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Catalysis by Ir(III), Rh(III) and Pd(II) metal ions in the oxidation of organic compounds with H_2O_2

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Catalytic activities of three transition metals, as iridium (III) chloride, rhodium (III) chloride and palladium (II) chloride, were compared in the oxidation of six aromatic aldehydes (benzaldehyde, *p*-chloro benzaldehyde, *p*-nitro benzaldehyde, *m*-nitro benzaldehyde, *p*-methoxy benzaldehyde and cinnamaldehyde), two hydrocarbons (viz. (anthracene and phenanthrene)) and one aromatic and one cyclic alcohol (cyclohexanol and benzyl alcohol) by 50% H_2O_2. The presence of traces (substrate: catalyst ratio equal to 1 : 62500 to 1 : 1961) of the chlorides of iridium(III), rhodium(III) and palladium(II) catalyze these oxidations, resulting in good to excellent yields. It was observed that in most of the cases palladium(II) chloride is the most efficient catalyst. Conditions for the highest and most economical yields were obtained. Deviation from the optimum conditions decreases the yields. Oxidation in aromatic aldehydes is selective at the aldehydeic group only and other groups remain unaffected. This new, simple and economical method, which is environmentally safe, also requires less time. Reactive species of catalysts, existing in the reaction mixture are also discussed. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: oxidation; aromatic aldehydes; hydrocarbons; transition metal catalysts; hydrogen peroxide

INTRODUCTION

Oxidation of organic compounds has been reported by various methods and oxidants.[1–5] Molecular oxygen in acidic[6] and alkaline[7] medium has frequently been used for the oxidation of organic compounds for synthetic purposes, but the drastic conditions required increase the cost and explosion hazard. Hydrogen peroxide as an oxidant is safer, cheaper and does not require a buffer. It has high active oxygen content and is clean since the by-product formed is water. H_2O_2 has been used for the oxidation of aromatic aldehydes,[8] benzyl chloride,[9] epoxidation of olefins,[10] hydroxylation of aromatics with $AlCl_3$,[11] oxidation of aromatic aldehydes by magnesium monoperoxypthalate,[12] etc. Oxidation of aromatic and aliphatic aldehydes in organic solvent in halide- and metal-free conditions using $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (PTC)[13] with a substrate : catalyst ratio of 1.1 : 2.5 and in benzyl alcohol to benzaldehyde under halide-free conditions in the presence of PTC,[14] with a substrate : catalyst ratio of 330 : 1 have been reported, but the system containing dimethyl sulfate, which is used to prepare PTC, is reported to be carcinogenic.[15] We have reported the efficiency of the ruthenium(III)–H_2O_2 system in the conversion of various organic compounds in acetic acid medium.[16,17] To explore the possibility of other transition metal ions, which are cheaper and are more readily available, herein we have compared the efficiency of chlorides of iridium(III), rhodium(III) and palladium(II) to activate hydrogen peroxide in the oxidation of various substrates, viz. six aromatic aldehydes (**a′–f′**), two hydrocarbons (**g′** and **h′**), one aromatic (**i′**) and one cyclic alcohol (**j′**) from the synthetic point of view.

EXPERIMENTAL

It is known that $IrCl_3$ in hydrochloric acid gives $IrCl_6{}^{3-}$ species.[18] It has also been reported that iridium(III) and iridium(I) ions are the stable species of iridium.[19] Further, the equation of $[IrCl_6]^{3-}$ gives $[IrCl_5H_2O]^{2-}$, $[IrCl_4\{H_2O)_2]^-$ and $[IrCl_3\{H_2O)_3]$ species.[20–22] Aquo species of palladium(II)

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such as $[\mathrm{PdC1_2(H_2O)OH}]^-$ or $[\mathrm{PdCI(OH)_2OH}]$ have been reported by Coe.[23] Similarly, Sarhon,[24] from a kinetic study of the reaction of palladium(II) with various dienes, has assumed the presence of reactive species of palladium(II) as $[\mathrm{PdC1_3(H_2O)}]^-$. This species has been considered to be an active species by Behari[25] also at low chloride ion concentrations, while $\mathrm{PdCl^{3-}}$ has been considered at higher chloride ion concentrations in acetic acid medium, depending on the amount of chloride ions present in the solution.[26] $\mathrm{RhCl_3.3H_2O}$ in hydrochloric acid gives $[\mathrm{RhCl_6}]^{3-}$ species, which on equation gives $\mathrm{RhCl_5(H_2O)}]^{2-}$, *cis*-$[\mathrm{RhCl_4(H_2O)_2}]^-$ and $\mathrm{RhCl_3(H_2O)_3}$.[27] Since no effect of acetic acid was found during the present study as acetic acid was used just to dissolve the organic substrates and no effect of change of its concentration on the yield was obtained, therefore, considering our experimental conditions and the efficiency of these catalysts in the oxidation of various functional groups, $[\mathrm{IrCl_5H_2O}]^{2-}$, $[\mathrm{RhCl_5(H_2O)}]^{2-}$ and $[\mathrm{PdC1_3(H_2O)}]^-$ have been considered to be the reactive species of different transition metal catalysts in the present study. It was observed that substrate : catalyst ratio ranging from 1 : 62 500 to was enough for the near quantitative conversion of aromatic aldehydes (a–d, Table 2) while a ratio of 1 : 1961 was required for good yields in the case of hydrocarbons and alcohols (g–j, Table 2). Formation of $\mathrm{HO_2}^{\cdot}$, $\mathrm{OH}^{\cdot}$ and OH^- during the catalytic decomposition of $\mathrm{H_2O_2}$ with metal ions is well documented.[28]

In all the cases IR spectra were taken with a Brucker Vector-22 IR spectrophotometer and ^{1}H NMR spectra with a Xeol 400 MHz. spectrophotometer in $\mathrm{CDCl_3}$ with TMS as internal standard. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Merck GF254 silica gel-coated plates. $\mathrm{IrCl_3}$, $\mathrm{RhCl_3}$ and $\mathrm{PdCl_2}$ (Jhonson-Matthey & Co.) were dissolved in minimum amount of hydrochloric acid and the final strengths of catalysts were 3.35×10^{-3}, 4.77×10^{-3} and 5.65×10^{-2} mol dm^{-3}. Purity and identification of products were confirmed by taking m.p., m.m.p., tlc, mol. wt determination, by neutralization equivalent, preparing derivatives, and IR and NMR 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 and catalyst, the requisite quantity of 50% $\mathrm{H_2O_2}$ was added and the mixture was heated for the required time. After completion of the reaction contents were cooled, separated and analyzed for the products. Benzaldehyde (**a′**, 9.8 mmol) was dissolved in glacial acetic acid (80.0 mmol). After adding $\mathrm{PdCl_2}$ (1.6×10^{-4} mmol), 50% $\mathrm{H_2O_2}$ (78 mmol) was added. The mixture was kept at 80 °C for 120 min. The contents were poured on the crushed ice. The precipitate was filtered and the filtrate was extracted with 10.0 ml ether. The extract was dried over anhydrous $\mathrm{MgSO_4}$. Solvent was removed under reduced pressure. After re-crystallization with hexane, benzoic acid **(a)** was obtained as a white solid (0.98 g. 82%); m.m.p., 120.5 °C (reported 122 °C), $\nu_{\max}$, 3008 nm ($\nu_{-\mathrm{OH}}$); 1687 nm ($\nu_{\mathrm{C=O}}$). *p*-Chlorobenzoic acid **(b)** was prepared similarly and re-crystallization with hot ethanol gave the compound as a white solid (1.05 g, 92%); m.p., 239.5 °C (reported 241 °C), IR $\nu_{\max}$.3095 nm($\nu_{-\mathrm{OH}}$), 1682 nm ($\nu_{\mathrm{C=O}}$), 765 nm$_{(\nu \mathrm{C-Cl})}$. *p*-Nitrobenzoic acid **(c)** was prepared similarly, and after re-crystallization with ether, *p*-nitrobenzoic acid was obtained as a white solid (1.01g. 92%); m.p., 239 °C (reported 241 °C). IR $\nu_{\max}$, 3115 nm ($\nu_{-\mathrm{OH}}$), 1690 ($\nu_{\mathrm{C=O}}$), 1581($\nu_{\mathrm{N=O}}$), 1351–1422 ($\nu_{\mathrm{N=O2}}$). *m*-Nitro benzoic acid **(d)** was prepared similarly; after re-crystallization the compound was obtained as a light yellow crystals (1.04 g, 94%); m.p., 139 °C (reported 142 °C). IR $\nu_{\max}$, 3092 nm ($\nu_{-\mathrm{OH}}$), 1692 ($\nu_{\mathrm{C=O}}$), 1582($\nu_{\mathrm{N=O}}$) and 1352 ($\nu_{\mathrm{N=O2}}$). 4-Methoxy benzoic acid **(e)** was prepared in the same manner. After extracting with diethyl ether and re-crystallizing with ethanol, the compound was obtained as a white solid (0.103 g, 6.9%); m.p., 181 °C (reported 184 °C), mol. wt, 150 (reported 152). IR $\nu_{\max}$, 2984 nm ($\nu_{-\mathrm{OH}}$), 1685 nm. ($\nu_{\mathrm{C=O}}$), 1601 nm ($\nu_{\mathrm{C=C}}$), 1301 nm ($\nu_{\mathrm{O-C=C}}$) and 1166 nm ($\nu_{\mathrm{O-C}}$). Cinnamic acid **(f)** was prepared in the same manner. After extracting with diethyl ether and re-crystallizing with hot water, the compound was obtained as a white solid (0.51g, 50%); m.m.p., 132.5 °C (reported 134 °C), compound gave the test for unsaturation, IR $\nu_{\max}$, 3027 nm ($\nu_{-\mathrm{OH}}$), 1680 nm ($\nu_{\mathrm{C=O}}$), 1494 nm ($\nu_{\mathrm{C=C}}$). Anthraquinone **(g)** was prepared similarly and re-crystallized with hot glacial acetic acid; needle-shaped yellowish crystals (0.17 g, 81%), m.p., 283.5 °C (reported 286 °C), NMR δ 7.049–8.21 (8Hm). Phenanthraquinone **(h)** was prepared similarly to **g**; needle-shaped yellowish orange crystals, identified by TLC (0.152 g, 73%), m.p., 206 °C (reported 210 °C), IR $\nu_{\max}$, 3053 nm ($\nu_{\mathrm{Ar.C-H}}$), 1674 nm.($\nu_{\mathrm{C=O}}$), 732 nm ($\nu_{\text{subs.benzene ring}}$). Cyclohexanone **(i):** the compound was prepared as above. Its hydrazone was separated and identified by TLC; m.p. of hydrazone 158 °C (reported 162 °C), 0.026 g, yield 26%; NMR δ 7.96–7.99 (1H, d), δ 8.27–8.31(1H, dd), δ 9.12–9.13 (1H, d), δ 1.71–2.5 (10H, m). Benzylaldehyde **(j):** the compound was prepared as above (0.052 g, 49%). Its hydrazone was separated and identified by TLC; m.p. of hydrazone, 238 °C (reported 241 °C). NMR, δ 11.2 (1H, s), δ 5.29 (1H, s), δ 9.1 (1H, d), δ 8.1–8.3 (2H, m), δ 7.2–7.9 (5H, m).

The present system is efficient and can be used to oxidize a variety of functional groups in the laboratory for demonstration purposes. Above all, it is cost-effective and environmentally benign as no harmful side product is formed. The system is effective for other organic compounds also containing a variety of functional groups, for which study is in progress.

DISCUSSION

The study was performed mainly to determine the efficiency with economy of the simple and novel, transition group metals–hydrogen peroxide system to oxidize various organic compounds like the easily oxidized aldehydes and the comparatively difficult hydrocarbons. To obtain the maximum

Table 1. Oxidation of benzaldehyde (a) (9.8 mmol.) with 50% H_2O_2 in acetic acid medium in presence of $IrCl_3$.

Entry Nos.	H_2O_2 (mmol.)	Acetic acid (mmol.)	$IrCl_3 \times 10^4$ (mmol.)	Temperature (°C)	Time (hours)	(%)Yield benzoic acid (1a)
1.	78	80	—	Room Temp.	24	<6
2.	78	80	1.6	-do-	24	<10
3.	78	80	0.4	80	2.0	50
4.	78	80	1.6	80	2.0	77
5.	78	80	3.2	60	2.0	51
6.	78	80	1.6	80	2.0	77
7.	78	80	1.6	100	2.0	82
8.	65	80	1.6	80	2.0	55
9.	78	80	1.6	80	2.0	77
10.	117	80	1.6	80	2.0	70

Table 2. Oxidation of various organic compounds by 50% H_2O_2 in aqueous acetic acid medium in the presence of $IrCl_3$(a), $RhCl_3$ (b), $PdCl_2$(c) (a'-9,8, b'-7.3, c'-6.6, d'-6.6, e'-9.8, f'-6.6, g'-1.0, h'-1.0, i'-1.0 and j'-1.0 mmol. of org. substrate was taken)

Organic substrate	Product	H_2O_2 (mmol)	Acetic acid (mmol)	catalyst $\times 10^{-4}$ (mmol)	Temp. (°C)	Time (hrs.)	% yield
Benzaldehyde (a′)	Benzoic acid (a)	78.0	80.0	1.6	80	2.0	77(a) 79(b) 82(c)
p-chloro benzaldehyde (b′)	p-chlorobenzoic acid (b)	46.0	32.0	1.6	100	2.0	90(a) 80(b) 92(c)
p-nitro benzaldehyde (c′)	p-nitrobenzoic acid (c)	80.0	16.0	1.6	80	1.5	92(a) 72(b) 92(c)
m-nitro benzaldehyde (d′)	m-nitro benzoic acid (d)	26.0	32.0	3.2	90	2.0	94(a) 78(b) 86(c)
p-methoxy benzaldehyde (e‘)	p-methoxy benzoic acid (e)	96.0	48.0	8.0	80	3.0	7.0(a) 5.1(b) 6.9(c)
Cinnamaldehyde (f′)	Cinnamic acid (f)	78.0	64.0	1.6	100	1.0	48(a) 44(b) 50(c)
Anthracene (g′)	Anthraquinone (g)	39.0	192	1.6	100	2.5	72(a) 64(b) 81(c)
Phenanthrene (h′)	Phenanthraquinone (h)	42.0	240	1.6	100	2.5	68(a) 60(b) 73(c)
Cyclohexanol (i′)	Cyclohexanone (i)	21.0	—	5.1	100	2.0	22(a) 17(b) 26(c)
Benzyl alcohol (j′)	Benzaldehyde (j)	28.0	—	1.6	100	3.0	45(a) 21(b) 49(c)

yield, five to eight sets were performed by changing the concentration or conditions of each component, which can affect the yield. Addition of H_2O_2 in small fractions at regular intervals or its continuous addition drop-wise showed negligible effect on the yield, thus the possibility of wasteful decomposition of H_2O_2 was eliminated if the whole amount was added at the beginning of the experiment. Change in the concentration of acetic acid does not affect the yield, indicating that it acts only as a solvent. Moreover, performing the reaction with or without adding the catalyst under optimum conditions for maximum yield does not give the desired results (entries 1 and 2, Table 1), showing that the system functions properly only under optimum conditions. This effect is clear from entries 6 and 7 in Table 1. It is seen that, with increasing amounts of oxidant, yield increases in the beginning, reaches a maximum and then further increase in the amount of oxidant decreases the yield (entries 8–10). This may be due to the wasteful decomposition of the oxidant at its higher concentrations or further oxidation of the products. Yield in all the cases reaches a maximum and then starts to decrease with further increase in catalyst concentration (entries 3–5, Table 1). This may be due to the unproductive decomposition of oxidant at higher concentrations of the catalyst. Increased rate of decomposition of oxidant at higher metal ion concentrations is well known. An electron abstracting group, when present in the ring, e.g. *p*-chloro group, facilitates the yield of acid. Thus, near-quantitative yield of *p*-chlorobenzoic acid (b compared with a in Table 2) was obtained. The double bond in the side chain makes oxidation difficult due to decreased electron density at the carbonyl carbon atom. Thus, a lower yield under similar conditions was obtained in the case of cinnamaldehyde. Poor yield of acid in the case of anisaldehyde may be due to electronic effects. In all the cases, by running the TLC plates no product other than that reported could be found.

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