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RUTHENIUM (III) CHLORIDE AS A GREEN CATALYST

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The aromatic compounds p-nitrobenzaldehyde, p-chlorobenzaldehyde, cinnamaldehyde, o-hydroxy benzaldehyde, 4-hydroxy-3 methoxy benzaldehyde, o-dihydroxy benzene, p-dihydroxy benzene naphthalene and phenanthrene dissolved in aqueous acetic medium or in aqueous medium were oxidized in quantitative to moderate yields by 50% $H_2 O_2$ in the presence of traces of $RuCl_3$ (10^{-8} mol, substrate : catalyst ratio 1488 : 1 to 387500 : 1) conditions for highest yield, in the most economical way were obtained. The yield is decreased owing to higher catalyst concentrations. Oxidation in aromatic aldehydes is selective at aldehydic group only while other groups remain unaffected. The oxidation in phenanthrene depends on the relative amount of substrate or temperature or both. This new, simple and economical method is environmentally safe and requires less time. The oxocentered carboxylate species of ruthenium (III) probably acts as a catalyst to the oxidation.

KEYWORDS : Oxidation, activated hydrogen peroxide, ruthenium (III) chloride, oxo-centered carboxylate species, aromatic oxidation.

INTRODUCTION

From the synthetic points of views, a large number of oxidants [1-5] have frequently been used for the oxidation of organic components. In catalyzed oxidation of aldehydes, it was recently observed that gold on carbon [6] in CCL_4 is more efficient than Pt- C system in H_2O or H_2O-CH_3CN used as solvents. Commonly used oxidants, apart from being harmful to the environment, also require drastic condition and are costly. Hydrogen peroxide has received continued interest as an oxidant and is found to be safer, cheaper and has high active oxygen content. since the by-product formed is water, it is clean and does not require a buffer. It is commonly used for the oxidation of aromatic aldehydes to carboxylic acid under strongly basic conditions [7], hydroxylation of aromatic with $AlCl_3$ [8], epoxidation of olefins [9], oxidation of Benzyl chlorides [10], oxidation of aromatic aldehydes by magnesium monoperoxypthalate, etc [11]. Recently, conversion of aromatic and aliphatic aldheydes to carboxylic acids in organic solvent-, halide – and metal-free conditions with $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (PTC) [12] and benzyl alcohol to benzaldehyde under halide free condition in the presence of (PTC) [13] have been reported. Ruthenuim-catalyzed oxidation of alcohol by

H_2O_2 [14], by perautic acid [15] in the presence of bimetallic catalyst [16] and under (PTC) conditions has also been reported. However, the systems containing dimethyl sulfate, that are used to prepare PTC, are reported to be carcinogenic. The efficiency of the Ru (III) H_2O_2 system in the conversion of aromatic alcohols, aldehydes, hydrocarbons, etc. in an acetic acid medium [18] have been reported. The potential of the present system for conversion of various other groups is explored both in aqueous and acetic acid medium. The oxidation by 50% H_2O_2 of p-nitrobenzaldehyde, p-chlorobenzaldheyde, cinnaalaldheyde, o-hdydroxybenzaldheyde, 4-hydroxy 3-methoxybenzaaldheyde, o-dihydroxybenzene, p-dihydroxybenzene, naphthalene and phenanthrene in the presence of traces of ruthenium(III) chloride is herein reported for the same. This study was carried out mainly to see the efficiency of economy of the simple and novel Ru(III)- H_2O_2 system to oxidize various organic compounds like the easy-to-oxidize aldehydes to the comparatively difficult –to- oxidize hydrocarbons in acetic acid and in aqueous media.

RESULTS AND DISCUSSION

The effect on the yield was negligible, both in the case of H_2O_2 addition in small amounts at regular intervals or continuous addition drop wise. The possibility of wasteful decomposition of H_2O_2 is thus eliminated if the whole amount of H_2O_2 is added at the starting of the experiment. Since the yield is not affecttted upon increasing the amount of acetic acid (above the minimum amount required to keep the reaction mixture homogenous in a, b, c, h, and i) it is clear that it acts only as a solvent. The addition of $RuCl_3$ in the case of aldehydes and hydrocarbons does not catalyze the reaction at the room temperature, indicating that $RuCl_3$ itself or $RuCl_6^{3-}$ species, which exist in aqueous acidic medium [19-20] at 25°C, may not catalyze the reactions. It was found that in all cases the yield first reaches a maximum and then starts decreasing with increase in the catalyst concentrations. This is probably due to the unproductive decomposition of H_2O_2, which increases with increase in the concentration of transition metal ions. The electron abstracting – NO_2 group, and – Cl group, when present in the ring, facilitates the yield of acid compared to the presence of electron donating –OH groups. Thus a quantitative yield of p-nitrobenzoic acid and p-chlorobenzoic acid was obtained at lower catalyst concentrations. Acetic acid was not used as a solvent since the aromatic dihydroxy alcohols are readily soluble in an aqueous medium. In all cases, the running of thin layer chromatography (TLC) plates showed no spot other than the unrelated compound or the product. It has been reported[21] that $RuCl_3$ may give rise to oxo-centered carboxylates $[Ru_3O(O_2C.CH_3)_6L_3]^+$ species (where L may be H_2O_2 py etc.) when heated at near-reflux temperature with acetic acid. These species may undergo reversible redox steps [22]. Trinuclear carboxylates have been reported to be an effective catalyst for the aerobic oxidation of aliphatic alcohols [23]. The catalytic activities of the above complexes are approximately 10 times higher than that of $RuCl_3$[24]. This is also observed in the present study, as a substrate: catalyst ratio ranging from 1488:1 to 387500:1 was good enough for the quantitative conversion of different functional groups including the hydrocarbons. The formation of HO_2, OH and OH^- during the catalytic decomposition of H_2O_2 with metal ions is well documented [25]. The presence of $RuCl_5\,(H_2O)^{2-}$ species, as reported by other workers[19,20], has been also considered to act as a catalyst in this study carried out in aqueous medium in the absence of the acetic acid. The ion-exchange technique confirmed that the ruthenium (III) chloride forms $RuCl_6^{3-}$ species [26-28] in hydrochloric acid medium and aquation of $RuCl_6^{3-}$ to $RuCl_5\,(H_2O)^{2-}$ takes only a few seconds [29, 30].

P-nitrobenzaldehyde (a^1, 0.66 m mol) was dissolved in glacial acetic acid (35 m mol). After adding $RuCl_3$ ($1.2x10^{-5}$ m mol), 50% H_2O_2 (155 m mol) was added. The mixture was kept at 80^0C for 90 min. The pouring of the contents on crushed ice resulted in a precipitate, which was then filtered. The filtrate after extracting with (3x10.0ml) ether, was dried over anhydrous $MgSo_4$ solvent was removed under reduced pressure. After recrystallyization with ethanol, p-nitrobenzic acid (a) was obtained as a white solid (110 mg, 100%); m.p. 237^oc (reported 241^oc) IR:V_{max} 3111 nm (V_{-0H}), 1694 nm ($\surd_e$=0); 1541 nm($\surd$-NO_2) p-chlorobenzoic acid (b) prepared similarly and recrystalization with hot ethanol gives the compound as a white solid (1.11 g, 100%) , m.p. 239°c (reported 241°c), IR $\surd_{max}$, 2974 nm ($\surd_-$ OH), 1685 nm ($\surd_{c=0}$).

Cinnamic acid (c) was prepared in the same manner. After extracting with diethyl ether and recrystalizing with hot water, a compound was obtained as white solid (1.15 g, 100%); m.p. 132^oc (reported 134^oc) compound gave the test for instauration, IR $\surd_{max}$ 3060 nm ($\surd_-$ OH), 1683 nm ($\surd_{c=0}$). O- hydroxy benzoic acid (d) prepared in the same manner was extracted with ethyl acetate and was dried with $MgSO_4$. The solvent was evaporated under relatively reduced pressure and with a portion of the reddish-yellow solution, GLC studies were performed. Peak 11, area (%) 0.219; RT, 25.38 min. the yield obtained was 14% (0.179 g). 4-hydroxy 3-methoxy benzoic acid (e), prepared in the same manner, was extracted with ethyl autate and dried with $MgSO_4$. The solvent was evaporated under relatively reduced pressure and with a portion of the reddish-yellow solution, GLC studies were performed. Peak 7, area (%), 1.05; RT, 44.07 min. the yield obtained was 59% (0.652 g). Polyphenal (f). reaction in this case was performed in an aqueous medium in the absence of any acid. Unfortunately, under the experimental conditions given in Table1, the reaction mixture polymerized. The IR spectra of the polymerized mass showed √max 3791 nm (√-oh phenlic), 3231 nm (√c=ch or Ar-H), 1272 nm (√c-oc), 874 nm (√disubstituted benzene). Quinhydrone (g). in this case, also the reaction was performed in the absence of an acid. The characteristic green crystals were washed repeatedly with some distilled water. The weight of dried precipitate was 446 mg (96%); m.p.: 170^oc (reported 174^oc) IR: $\surd_{max}$ 3622 nm ($\surd_{-O-H-O}$) bounded), 3232 nm ($\surd_{-OH}$), 3063 nm ($\surd_{c=c}$), 2749 nm ($\surd_{-CH}$), 1629 nm ($\surd_{-c=o}$), 874-832 nm ($\surd_{\text{disubstitutd benzene}}$). α–naphthol (h) was prepared in the same manner. The mixture was diluted with water to separate unreacted naphthalene, and on extracting the remaining solution with diethyl ether (3 × 25 ml), the product was obtained as black mass, which was then recrystallized with benzene (17 mg, 15 %); m.p. 77°C (reported 80°C). The compound gave a positive test for phenolic group. IR $\surd_{max}$ 3053 nm ($\surd$ $-_{c=CH}$),1146 nm($\surd_{c-o}$),904 – 761 ($\surd_{\text{subs. benzene ring}}$) , NMR , δ 7.73 – 7.67 (3 Hm) , δ 7.43 – 7.38 (4 Hm)

Phenanthraquinone (i): prepared similarly as h to give needle shaped yellowish orange crystals, which were identified by TLC (0.165 g, 80 %); m.p 207^0 C (Reported 210^0 C)

The present system (Scheme 1) is easy & efficient and can be used for the oxidation of a wide variety of functional groups from the synthetic view and also in the laboratory for demonstration purpose. The present system require more oxidents but is still more economicalal than many other prevailling methods because of the nominal cost of the catalyst.(catalyst: substrate ration is 1:1488 to 1:387500) and the catalyst and acetic acid (wherever used to solvent) can be regenerated it is environmentally benign, as no harmful side products is formed. The system is similarly effective for several other organic compounds containing a wide variety of functional groups, the study for which is in progress.

EXPERIMENTAL

In all cases the IR spectra were taken with a brucker vector – 22 IR spectrometer and HNMR spectra were taken with a xelol 400 MH_z spectrophotometer on $CdCl_3$ with tetramethyl silane as internal standard gas liquid chromatography (GLC) studies were performed with a varian vista 6000 commercially obtained reagents were used and without further purification all reactions were monitored by TLC with merck GF254 Silica – gel – coated plates. $RuCl_3$ (Johnson mathy & Co.) was dissolved in the minimum amount of HCl, and the final strengths of the acid and catalyst were 4.82×10^{-3} M and 4.0×10^{-3} M respectively. The identification and purity of the products were confirmed by melting point, molecular weight determination, mixture melting point TLC, by neutralization equivalent, preparing derivative, IR, NMR and GLC studies. To obtain the maximum yield , five to eight concentration or conditions of each component , which can affect the yield In general , to the mixture or organic compound in aqueous acetic acid (a , b , c , h and I) , in water (d, e , f and g) and catalyst , the requisite quantity of 50 % H_2O_2 was added and the mixture was heated for the required time after completion of the reaction the content were cooled , separated and analyzed for the products.

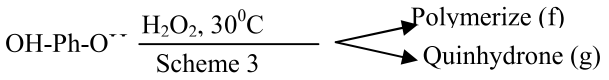
Table 1. Oxidation of various organic compounds 50 % H_2O_2 in aqueous acetic acid (a, b, c, h and I), aqueous (d, e, f, g) media in the presence $RuCl_3$ (Organic subtracts taken : a' 0.66 m mol b' 6.1 m mol , c' 7.1 m mol , d ' 9.3 m mol e' 7.0 m mol, f' 4.5 m mol, g' 4.6 m mol h' 0.78 m mol, i' 1.1 m mol).

Organic Substrate	**products**	**H_2O_2 m mol**	**Acetic Acid m mol**	**$RuCl_3$ 10^{-5} m mol**	**Temp °C**	**Time H**	**Yield %**
P – Nitrobenzaldehyde (a')	P – nitrobenzoic acid (a)	155	35	1.2	80	1.5	100
P – Chlorobenzaldehyde (b')	P – chlorobenzoic acid (b)	140.6	43.7	1.2	80	1.5	100
Cinnamaldehyde (c')	Cinnamic acid (c)	140.6	87.5	2.8	100	1.0	100
O – hydroxy benzaldehyde (d')	0 – hydroxybenzoic acid (d)	159	87.5	2.4	80	1.5	14
4 – hydroxy – 3 – methoxy – benzaldehyde (e')	4 – hydroxy – 3 methoxy – benzaldehyde (e)	159	1.7	2.4	80	1.5	57
O – dihydroxy benzene (f')	Polymerized (f)	14	-	307	30	2.0	-
P – di hydroxyl benzene (g')	Quinhydrone (g)	14		153.6	30	1.0	90
Naphthalene (h')	α- naphthol (h)	210	350	19.6	100	4.0	15
Phenamthracene (i')	Anthraquinone (i)	70.5	175	19.2	80	2.0	80

Scheme 1 Oxidation routes of the various organic substrates

$$X-Ph-CHO \xrightarrow[\text{Scheme 1}]{AcOH,\ H_2O_2,\ 30°C} X\text{-}Ph\text{–}COOH \quad (a, b, c, d)$$

$$X\text{-}Ph \xrightarrow[\text{Scheme 2}]{AcOH,\ H_2O_2,\ 30°C} X\text{-}Ph\text{-}OH \quad (h \ \&\ i)$$



$RuCl_3$ (~ 10^{-8} mol) : X = NO_2 (a), Cl (b)
H (c), -OH (d & e), Ph = Ph (f, g, h & i)

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