APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 1079–1082
Materials, Nanoscience and Catalysis AOC

Simple one-pot conversion of organic compounds by hydrogen peroxide activated by ruthenium(III) chloride: organic conversions by hydrogen peroxide in the presence of ruthenium(III)

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Received 10 March 2004; Revised 20 March 2005; Accepted 9 May 2005

The aromatic compounds *p*-nitrobenzaldehyde, *p*-hydroxybenzaldehyde, naphthalene, toluene, catechol, quinol, aniline and toluidine dissolved in aqueous acetic acid or aqueous medium were oxidized in quantitative to good yields by 50% H_2O_2 in the presence of traces of $RuCl_3$ ($\sim 10^{-8}$ mol; substrate/catalyst ratio 1488 : 1 to 341 250 : 1). Conditions for highest yields, in the most economical way, were obtained. Higher catalyst concentrations decrease the yield. Oxidation in aromatic aldehydes is selective at the aldehydic group only. In the case of hydrocarbons, oxidation results in the introduction of a hydroxyl group with >85% (in the case of toluene) selectivity for the ortho position. Formation of low-molecular-weight polyaniline was reduced to 10%, along with 90% formation of higher molecular weight polyaniline. In this new, simple and economical method, which is environmentally safe and requires less time, oxo-centered carboxylate species of ruthenium(III) in acetic acid medium and hydrated ruthenium(III) chloride in aqueous medium probably catalyze the oxidation. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: activated hydrogen peroxide; ruthenium(III) chloride; oxo-centered carboxylate species; aromatic oxidation; low and higher molecular weight polyanilines

INTRODUCTION

From the synthetic point of view, a large number of oxidants[1–5] have frequently been used for the oxidation of organic compounds. 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 conditions and are costly. Hydrogen peroxide, which has received continued interest as an oxidant, is safer, cheaper, has high active oxygen content, does not require a buffer and is clean, since the by-product formed is water. It has been used for the oxidation of aromatic aldehydes to carboxylic acids under strongly basic conditions,[7] epoxidation of olefins,[8] hydroxylation of aromatics with $AlCl_3$,[9] oxidation of benzyl chlorides,[10] oxidation of aromatic aldehydes by magnesium monoperoxypthalate, etc.[11] Recently, conversions of aromatic and aliphatic aldehydes 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 conditions in the presence of PTC[13] have been reported. Ruthenium-catalyzed oxidation of alcohols by H_2O_2,[14] by peracetic acid[15] under PTC conditions and in the presence of bimetallic catalyst[16] has also been reported, but the systems containing dimethyl sulfate, which is used to prepare PTC, are reported to be carcinogenic.[17] We have reported the efficiency of the $Ru(III)–H_2O_2$ system in the conversion of aldehydes, hydrocarbons, aromatic alcohols, etc. in an acetic acid medium.[18] To explore the potential of the present system for conversion of various other groups, both in acetic acid and in an aqueous medium, herein the oxidation

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Contract/grant sponsor: U.G.C.; Contract/grant number: F.12-97/2001(SR-I).
Contract/grant sponsor: C.S.T.; Contract/grant number: CST/D-3205.

of *p*-nitrobenzaldehyde, *p*-hydroxybenzaldehyde, naphthalene, toluene, catechol, quinol, aniline and toluidine by 50% H_2O_2 in the presence of traces of ruthenium(III) chloride is reported. This study was performed mainly to see the efficiency with 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

Whether H_2O_2 was added in small amounts at regular intervals or by continuous addition dropwise, there was a negligible effect on the yield; thus, the possibility of wasteful decomposition of H_2O_2 is eliminated if the whole amount is added at the beginning of the experiment. Increasing the amount of acetic acid (above the minimum amount required to keep the reaction mixture homogeneous in **a** to **d**) does not affect the yield, indicating that it acts only as a solvent. Addition of $RuCl_3$ at the room temperature in the case of aldehydes and hydrocarbons does not catalyze the reaction, indicating that $RuCl_3$ itself or $RuCl_6{}^{3-}$ species, which exist in aqueous acidic medium[19,20] at room temperature, may not be catalyzing the reactions. It was observed that in all cases the yield reaches a maximum and then starts decreasing with increasing catalyst concentrations, probably due to unproductive decomposition of H_2O_2, which increases with increasing concentration of transition metal ions. The electron abstracting $-NO_2$ group, when present in the ring, facilitates the yield of acid compared with the presence of the electron donating –OH group. Thus, a quantitative yield of *p*-nitrobenzoic acid was obtained at lower catalyst concentrations. In the case of toluene the overall yield of cresols was 48% with 85% selectivity for the ortho position. Aromatic dihydroxy alcohols are readily soluble in an aqueous medium, hence acetic acid was not employed as a solvent. Unfortunately, the reaction mixture polymerized to a black mass in the case of catechol. Hydrochloric acid was used to make the medium acidic in the case of aniline and toluidine. In all cases, the running of thin-layer chromatography (TLC) plates showed no other spot other than the unreacted compound or the product. It has been reported[21] that, when heated at near-reflux temperature with acetic acid, $RuCl_3$ may give rise to oxo-centered carboxylates $[Ru_3O(O_2C{\cdot}CH_3)_6\ L_3]^+$ (where L may be H_2O, Py etc.) species that may undergo reversible redox steps.[22] Trinuclear caboxylates have been reported to be effective catalysts for the aerobic oxidation of aliphatic alcohols.[23] The catalytic activities of these complexes are approximately 10 times higher than that of $RuCl_3$.[24] This also seems to be true in the present study, as a substrate/catalyst ratio ranging from 1 : 1488 to 1 : 341 250 was enough for the good to quantitative conversion of different functional groups including the hydrocarbons. The formation of $HO_2^{\cdot}$, $OH^{\cdot}$ 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 also been considered to act as a catalyst in the present study also, which was performed in aqueous medium in the absence of acetic acid. The ion-exchange technique has confirmed that 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′**, 0.66 mmol) was dissolved in glacial acetic acid (35 mmol). After adding $RuCl_3$ (1.2×10^{-5} mmol), 50% H_2O_2 (155 mmol) was added. The mixture was kept at 80 °C for 90 min. Pouring of the contents on crushed ice resulted in a precipitate, which was filtered. The filtrate, after extracting with (3 × 10.0 ml) ether, was dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure. After recrystallization with ethanol, *p*-nitrobenzoic acid (**a**) was obtained as a white solid (110 mg, 100%); m.p.: 237 °C (reported 241 °C). IR: ν_{max} 3111 nm (ν_{-OH}); 1694 nm ($\nu_{C=O}$); 1541 nm (ν_{-NO2}).

p-Hydroxybenzoic acid (**b**) was prepared similarly, and recrystallization with hot ethanol gives the compound as a white solid (0.27 g, 24%); m.p: 239 °C (reported 241 °C). IR: ν_{max}·3387 nm ($\nu_{-OH\ phenolic}$), 1677 nm ($\nu_{C=O}$), 2989 nm ($\nu_{-OH\ acid}$), 768 nm ($\nu_{disubstituted\ benzene}$).

α-Naphthol (**c**) 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 a black mass, which was recrystallized with benzene (17 mg, 15%); m.p.: 77 °C (reported 80 °C). The compound gave a positive test for phenolic groups. IR: ν_{max}·3053 nm ($\nu_{-C=CH}$), 1146 nm. (ν_{C-O}), 904–761 (ν subs. benzene ring); NMR; δ 7.73–7.67 (3H m), δ 7.43–7.38 (4H m).

o-, *m*-, *p*-Cresols (**d**) were identified after completion of the reaction with the help of a TLC plate, which showed three spots corresponding to three isomers. The gas–liquid chromatogram showed that *o*-:*m*-:*p*-cresols were in the ratio 85 : 1 : 14.

Polyphenol (**e**). Reaction in this case was performed in the absence of any acid in an aqueous medium. Unfortunately, under the experimental conditions given in Table 1, the reaction mixture polymerized. The IR spectra of the polymerized mass showed ν_{max}·3791 nm ($\nu_{-OH\ phenolic}$), 3231 nm ($\nu_{C=CH\ or\ Ar-H}$), 1272 nm (ν_{C-O-C}), 874 nm ($\nu_{disubstituted\ benzene}$).

Quinhydrone (**f**). In this case, also, the reaction was performed in the absence of any acid. Characteristic green crystals were washed repeatedly with distilled water. The weight of dried precipitate was 446 mg (96%); m.p.: 170 °C (reported 174 °C). IR: ν_{max}·3622 nm ($\nu_{-O-H-O\ bounded}$), 3232nm. (ν_{-OH}), 3063 nm ($\nu_{C=C}$), 2749 nm (ν_{-CH}), 1629 nm ($\nu_{-C=O}$), 874–832 nm ($\nu_{disubstituted\ benzene}$).

Polyaniline (**g**). In this case the reaction was performed in an aqueous hydrochloric acid medium. The filtrate gave a negative test for aniline. The filtered precipitate (bluish-black) was washed with 0.5 M HCl (3 × 25 ml.) to dissolve the low-molecular-weight polyaniline. The precipitate was

Table 1. Oxidation of various organic compounds by 50% H_2O_2 in aqueous acetic acid (**a**–**d**), aqueous (**e** and **f**), aqueous HCl (**g** and **h**) media in the presence of $RuCl_3$ (organic substrates taken: **a′**, 0.66 mmol; **b′**, 8.19 mmol; **c′**, 0.78 mmol; **d′**, 6.5 mmol; **e′**, 4.5 mmol; **f′**, 4.55 mmol; **g′**, 4.6 mmol; **h′**, 4.6 mmol)

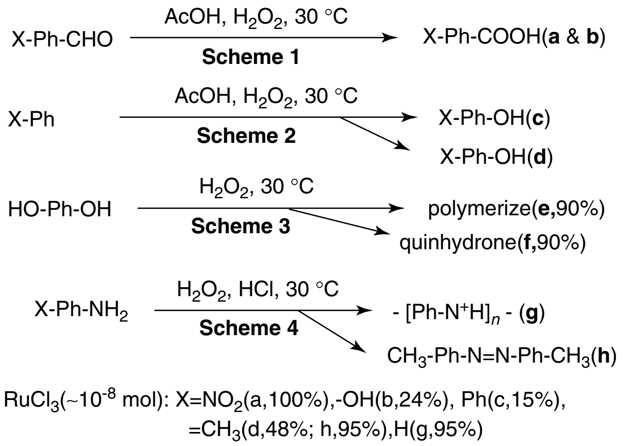
Organic substrate	Product	H_2O_2 (mmol)	Acetic acid or HCl (mmol)	$RuCl_3 \times 10^{-5}$ (mmol)	Temp. (°C)	Time (h)	Yield (%)
p-Nitrobenzaldehyde (**a′**)	*p*-Nitrobenzoic acid (**a**)	155	35	1.2	80	1.5	100
p-Hydroxybenzaldehyde (**b′**)	*p*-Hydroxybenzoic acid (**b**)	159	87.5	2.4	80	1.5	24
Naphthalene (**c′**)	α-Naphthol (**c**)	210	350	19.2	100	4.0	15
Methyl benzene (**d′**)	(*o*-, *p*-, *m*-) Cresols (**d**)	210	87.5	2.4	65	4.0	48[b]
o-Dihydroxybenzene (**e′**)	Polymerized (**e**)	14	—	307	30	2.0	—
p-Dihydroxybenzene (**f′**)	Quinhydrone (**f**)	14	—	153.6	30	1.0	90
Aniline (**g′**)	Polyaniline (**g**)	7.05	2.5[a]	307	30	1.0	95
Toluidine (**h′**)	Azotoluene (**h**)	14	5.0[a]	307	30	2.0	95

[a] HCl.
[b] Combined (*o*-, *p*-, *m*-) yield.

dried at room temperature (90 mg, 90%); m.p.: >300 °C. The negative test for aniline and the bluish-black washings with HCl indicate that, in this case, 10% low-molecular-weight polyaniline was produced along with 90% high-molecular-weight polyaniline. IR: ν_{max}·3335 nm ($\nu_{=NH}$), 3049 nm ($\nu_{=CH}$), 1494 nm ($\nu_{C=C}$), 834 ($\nu_{\text{disubstituted benzene}}$).

Azotoluene (**h**). After completion of the reaction, performed in an aqueous hydrochloric acid medium, the mixture was diluted with 0.5 M HCl. The powdery pinkish precipitate after washing with 0.5 M HCl (3 × 25 ml.) was dried at room temperature (466 mg, 95%). The product sublimed at 170 °C (reported 180 °C). IR: ν_{max}·3030 nm ($\nu_{=CH}$), 2921 nm (ν_{C-H}), 1630 ($\nu_{N=N}$), 872 nm ($\nu_{\text{disubstituted benzene}}$), 35–809 nm (ν subs. benzene ring).

The present system (Scheme 1) is easy and efficient and can be used to oxidize a variety of functional groups from the synthetic point of view, and also in the laboratory for demonstration purposes. Even with the drawback that more oxidant is required, the present system is more economical than many other methods because the cost of the catalyst is nominal (catalyst/substrate ratio is 1 : 1466 to 1 : 341 250) and the catalyst and acetic acid (wherever used as solvent) can be regenerated. It is environmentally benign, as no harmful side product is formed. The system is also effective for other organic compounds containing a variety of functional groups, the study of which is in progress.



Scheme 1. Oxidation routes of the various organic substrates.

EXPERIMENTAL

In all cases the IR spectra were taken with a Brucker Vector-22 IR spectrophotometer, and ^1H NMR spectra were taken with a Xeol 400 MHz spectrophotometer in $CDCl_3$ with tetramethylsilane as internal standard. Gas–liquid chromatography (GLC) studies were performed with a Varian Vista 6000. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Merck GF254 silica-gel-coated plates. $RuCl_3$ (Johnson-Matthey & Co.) was dissolved in a minimum amount of HCl and the final strengths of the catalyst and acid were 4.0×10^{-3} M and 4.82×10^{-3} M respectively. The purity and identification of the products were confirmed by melting point, mixture melting point, TLC, molecular weight determination, by neutralization equivalent, preparing derivatives, IR, NMR and GLC studies. To obtain the maximum yield, five to eight sets were performed by changing the concentration or conditions of each component, which can affect the yield. In general, to the mixture of organic compound (in aqueous acetic acid (**a** to **d**), in water (**e** and **f**) and 0.5 M HCl (**g** and **h**)) 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 contents were cooled, separated and analyzed for the products.

Acknowledgements

R.B. and A.K.S. are grateful to U.G.C. and C.S.T., U.P. (grant nos. F.12-97/2001(SR-I) and CST/D-3205 respectively) for financial assistance, to C.D.R.I., Lucknow for glc and IIT, Kanpur for IR and NMR studies.

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