed when a carboxylic acid bearing C=O group in β-position, is heated to 150° C conventionally (Ucalgary.ca). The C=O group may be the part of aldehyde, ketone ester or carboxylic acid group itself as in the present case. The reaction takes place through six member cyclic transition states. We cannot rule out the possibility of the same mechanism operating here also especially in the light of the fact that ionic path is a remote possibility in non-aqueous medium of less polar solvents like dioxane and tetrahydrofuran. The presence of organic moiety in the products does not depend only on their stability but also on their ability to function as ligands. The absence of aldehydic products may be explained on the basis of their poor record as ligands though they are very much expected to be formed before their final conversion to acids. The absence of proposed products like ketomalonic acid etc does not clearly indicate their absence in the oxidation products. It may again be due to their inability to function as potential ligands. The above mentioned observations are in conformity to the observations of earlier investigators (Wang,2006; Belousor,1959; Zhabolinsky, 1964; Neuman *et al.,* 1997*)*

The Table 2 shows that the common oxidation products i.e. oxalic acid and formic acid are formed during the process along with water. The formation of acetic acid in almost all the cases is a striking observation which might have been the result of accompanying β-decarboxylation of the substrate. As regards the solvents the process of oxidation is more efficient in THF while it is more controlled in presence of dioxane. Chromium (VI) is largely reduced to Cr (III). The proper selection of solvent for the products and subsequent studies of magnetic, photometric, cryoscopic and other properties may lead to valuable information(Neeraj *et al*.,2009 : Singh & Pandey, 2010)

Acknowledgements:

The authors are thankful to SAIF, IIT Mumbai, CIF; BIT Mesra for thermogravimetric analysis and SAIF, CDRI, Lucknow for providing useful data on elemental analysis and FTIR spectra.

References

Belousov, B.P. (1959). A periodic reaction and its mechanism. Compilation of Abstracts on Radiation medicine 145-147

Drummond A.Y. and Waters W.A. (1954): Oxidation of malonic acid and its analogue*. J. Chem. Soc.* 2456-2467

Hayes B.L. (2002): Microwave synthesis, *Chemistry at the speed of light*. CEM Publishing, Mathews.

Table-2 Showing various products

Product code	**Colour**	**Solubility in water**	**Empirical formula**	**Proposed formulation**
M-1	Dull green	Sparingly soluble	$Cr_2C_5H_{13}O_{10}$	$Cr_2O_3.CH_3COOH.CH_2(COOH)_2.H_2O$
M-2	Light brown	,,	$Cr_2C_5H_{13}O_{11}$	$Cr_2O_3.CH_3COOH.CH_2(COOH)_2.2H_2O$
M-3	Reddish brown	,,	$Cr_2C_4H_{14}O_{15}$	$Cr_2O_3.2(COOH)_2.4H_2O$
M-4	Ash grey	Soluble	$Cr_2C_5H_{12}O_8$	$Cr_2O.CH_3COOH.CH_2(COOH)_2.H_2O$
M-5	Dull green	Insoluble	$Cr_2C_6H_{15}O_{13}$	$Cr_2O_3.2CH_3COOH.(COOH)_2.2H_2O$
M-6	Light brown	Sparingly soluble	$Cr_2C_2H_{10}O_8$	$Cr_2O_3.\ CH_3COOH\ .3H_2O$
M-7	Ash green	,,	$Cr_2C_5H_{12}O_8$	$Cr_2O.CH_3COOH.CH_2(COOH)_2.H_2O$
M-8	Light brown	Insoluble	$Cr_2C_5H_{13}O_{11}$	$Cr_2O_3.CH_3COOH.CH_2(COOH)_2.2H_2O$
M-9	,,	,,	$Cr_2C_3H_{11}O_7$	$2CrO.CH_3COOH.HCOOH.H_2O$

Neeraj, Pandey, H.O and G D Mishra, (2009) : Study of oxidation of some naturally occurring amino-acids by chromium containing oxidant-A. *J. Chemtracks*, **11 (1),** 251-256.

Neumann, B; Oliver, S ; Muller S.C and Dalal N.S. (1997): Stoichiometric Fingerprinting as an aid in understanding complex reactions-The oxidation of malonic acid by Cerium(IV). *J. Phys. Chem, A* **101**, 2743-2745.

Singh R. and Pandey H.O. (2010) : Study of the compounds formed by the oxidation of some organic compounds with non-classical Cr and Mn based oxidants. Thesis; Ranchi University, Ranchi.

Rao I, Mishra S.K. and Sharma P.D. (1992) : Kinetics and mechanism of oxidation of malonic acid by chromium (VI) in aqueous perchlorate medium. *Transition met. Chem*. **17**, 449-454.

Senapati, M; Panigrahi, G.P and Mahapatro, S.N. (1985): Pathways in chromic acid oxidation; kinetics and mechanism of oxidation of malonic acid. *J. Org. Chem.* **50**: 3651-3655.

Tierney J.P. and Lidstrom, P. (2004). *Microwave Assisted Organic Chemistry*. Taylor and Francis Group, Abingdon.

Ucalgary.ca/course/350/Carey5th/chapter19/Ch19-3-4.html

United States Environmental Protection Agency Retrieved (2006). *The 12 principles of Green Chemistry* pp-07-31

Y.Wang (2006) : Https:// jscholarship. library. jhu.edu/ bitstream/ handle/ 1774.2/ 858 Reduction of MnO_2 (birnessite) by Malonic acid, Acetoacetic acid, Acetylacetone and Structurally related compounds Chapter- 4[1].Malonate pp 143 (pdf).

Zhabotinsky, A.M. (1964). Periodic process of malonic acid oxidation in liquid phase. *Biofizika.* **9,** 306-311.