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Microwave assisted oxidation of aromatic hydrocarbons, aldehydes and phenols by cerium (IV) sulphate catalyzed by ruthenium (III) chloride for industrial point of view

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ABSTRACT

The reported new oxidation system is highly efficient, and also can be used to oxidize a variety of other functional group such as aromatic hydrocarbons, aromatic aldehydes and phenols by cerium (IV) sulphate as oxidant in the presence of Ru (III) chloride as catalyst under ecofriendly green synthetic method. In case acetophenone (88.3%), 1-phenyl 2-propanone (72.5%), 3,4 dimethoxybenzoic acid (49.7), 3,4,5 tri methoxybenzoic acid (70.2%), *p* hydroxybenzaldehyde (94.8%) and benzoquinone (73.9%). In the case of phenol and resorcinol the product will be polymerized. Identification of products was confirmed by TLC, M.P. of the derivatives and by their IR and NMR spectra.

1. Introduction

Ruthenium-catalyzed oxidation of alcohols by H_2O_2[1] converted to peracetic acid[2] under PTC conditions and in the presence of bimetallic catalyst[3] has been reported, but the systems containing dimethyl sulfate, which is used to prepare PTC, are reported to be carcinogenic.[4] The excellent efficiency of the Ru(III)–H_2O_2 system in the conversion of aldehydes, hydrocarbons, aromatic alcohols, etc. in an acetic acid medium.[5]

Oxidation of organic compounds with cerium (IV) is quite interesting since cerium (IV) is an unusually strong, one electron transfer oxidant. Ruthenium (III) chloride shows sluggish catalytic activity in acidic medium and thus it was given little attention till now.[6,7] During kinetic studies it was observed that ruthenium(III) chloride-cerium(IV) sulphate system, in acidic medium, is more efficient compared to osmium teroxide in alkaline medium.[8,9] This system, when tried from the synthetic point of view, proved to be highly efficient in the oxidation of many organic compounds, which were otherwise difficult to oxidize. Various functional groups in the organic compounds have been oxidized with different species of cerium (IV). Oxidation of 1-butanol to 4-butanone has been reported with CeO_2/MgO catalyst with 25.5% yield.[10] Ceric ammonium nitrate a versatile oxidant for synthetic organic chemistry has been used as a catalyst also in a number of synthetic reactions[11] .Liquid phase oxidation of cyclohexane was carried out over mesoporous Ce-MCM-41 catalysts using aqueous hydrogen peroxide as oxidant and acetic acid as solvent without adding any initiator.[12] CAN catalyzed oxidation of alkyl aromatics giving rise to aldehydes, ketones, acids or alcohols with potassium bromate has been reported.[13] Most of the synthetic work related with cerium(IV) deals with un-catalyzed oxidations, while catalyzed organic synthesis with cerium(IV) as an oxidant, has not been attended properly. Here we report the microwave assisted oxidation of propyl benzene, naphthalene, dimethoxy and trimethoxy benzaldehydes, cresol, quinol, phenol and resorcinol by cerium (IV) sulphate in the presence of traces of ruthenium (III) chloride.

2. Experimental

Solution of $RuCl_3$ (Johnson-Matthey & Co.) was dissolved in a minimum amount of HCl and the final strengths of the catalyst and strength of HCl in catalyst solution were 0.00586 M and 6.45×10^{-3} M respectively. Cerium (IV) sulphate, prepared by dissolving the calculated amount of cerium (IV) sulphate in 1:1 sulphuric acid, was standardized by titrating it with a freshly prepared standard solution of ferrous ammonium sulpahate using ferroin as an external indicator. For getting the maximum yield 3 to 7 sets were performed by changing the concentration or conditions of each component, which can affect the yield. In the case of synthesis of acetophenone from ethylbenzene under microwave irradiations. For performing the reactions in the solid phase, calculated amount of ethylbenzene, cerium (IV) sulphate and ruthenium (III) chloride was adsorbed on montmorillonite K 10 under microwave irradiation at desired temperature, power and time. Contents were cooled and extracted with appropriate solvents. Extract was dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure and the product was obtained

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∗ Corresponding author. Tel.: +917737559546; fax: +91-1438-228365; e-mail: sagermaniah1@gmail.com identified by appropriate method. IR (in KBr; Brucker Vector-22 IR spectrophotometer) and ^{1}H NMR (Xeol 400 MHz in $CdCl_3$ with TMS as internal standard) spectra were recorded and reactions were monitored with TLC (Merck GF254 silica gel-coated plates). Purity and identification of products were confirmed by TLC, mp. of the derivatives and by their IR and NMR spectra.

3. Results and discussion

On running TLC plate with organic part only one spot corresponding to product was obtained. In the case of reaction mixture was extracted (15 ml × 3) with ether. Reaction conditions in which various experiments were performed are summarized in **Table 2**, while the general procedure for performing the reactions in solid phase under microwave irradiations is given in the experimental section. 2,4-dinitrophenylhydrazone derivative in the case of ethylbenzene **(a)** and propylbenzene **(b)** was prepared by standard method[14] and was re-crystallized with ethanol.

Acetophenone **(a')** from ethylbenzene **(a)** corresponding to yield of the product is 88.3%. Mp of hydrazone derivative 246°C (reported 250°C); NMR; δ 2.27 (3H, s), 7.26-7.99 (5H, m)

1Phenyl2propanone **(b')** from propylbenzene **(b)** corresponding to yield 72.5% of the product. M.P. of hydrazone derivative 152^{o}C (reported 156^{o}C) NMR; δ 2.126 (3H, s), 2.694 (2H, s), 7.12-7.28 (5H, m)

3,4 dimethoxybenzoic acid **(c')** from 3,4 dimethoxybenzaldehyde **(c)** corresponding to yield of the product is 49.7%. M.P. of 3,4 dimethoxybenzoic acid 179°C (reported 181°C). NMR; δ 3.96 (6H, s), 6.92- 6.94 (2H, dd), 7.87-7.6 (1H, dd), 9.88 (1H, s); IR ν_{max}. 845.9($\nu_{\text{C-C str.}}$), 1236($\nu_{\text{C-O}}$), 1506($\nu_{\text{benzene ring}}$), 1589($\nu_{\text{C=C}}$), 1686($\nu_{\text{C=O}}$), 2847($\nu_{\text{CH3 str.}}$), 2944 cm^{-1} ($\nu_{\text{o-H str.}}$).

3,4,5trimethoxybenzoic acid **(d')** from 3,4,5trimethoxybenzaldehyde **(d)** corresponding to yield of the product is 70.2% M.P. of 3,4,5trimethoxybenzaldehyde 141 °C (reported 144 °C). NMR: δ 3.94 (9H, s), δ 7.14 (2H, s), δ 9.88 (1H, s).

4-hydroxybenzaldehyde **(e')** from *p*-cresol **(e)** corresponding to yield of the product is 94.8 %. M.P. of product 115 °C (reported 117 °C). IR ν_{max}. 813.8($\nu_{\text{C-C}}$), 1456.8($\nu_{\text{C=C}}$), 1605($\nu_{\text{benzene ring}}$), 1661.8($\nu_{\text{C=O}}$), 2924($\nu_{\text{C-H aldehyde}}$), 3397 cm^{-1} ($\nu_{\text{OH}}$).

Benzaquinone (f') from quinol (f) corresponding to yield of the product is 73.9%. M.P. of benzaquinone 113 °C (reported 116 °C). NMR; δ 6.5 (2H, s), 6.8 (2H, s).

Phenol **(g)** and resorcinol **(h)** polymerized under the reaction conditions. It was observed that catalyst: substrate ratio ranging from 1: 80 to 1: 197 was enough for the conversion of aromatic hydrocarbons (a and b Table 2) while 1: 78 to 1: 153 ratio was required for good yields in case of aromatic aldehydes (c and d, Table 2). For cresol and quinol catalyst: substrate ratio was found to be 1: 98 and 1: 162 respectively. The study was performed mainly to determine the efficiency and selectivity of the novel, simple and one pot cerium (IV) sulphate-ruthenium (III) chloride system to oxidize various organic compounds.

Three to seven sets were performed to obtain the maximum yield by changing concentration or conditions of each component, which can affect the yield (Table 1). Change in the concentration of acetic acid does not affect the yield (entries 4 and 5, Table 1) indicating that it acts as a solvent to dissolve the hydrocarbons. Yields in all the cases reached to a maximum and then started to decrease with further increase in the concentrations of catalyst (entries 5, 6 and 7, Table 1) and the oxidant (entries 5, 8 and 9, Table 1) or increasing duration of experiment and temperature (entries 5 and 10, Table 1) indicating that optimum conditions are required to get the highest yield. It may also be possible that some un-reactive complex is formed at higher concentrations of the catalyst and oxidant. No formation of the desired products, after prolonged heating in the absence of oxidant (entry 2, Table 1) or leaving the mixture for 48 hrs at room temperature (entry 3, Table 1) excludes aerial oxidation of the organic compound under experimental conditions and indicates that control of reaction conditions was a must for getting the product with desired yield. It has been reported that cerium (IV) is a typical one-equivalent oxidant which removes one electron at a time from the substrate. In this regard it shares certain similarities in reaction patterns with Mn (III), Co (III) and V (V).

In one-equivalent oxidation of neutral or anionic organic species, cation radicals or free radicals are generated[15] normally these intermediates undergo rapid oxidation to afford neutral products by electron transfer (outer sphere reaction) or by ligand transfer (inner sphere reaction) because cerium (IV) oxidations deal most frequently with neutral organic compounds radical intermediates. The fates of these intermediates to undergo C-H, C-C bond cleavage or hydrogen transfer, depend on their structure. In the oxidation of alcohols[16] and aromatic aldehydes[17] with cerium (IV) in aqueous acetic acid involvement of both 1:1 and 2:1 inner-sphere complexes has been reported.

Table 1: Effect of various factors on the yield of acetophenone (a') from ethyl benzene (a) (1.0mmol) with cerium (IV) sulphate in aqueous acetic acid medium in the presence of ruthenium (III) chloride

Entry No.	Cerium(IV) sulphate (mmol)	Acetic acid (mmol)	$RuCl_3$ (mmol)	Temperature (°C)	Time (min)	MW Power	(%)Yield Acetophenone(a')
1.	2.0	3.4	-	100	3.0	80	>10
2.	-	3.4	6.6×10^{-3}	100	3.0	80	0.0
3.	2.0	3.4	6.6×10^{-3}	Room Temp.	4.8	-	0.0
4.	2.0	3.4	6.6×10^{-3}	100	3.0	80	55.6
5.	2.0	3.4	6.6×10^{-3}	100	3.0	80	88.3
6.	2.0	3.4	10.0×10^{-3}	100	3.0	100	44.3
7.	2.0	3.4	4.0×10^{-3}	100	3.0	120	34.5
8.	1.0	3.4	6.6×10^{-3}	100	3.0	80	28.6
9.	3.0	3.4	6.6×10^{-3}	100	3.0	80	38
10.	2.0	3.4	6.6×10^{-3}	70	3.0	80	45.4
11.	2.0	-	6.6×10^{-3}	-	3.0	60	38.2

Table 2: Oxidation of ethylbenzene (1.0mmol) by cerium (IV) sulphate in presence of ruthenium (III) chloride under microwave irradiation

Organic Substrate	Product	Cerium (IV) sulphate (mmol)	Acetic acid mmol	Ru(III) $\times 10^3$ (mmol)	Temp.(°C)	Time (min)	% Yield
Ethyl benzene	Acetophenone	2.0	3.4	6.6×10^{-3}	80	3.0	88.3
Propyl benzene (a)	1-phenyl2-propanone (a’)	2.5	3.4	13.2×10^{-3}	100	3.5	72.5
3,4dimethoxy benzaldehyde (c)	3,4dimethoxy benzoic acid (c’)	3.0	3.4	13.2×10^{-3}	120	4.0	49.7
3,4,5trimethoxy benzaldehyde (d)	3,4,5trimethoxy benzoic acid (d’)	2.0	3.4	8.8×10^{-3}	100	3.0	70.2
p-cresol (e)	p-hydroxy benzaldehyde (e’)	3.0	3.4	6.6×10^{-3}	80	3.0	94.8
Quinol(f)	p-benzaquinone(f’)	2.0	3.4	11.0×10^{-3}	80	3.5	73.9
Phenol (g)	Polyphenol (g’)	4.0	3.4	11.0×10^{-3}	100	4.0	Polymerized
Resocinol (h)	Polyresorcinol (h’)	4.0	3.4	11.0×10^{-3}	100	4.0	Polymerized

4. Conclusion

The reported novel one pot synthesis is highly efficient, easy and can be used to oxidize a variety of other functional groups Selectivity for the oxidation of methyl group in the case of p-cresol and α-carbon in propylbenzene makes the system highly attractive for synthetic point of view.

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