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Research Article

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Ru (III) Catalysed Oxidative Degradation of Sodium Bisulphite Derivatives of Aromatic Aldehydes by Potassium Hexacyano Ferrate (III) in Aqueous Alkaline Medium

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ABSTRACT

Introduction: The catalysed oxidation of the derivatives of aromatic aldehydes with inorganic moieties is still unstudied with economically cheaper oxidant like potassium hexacyano ferrate (III). The catalyst like ruthenium (III) chloride is very much effective at very low concentration for the oxidation reactions.

Aims: The study is carried out to observe and to get the results about the oxidative degradation of derivatives of organic and inorganic moieties.

Methodology: Benzaldehyde sodium bisulphite (BSS) and substituted aromatic aldehyde sodium bi sulphite like p-chloro benzaldeyde sodium bisulphite, p-methyl benzaldehyde sodium bisulphite, etc. are dissolved in water, can be oxidized in good yield by potassium hexacyanoferrate (III) as PHF in aqueous alkaline medium in presence of ruthenium (III) chloride. Result: The process requires lesser time and probably intermediate complex of ruthenium (III) chloride, substrate and oxidant give the products.

Conclusion: Oxidative degradation of Benzaldehyde sodium bisulphite (BSS) and substituted aromatic aldehyde sodium bisulphite like p-chloro benzaldeyde sodium bisulphite, p-methyl benzaldehyde sodium bisulphite, etc. give moderate to good yield of corresponding aromatic acids in presence of potassium hexacyanoferrate (III) and ruthenium (III) chloride.

Key Words: PHF, Ruthenium (III) catalysis, BSS, Aromatic Acids, Intermediate complex, Oxidation

INTRODUCTION

A large number of oxidant[1,2,3] till now have been used in the oxidation of organic compounds like perchloric acid, lead tetra acetate, trivalent manganese, chromium (VI), osmium tetroxide, ferricyanide, cerium (IV) including molecular oxygen in acetic acid[4]and alkaline[5]mediaetc.From the synthetic point of view there is a need to study these potentially boosted oxidants with transition metal catalysts to get cheaper path of synthesis and to get high amount of yields which are environmentally less harmful. Communally used oxidant apart from being costly and requires drastic conditions. As an oxidant PHF is cheaper and safer. PHF is used for oxidation of aliphatic alcohols, acid, aromatic acid and phenol but it is not used for aromatic aldehydes having inorganic moiety. Transition group metals like Osmium, Iridium, Tungsten, etc. have successfully been used as homogeneous catalysts. Osmium is injurious in acidic medium and restricted in alkaline media only, therefore ruthenium[6] compounds were preferred and their catalytic activities were widely studied[7,8] in acidic as well as in alkaline media. Comparison of catalytic virtues of ruthenium (III) [9a] and ruthenium (VIII)[9b] in acidic media were reported by Krishana and Tandon. Latter on the oxidation of aliphatic hydroxyl compounds along with diols has been reported with ruthenium (VIII). Moreover osmium adds to the multiple bonds whereas ruthenium breaks the double bonds.[10] Catalysis in single and uniform medium by ruthenium and osmium and other precious transition metals were reported by many workers. Several workers have studies the oxidation of inorganic species by PHF.[11,12] The aromatic aldehydes with inorganic moiety have more virtues to form a homogeneous medium to form the intermediates with PHF and ruthenium (III) to form the required product.

MATERIALS AND METHODS

IR spectra were taken with Bruker Vector 22 IR spectrophotometer and ^{1}NMR spectra with a xeol 400 MHz

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spectrophotometer in $CDCl_3$ with TMS as internal standard. Commercial reagents used as such supplied by traders. All reaction and product identification were observed with the help of TLC with Merck silica gel-coated plates. MP, mmp and other identification parameters were done by as usual methods. The sodium bi sulphite derivative of each aromatic aldehyde was prepared by saturated solution of sodium bi sulphite. Yields of the product of corresponding aldehydes of sodium bi sulphite are given in table number 1.

Benzaldyhyde sodium bi sulphite (4.70 mmol) was taken in the round bottom flask with $1.0*10^{-5}$M of ruthenium (III) chloride and 20 ml of N/2 NaOH. 10 mM of PHF was added to it. The solution was left for two hours at required temperature then this was acidified with N/2 HCl until the NaOH in the solution fully neutralize and was extracted with ether dried over magnesium sulphate and solvent was removed under reduced pressure. The obtained benzoic acid was recrystallised in ethanol. Yield of this white benzoic acid was 70% (0.40 g). Mmp 121^{0}C (Reported 122 ^{0}C). In this case NMR spectra was taken 1HNMR (CDCl3 400 mhz) and IR in KBr. IR max 3068 nm (for OH); 1609 nm (for C=O); NMR ppm; 7.48 (2H, t); 7.62(1H, t) 8.12 (2H, d).

p-Nitro bernzaldehyde sodium bi sulphite was oxidized to p- Nitro benzoic acid similarly as above. The mmp was 235 ^{0}C (Reported 237 ^{0}C). IRmax 3111 nm (for OH), 1694 nm (for C=O) & 1541 nm (for NO_2)

p-Methoxy benzaldehyde sodium bi sulphite was oxidized to p- Methoxy benzoic acid similarly as above. The mmp was 181 ^{0}C (Reported 184 ^{0}C). IRmax 2982 nm (for OH), 1683 nm (for C=O), 1601 nm (for C=C), 1297 nm (for O-C=C) & 1164 nm (for O-C).

p- Chloro benzaldehyde sodium bi sulphite was oxidized to p- Chloro benzoic acid in a same manner as above. The mmp was 238 ^{0}C (Reported 241^{0}C). IRmax 2975 nm (for OH) & 1684 nm (for C=O),

p- Bromo benzaldehyde sodium bi sulphite was oxidized to p- Bromo benzoic acid similarly as above. The mmp was 148 ^{0}C (Reported 150 ^{0}C). IRmax 2982 nm (for OH), 1683 nm (for C=O), 1601 nm (for C=C), 1297 nm (for O-C=C) & 1164 nm (for O-C).

p- Methyl benzaldehyde sodium bi sulphite was oxidized to p- Methoxy benzoic acid similarly as above. The mmp was 178 ^{0}C (Reported 181 ^{0}C). IRmax 2989 nm (for OH) & 1685 nm (for C=O).

Cinnamaldehyde sodium bi sulphite was oxidized to cinnamic acid similarly as above. The mmp was 131^{0}C (Reported 134 ^{0}C). IRmax 3061 nm (for OH), 1683 nm (for C=O) & 1493 nm (for C=C).

RESULTS AND DISCUSSION

BSS and other substituted aldehydes of sodium bisulhites are soluble in water and alkaline solution. The oxidation of BSS and other substituted aldehydes of sodium bisulhites yield substituted aromatic acids in which all parameters are checked and it has seen that ruthenium (III) chloride is an important factor as a catalyst in this oxidation. The concentration of catalyst increases the formation of product of reaction. Ruthenium as a catalyst enhances the extent of completion of reaction in less than stipulated rime at very low concentration. So the reduction of oxidant in time and to obtain maximum yield both the things is achieved. Ruthenium (III) catalysed oxidation of the given aldehydes sodium bisulphate was done under the constant ionic strength where the uncatalysed reaction is under observation. The obtained results were confirmed by studying the individual sets in each variation at two different concentrations of catalysts. In the individual runs also it was observed that with progress of the reaction, there is an increase of potassium hexacyano ferrate (II) in the reaction due to this the reaction slows down and ultimately stops. It has been reported that the complex formation between ruthenium (III) and substrate molecules for oxidation due to the exchange of hydroxide ion.[13] Electronic spectra[14] studies have confirmed that rathenium(III) chloride exists in the hydrated form as $[Ru(H_20)_6]^{3+}$. In alkaline medium $[Ru(H_2O)_6]^{3+}$ also exists in the form of $[Ru(H_20)_5OH]^{2+}$. There is very much less effect of concentration of sodium hydroxide on the formation of corresponding acids for corresponding bi sulphite aldehydes.

Table 1: Oxidation of various organic compounds by Potassium Hexacyano Ferrate (III) (PHF) in aqueous alkaline medium in the presence of $RuCl_3$

Organic Compounds	Products	PHF (mmol)	NaOH (mmol)	$RuCl_3$ x 10^{-5} mol	Temp. (^{o}C)	Time (In Hours)	Yield (%)
Benzaldihyde sodium bi sulphite (4.70 mmol)	Benzoic acid	10 mmol	10 mmol	1.0	50	2.0	70 (0.40g)
p-Nitro bernzaldehyde sodium bi sulphite (3.90 mmol)	p-Nitro benzoic acid	10 mmol	10 mmol	1.0	50	2.0	64 (0.41g)
p-Methoxy benzaldehyde sodium bi sulphite (4.10 mmol)	p-Methoxy benzoic acid	10 mmol	10 mmol	1.0	50	2.0	56 (0.35g)

Table 1: *(Continued)*

Organic Compounds	Products	PHF (mmol)	NaOH (mmol)	$RuCl_3$ x 10^{-5} mol	Temp. (°C)	Time (In Hours)	Yield (%)
p- Chloro benzaldehyde sodium bi sulphite (4.08 mmol)	p- Chloro benzoic acid	10 mmol	10 mmol	1.0	50	2.0	60 (0.38g)
p- Bromo benzaldehyde sodium bi sulphite (3.46 mmol)	p- Bromo benzoic acid	10 mmol	10 mmol	1.0	50	2.0	62 (0.43g)
p- Methyl benzaldehyde sodium bi sulphite (4.46 mmol)	p- Methyl benzoic acid	10 mmol	10 mmol	1.0	50	2.0	60 (0.36g)
Cinnamaldehyde sodium bi sulphite (3.78 mmol)	Cinnamic acid	10 mmol	10 mmol	1.0	50	2.0	55 (0.30g)

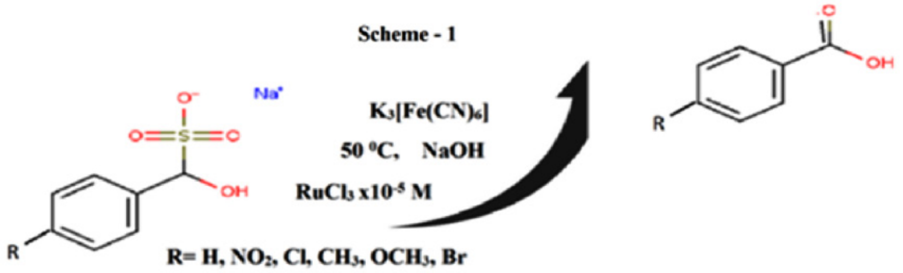

Figure 1

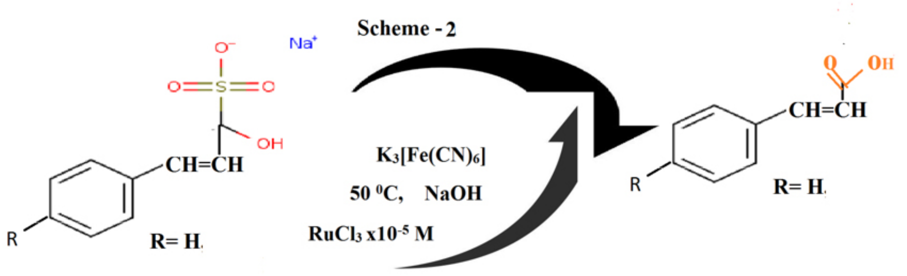

Figure 2

Table 2: Oxidation of Benzaldehyde Sodium bi sulphite by Potassium Hexacyano Ferrate (III) (PHF) in aqueous alkaline medium in the presence of $RuCl_3$

S.N.	PHF (mmol)	NaOH (mmol)	$RuCl_3$ x 10^{-5} mol	Temp. (°C)	Time (In Hours)	Yield (%)
1	10 mmol	10 mmol	0.25	50	2.0	39
2	10 mmol	10 mmol	0.05	50	2.0	56
3	10 mmol	10 mmol	1.00	50	2.0	70
4	10 mmol	10 mmol	2.00	50	2.0	82
5	10 mmol	10 mmol	3.00	50	2.0	84
6	10 mmol	10 mmol	4.00	50	2.0	86
7	10 mmol	10 mmol	5.00	50	2.0	86
8	10 mmol	10 mmol	6.00	50	2.0	86

In the table 1 the oxidation of various sodium bisulphate derivatives of aromatic aldehydes is shown by the use of potassium hexacyano ferrate (III) (PHF) in aqueous alkaline medium in the presence of $RuCl_3$ and in the table 2 the oxidation of Benzaldehyde Sodium bi sulphite by Potassium Hexacyano Ferrate (III) (PHF) in aqueous alkaline medium in the presence of different concentration of $RuCl_{3.}$ In the structural representation of figure 1 the oxidation of sodium bisulphite derivative of substituted aromatic aldehydes at para position is shown whereas in figure 2 there is a representation of oxidation of sodium bisulphite derivatives of aromatic aldehyde with unsaturated side chain.

CONCLUSIONS

The above study shows that the obtained results are very much important from the academic as well as industrial point of view along with environmental friendly. The ruthenium (III) is used in very low concentration as catalysts as compare to other transition metal catalysts. The obtained results of the product formation are quite compatible with other process of preparations.

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REFERENCES

1. Jonge M. De. Organic Synthesis by Oxidation with Metal Compounds, Plenum, Newyork, 1986, 839-876.
2. Hundicky M., Oxidations in Organic Chemistry, Am. Chem. Soc., Washington, 1990, 838-840.
3. Rappoport Z., Second Eds, Synthesis of Carboxylic Acids, Esters, their Derivatives, Wiley Chichester 1991, 357-360.
4. Russel G.A., Selective Oxidation Processes. Am. Chem. Soc., Washington DC, 1965, 112-173.
5. Sonsnovasky D., In Organic Peroxides, Wiley Interscience USA, Vol. 1, Sweren D (ed) 1970, 517-560.
6. March J., Advansed Organic Chemistry, McGraw Hill Inc. 2004, 698, 1162, 1167, 1169, 1181-1182, 1191-1192 – 1196, 1200 &1235.
7. Singh M, Singh H.S, Verma M.K.; Kinetics and mechanism of the ruthenium(III) chloride catalyzed oxidation of butanone-2 and pentanone-3 by cerium(IV) sulfate in aqueous sulfuric acid medium, J. phys. Chem., 1980, 84, 3, 256-159
8. Tandon P. K., Manibala, Singh H.S., Krishna B., Mechanism of Ruthenium(III) chloride Catalysed Oxidation of Cyclopentanol, Cyclohexanol and Cycloheptanol by Cerium(IV) Sulphate in Aqueous Sulphuric Acid Medium, Z. phys. Chemie, Leipzig, 1984), 3, S. 265, 609-61
9. (a) Srisailam V., Rao M.A., Kinetics and mechanism of the ruthenium (III)-catalysed oxidation of aliphatic acids by peroxodiphosphate in acetate buffers. Transition Met Chem, (1994) 19, 257–259 (b) TeresaM., Nunez and Martin Victor S., Efficient oxidation of phenyl groups to carboxylic acids with ruthenium tetraoxide. A simple synthesis of (R)-.gamma.-caprolactone, the pheromone of Trogoderma granarium, *J Org. Chem,* **1990,** *55*, 6, 1928-1932 (b)
10. Barkowitz L.M., Rylander P.N., Use of Ruthenium Tetroxide as a Multi-purpose Oxidant, J. Am. Chem. Soc., 1958, 80, 24, 6682-6684
11. Friedman H.B., Anderson B. E., Neutral Salt Action. I. The Effect of Neutral Salts on the Velocity of the Reaction $2Fe(CN)_6^{\equiv}$ + $3I^-$ → $2Fe(CN)_6^{[UNK]}$ + I_3^-, J. Am. Chem. Soc. 1939, 61, 1, 116-118.
12. Wagner C., Der Mechanismus der Oxydation des Jodions durch Ferricyanion und Ferriion, Z Phys Chem, 1924, 113, 261-274
13. Singh H. S. , Singh R. K., Singh S. M., Sisodiya A. K., Kinetics and mechanism of the ruthenium(III) chloride catalyzed oxidation of butan-2-ol and methyl-1-propanol by the hexacyanoferrate(III) ion in an aqueous alkaline medium, J. Phys. Chem. (1977), 81, 11, 1044–1047
14. Cotton F. A., Wilkinson G., Advanced Inorganic Chemistry, 2rid Edition, 1980, 918 & 919