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Catalytic oxidation of aromatic and cyclic hydrocarbons by in situ generates zinc dichromate trihydrate used the Ag (I) and Cu (II) metal ions under microwave irradiation

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ABSTRACT

Oxidations of various hydrocarbons and alcohols with in situ generate zinc dichromate trihydrate in the presence of metal ion catalysts like silver and copper were examined. Naphthalene, anthracene, phenanthrene, cyclohexane and toluene dissolved in minimum amount acetic acid by in situ generate zinc dichromate trihydrate in the presence of traces of Ag(I) catalyst: substrate ratio (1: 70 to 1: 300) and Cu(II) catalyst: substrate ratio (1: 60 to 1: 250) under microwave irradiation. All the synthesized containing Cu (II) catalytic system gave higher yield as compare to Ag (I) catalytic system. Phenanthrene was oxidized in 9-Fluorenone instead of phenanthraquinone to get the benzylic rearrangement.

KEYWORDS

Oxidation;
In situ generate zinc dichromate trihydrate;
Silver and copper catalyst
microwave irradiation.

INTRODUCTION

The oxidation of aromatic hydrocarbons and alcohols has been of latest interest because of wide-ranging potentials in organic chemistry and industrial output, and is recognized a fundamental reaction[1-5]. The oxidation of aromatic hydrocarbons yields carbonyl compound although over-oxidation yields carboxylic acids as a final product. A variety of chromium (VI) oxides derived from CrO_3 were long among the most popular reagents for oxidation of aromatic hydrocarbons and alcohols to carbonyl compounds.

Number of organic substrates were oxidized in the presence of chromate salts and other chromium (VI) oxides have been reported[6-7] including aromatic hydrocarbons and alcohols[8]. Generally these oxidizing agents are used in large excess[9] but also can be used at catalytic scale in conjunction with oxidants[10] at present time several chromium (VI) reagents such as; collins reagent (CrO_3. Py),[11] jones reagent (CrO_3/H_2SO_4/acetone),[12] pyridinum chlorochromate (PCC),[13] trim ethyl silylchlorochromate[14], zinc chlorochromate nonhydrate[15], Zinc dichromate trihydrate[16], 3-carboxypyridinum chlorochromate[17] and 4-(dimethylamino) pyridinum chlorochromate[18] are synthesized and play an important role in the oxidation of organic compounds. The main concern with the utilization of Cr(VI) complexes as oxidant are the lack of selectivity in oxidations, safety hazards related to the utilization of enormous quantities of poisonous chemicals, and in isolation of product and waste disposal.

To overcome of these troubles researchers developed many reagents on solid supports such as pyridinium chlorochromate on Al_2O_3[19], CrO_3 adsorbed on Al_2O_3[20] and SiO_2,[21] chromyl chloride adsorbed on Al_2O_3[22], polyvinyl pyridinium chlorochromate[23] and polyvinyl pyridinium dichromate[24], Cr(VI) oxide[25] synthesized and utilize in the oxidation reactions. In this paper, we tend to report the ZDT with silver and copper catalyst as an expedient and reasonable reagent for the oxidation of aromatic hydrocarbons to carbonyl compounds in acetic acid medium.

Usually Chromium (VI) reagents involves exchange of three electrons in the system for the oxidation of organic compounds, whereby reduction of Chromium (III) species to Chromium (VI)[26-28]. The more reactive complex has been formed with Chromium (V) and Chromium (VI), if oxidation reaction is performed in the presence of the catalyst. Although in order to have a view with synthetic point, a large number of organic compounds could be oxidized with Cr(VI) oxidants in the presence of homogeneous catalyst in acidic media.

Firouzabadi et al. reported a novel, convenient and highly strong oxidant zinc dichromate trihydrate Number of compounds can be oxidized with ZDT[29] it has been used for the oxidation of acetylenes, sulfides, aromatic hydrocarbons, cyclic ethers, primary and secondary alcohols, and etc[30].

The selective oxidation of a variety of organic compounds using silver catalyst become ever more important subject to the researchers for the preparation of industrially remarkable products including hydrocarbons, ketones and aldehydes[31-32]. Copper as a catalyst has been always a innovative concern for researchers in a variety of chemical reactions due to their high activity related to facile electron transfers between copper in various oxidation states (Cu^{1+} and Cu^{2+}). Oxidation of aromatic hydrocarbons, aldehydes and cyclic alcohol by sodium ferrate in presence of copper nano particle has been reported[33-34]. Mesoporous Ce-MCM-41 was use as a catalyst with aqueous hydrogen peroxide as oxidant for the liquid phase oxidation of cyclohexane in an acetic acid media without adding any initiator[35]. Ganin E, and coworkers reported the synthesis of alcohols, carbonyl compounds and acids from the liquid phase oxidation of alkyl aromatics with potassium bromated catalyzed by cerric ammonium nitrate[36]. It has been shown that oxidation of aromatic hydrocarbons with cerium (IV) results in their conversion to quinones. Naphthalene is converted to 1, 4-Napthoquinone (90%). In case of hydrogen peroxide[37] naphthalene is converted to α-naphthol.

As we have already reported the oxidation of some hydrocarbons with Ce (IV)-Ir (III) system[38-39]. Currently in this study we have reported a novel ZDT-Cu (II) and ZDT- Ag (I) system for the oxidation of hydrocarbons. This system is a more convenient, one-pot quick reactions, environmental friendly and reasonable. Requirement of additional oxidant within the reaction is the limitation of the system, but the system is still more economical as the cost of catalyst is nominal and the solvent.

EXPERIMENTAL SECTION

Preparation of oxidant and catalysts

In a typical procedure, in situ generate zinc dichromate trihydrate was first prepared by adding zinc carbonate to the cold solution of chromic acid, dark red solution obtained, then evaporate the solvent under rota vapor, obtained reddish orange slurry was dried over clay plate. Silver (I) catalyst was prepared by dissolving the silver (I) nitrate in deionized water, the final strength of catalyst is 1.62 mmol and Copper catalyst was prepared by dissolving the copper (II) sulphate pent hydrate in de-ionized water; the final strength of catalyst is 1.0 mmol respectively.

Synthesis of the compounds

A CEM Discover Microwave synthesizer was used for carrying out the reactions under microwave irradiation. In order to achieve the maximum yield, five to seven sets of experiments were performed with each substrate by varying significantly the concentration of oxidant, catalyst, time, temperature and microwave power of reactions. IR spectra were recorded in KBr on a Perkin-Elmer 8201 FTIR spectrophotometer. ^{1}H-NMR spectra were recorded at ambient temperature using a Bruker spectroscopic DPX-300 MHz spectrophotometer using DMSO as solvent and TMS as an internal standard (chemical shift in δ ppm).

Synthesis of cyclohexanone from cyclohexane

In solution phase, 0.20 mmol of Ag (I) was mixed with 2.5mmol in situ generate zinc dichromate trihydrate and added to 3.4 mmol of acetic acid solution containing 1.0 mmol of cyclohexane. The mixture was kept at a 100°C temperature for the 5.0 min under microwave irradiation. Contents were cooled and extracted with appropriate solvents. The extract was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. Prepared hydrazone[26] derivative of the product and noted the achieved yield to obtain the final product. Similarly oxidation of ethyl benzene was carried out by changing the 0.25 mmol concentration of Cu (II) catalyst. All the compounds were routinely checked by IR, and ^{1}H-NMR spectrometries.

RESULTS AND DISCUSSION

Results and discussion

Physical and Analytical characterization of the compounds

Oxidation of cyclohexane; yield with copper catalytic system (38.25%) and catalytic system (31.94%).

R (KBr) cm^{-1}; 2938.1 cm^{-1} (v_{C-H}, str$^{.}$), 1711.4 cm^{-1} ($\nu_{C=O}$), 1450 cm^{-1} (v_{C-H}, bend). ^{1}H-NMR ($CdCl_3$); δ 1.69 to 2.7 (10H, m), δ 7.89 to 8.01 (1H, d), δ 9.02 to 9.15 (1H, d), δ 8.19 to 8.29 (1H, dd).

Oxidation of toluene; yield with copper catalytic system (48.11%) and in silver catalytic system (42.54) IR (KBr) cm^{-1}; 2737.2 cm^{-1}(v_{C-H}, aldehydes str.), 3064.7 cm^{-1} (v_{C-H}, str$^{.}$), 1701.0 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR ($CdCl_3$); δ 6.9 to 7.8 (5H, m), δ 8.9 (1H, d), δ 10.8 (1H, s), δ 5.30 (1H, s), δ 7.8 to 8.4 (2H, m).

Oxidation of naphthalene; yield with copper catalytic system (24.68%) and silver catalytic system (19.68%).

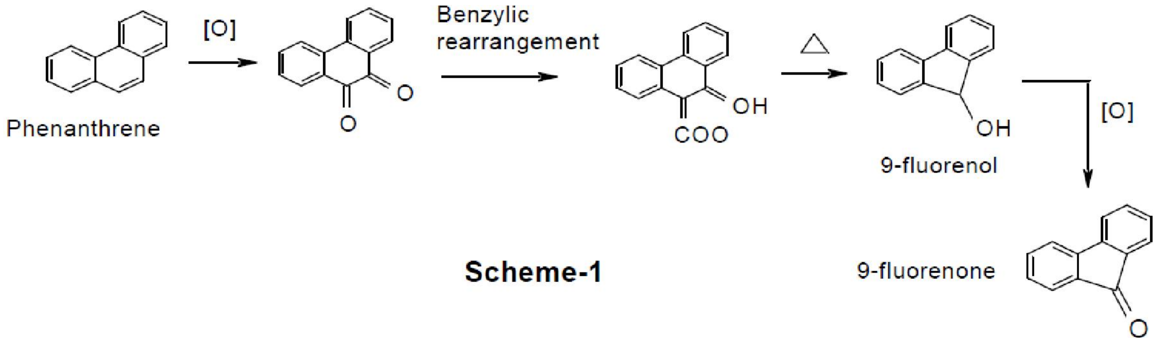
IR (KBr) cm^{-1}; 1651 cm^{-1} ($\nu_{c=o\ quinone}$), 3007 cm^{-1} ($v_{C-H,\ str.aromatic}$), 765cm^{-1} ($v_{C-H,\ bend\ aromatic}$), and 1513 cm^{-1}($V_{C=C,\ Str.\ atm}$)$_{.}$ ^{1}H-NMR ($CdCl_3$); δ 7.22 to 8.24 (6H, m).

Oxidation of anthracene; yield with copper catalytic system (93.5%) and in silver catalytic system (87.02%). IR (KBr) cm^{-1}; 1673 cm^{-1} ($\nu_{c=o\ quinone}$), 3072 cm^{-1} ($v_{C-H,\ str.aromatic}$), and 1581 cm^{-1}($V_{C=C,\ Str.\ atm}$) 940–810 cm^{-1} ($\nu_{subs.\ benzene\ ring}$). ^{1}H-NMR ($CdCl_3$); δ 6.92 to 8.20 (8H, m).

Oxidation of phenanthrene; yield with copper catalytic system (83.4%) silver catalytic system (80.25%). IR (KBr) cm^{-1}; 1671 cm^{-1} ($\nu_{c=o}$), 3057 cm^{-1} ($v_{C-H,\ str.aromatic}$), 756, and 866.881 cm^{-1} ($v_{C-H,\ bend\ aromatic}$), and 1600 cm^{-1}($V_{C=C,\ Str.\ atm}$)$_{.}$ ^{1}H-NMR ($CdCl_3$); δ 7.24-8.70 (8H, m).

Oxidation of phenanthrene generally results in the formation of 9, 10- phenanthraquinone which undergoes benzylic rearrangement in basic medium and finally gives 9-fluorenone in heating conditions through the formation of 9-hydroxyfluorene-9-carboxylic acid (Figure 1: Mechanism - 9, 10-Phenanthraquinone converted to 9-fluorenone).

9, 10-Phenanthraquinone (generally obtained by oxidation of phenanthrene) when warmed with al-



Scheme-1

Figure 1 : Mechanism - 9, 10-Phenanthraquinone converted to 9-fluorenone

kali undergoes benzylic rearrangement gives 9-hydroxyfluorene-9-carboxylic acid, which gives finally 9-fluorenone in heating conditions[13].

Discussion

It was notice that catalyst substrate ratio ranging from 1: 70 - 1: 300 was enough for the conversion of aromatic hydrocarbons with silver catalyst while in case of copper catalyst the ratio needed was 1: 60 - 1: 250 to obtain product in good yield. Although the purpose of study was to determine the selectivity and efficiency of the new ZDT-silver(I) nitrate and ZDT-copper(II) sulphate system for the oxidation of various functional groups in compounds. In order to achieve the product in high amount, variations (in temperature, pressure, time concentration) were done taking six sets that could influence the yield (TABLE 1). As aromatic hydrocarbons are insoluble in aqueous medium, therefore, acetic acid was used as a solvent to create the system homogeneous. In TABLE 1, it has been shown that initially on increasing the various factors in reaction under microwave irradiation, yield increases and reaches to utmost and after that shows the decline graph with further increase in concentration. Increasing duration of experiment and temperature indicating that optimum conditions are required to get the most noteworthy yield. Desired product was not formed, if reaction was over heated in absence of oxidant under experimental conditions, excludes aerial oxidation. This predicts that control of reaction conditions was an unquestionable requirement for sought yield of product. The study was performed mainly to verify the effectiveness of the simple chromium (VI)-silver (I) and chromium (VI)-copper (II) system for the oxidation of aromatic and aliphatic cyclic hydrocarbons. In the case of oxidant variation increase the concentration of ZDT decrease the yield of the product because at high concentration un-reactive species is formed so the rate of reaction is decrease, yield is decrease (TABLE-1, entry 4 and 5). And in case of catalyst variation increase the concentration of catalyst decrease the yield of the product because at high concentration un-reactive species is formed so the yield of product is decrease (TABLE-1, entry 4 and 5). In the absence of catalyst the yield of product was found to be zero (TABLE-1, entry 6) i.e., the reaction was not occurred.

UV-Visible spectral study we get the complex formed between the organic substrate and oxidant. In Figure-2 the bar diagram show that in case of copper(II) catalyst give the higher yield as compare to silver(I) catalyst because the electronic configuration of Ag(I) is $4d^{10}5s^1$ and Cu(II) is $3d^9$. The electrode potential of the Ag(I) is +0.80 and Cu(II) is +0.34. The electrode potential of Ag(I) is higher than compare to Cu(II) electrode potential, so Cu^{2+} oxidation state is more stable and more reactive than Ag+. Although, of these two metals, silver releases electrons slowly and copper releases rapidly. In a cell, the copper would have the greater build up of electrons, and be the negative electrode. If the silver and copper were connected by a bit of wire, flow of electrons would electrons would flow from the copper to the silver. In TABLE 2, Figure 2 show that comparative study of silver (I) nitrate and cop-

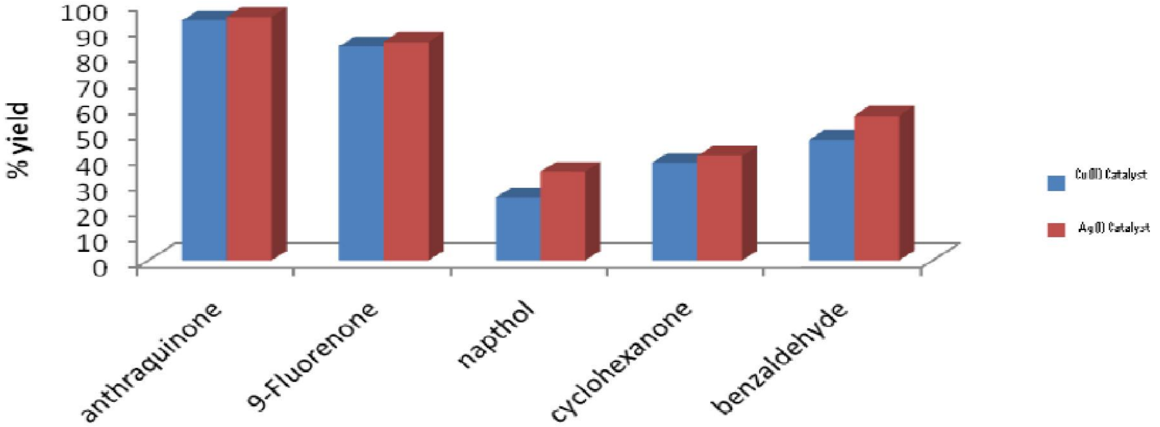


Figure 2 : Effect of variant of copper and silver catalyst on the yield of compounds

TABLE 1 : Factors effecting on the yield of cyclohexanone resulting from cyclohexane (1.0 mmol) by silver (I)-ZDT and copper (II)-ZDT catalytic system in acid medium in solution phase under microwave irradiation

S.No.	Acetic acid (mmol)	ZDT (mmol)	Cu(II)x10^{3} catalyst^{a} (mmol)	Ag(III)x10^{3} catalyst^{b} (mmol)	Time (min.)	Temp. (^{o}C)	MW power (W)	% yield With Cu(II) catalyst^{a}	% yield With Ag(I) catalyst^{b}
1.	3.4	2·0^{a} 2·0^{b}	0.05	0.05	3.0^{a} 3.0^{b}	60^{a} 60^{b}	100^{a} 100^{b}	20.37	18.30
2.	3.4	2·0^{a} 2·0^{b}	0.08	0.08	5.0^{a} 5.0^{b}	120^{a} 120^{b}	100^{a} 100^{b}	39.26	27.41
3.	3.4	2·0^{a} 2·0^{b}	0.10	0.10	5.0^{a} 5.0^{b}	100^{a} 100^{b}	80^{a} 80^{b}	48.11	35.32
4.	3.4	2·5^{a} 2·5^{b}	0.20	0.20	5.0^{a} 5.0^{b}	100^{a} 100^{b}	100^{a} 100^{b}	38.25	31.94
5.	3.4	3·0^{a} 3·0^{b}	0.25	0.25	7.0^{a} 7.0^{b}	120^{a} 120^{b}	120^{a} 120^{b}	29.12	26.15
6.	4.0	3.5^{a} 3.5^{b}	0.30	0.30	5.0^{a} 5.0^{b}	100^{a} 100^{b}	100^{a} 100^{b}	30.92	27.67

Reaction condition: 1.0 mmol of substrate was used in all cases, Conditions used in copper case b- Conditions used in silver case

TABLE 2 : Comparative study of silver (I) nitrate and copper (II) sulphate as catalyst in solution phase for oxidation of hydrocarbons by ZDT dissolve in acetic acid under microwave irradiation, Conditions used in copper case b- Conditions used in silver case

Organic Substrate	Product	Acetic acid (mmol)	ZDT (mmol)	Au(III)x10^{3} catalyst (mmol)	Cu(II)x10^{3} (mmol)	Time (min)	Temp (^{O}C)	MW Power (W)	% Yield With Cu(II) catalyst^{a}	% Yield With Ag(I) catalyst^{b}
Cyclohaxane (A)	Cyclohexanone (A')	3.4	2.5^{a} 2.5^{b}	0.20	0.20	5.0^{a} 5.0^{b}	100^{a} 100^{b}	80^{a} 80^{b}	38.25	31.94
Toluene (B)	Benzaldehyde (B')	3.4	2.0^{a} 2.0^{b}	0.30	0.30	5.0^{a} 5.0^{b}	100^{a} 100^{b}	80^{a} 80^{b}	48.11	42.54
Naphthalene (C)	Naphthoquinone (C')	3.4	6.0^{a} 6.0^{b}	0.10	0.10	3.0^{a} 3.0^{b}	80^{a} 80^{b}	60^{a} 60^{b}	24.68	19.68
Anthracene (D)	Anthraquinone (D')	3.4	4.0^{a} 4.0^{b}	0.08	0.08	3.0^{a} 3.0^{b}	100^{a} 100^{b}	80^{a} 80^{b}	93.5	87.02
Phenanthrene (E)	9-Fluorenone (E')	3.4	4.0^{a} 4.0^{b}	0.05	0.05	3.0a 3.0b	80^{a} 80^{b}	80^{a} 80^{b}	83.4	80.25

per (II) sulphate as catalyst in solution phase for oxidation of hydrocarbons by ZDT dissolve in acetic acid under microwave irradiation.

CONCLUSIONS

An efficient system for the copper and silver-catalyzed oxidation of aromatic and aliphatic hydrocarbons has been developed using Zinc dichromate trihydrate as an oxidant. The reported novel catalyst-oxidant system is highly efficient, well handled. The main advantage of using the catalyst-oxidant system is too safe the time of reaction with the use of small quantity of catalyst and oxidant. The fascination of used novel system is due to the excellent yield of the carbonyl group. Microwave reaction is also important from the environmental point of view because using very less amount of solvent and not uses the hazarded chemical in reaction.

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