Oxidation of organic compounds by in situ generated sodium ferrate in presence of Cu NPs adsorbed on Al2O3 under microwave irradiation

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ABSTRACT

Admirable yields with selectivity were obtained in the oxidation of anthracene, phenanthrene ethylbenzene, ethylbenzene, cyclopentanol, p-methylcyclohexanol, p-methoxy benzaldehyde and p-hydroxy benzaldehyde with in situ generated sodium ferrate in the presence of Cu NPs adsorbed on Al2O3 under microwave irradiation. Present one pot system does not require tedious separation of ferrate and is quicker and environmentally benign.

KEYWORDS:
Oxidation, in situ generated sodium ferrate, Cu NPs, Al2O3, green synthesis.

1. INTRODUCTION

The oxidation of organic functionalities, generally require rigorous control of the experimental conditions added with their lack of selectivity.1 Oxidants based on chromium2 and on manganese are corrosive, and they are irritants for the skin and for sensitive body parts such as the eyes. They are violently toxic to man and to the environment. Derivatives of chromium(VI) in particular are well-known carcinogens.3 Fe(VI) is a powerful oxidizing agent throughout the entire pH range with a reduction potential (Fe(VI)/Fe(III) couple) varying from +2.2 V to +0.72 V versus NHE in acidic and basic solutions, respectively. Fe(VI) is also a selective oxidant for a large number of organic compounds with Fe(III) as a by-product and therefore has a role in cleaner technology for organic synthesis. Other applications of Fe(VI) include production of ferrate(V) by pulse radiolysis, 'super-iron' batteries, in wastewater treatment processes as a disinfectant, antifloculant, and coagulant etc. In aqueous solution, the ferrate dianion FeO42− remains monomeric.4 In basic solution, the rate of decomposition of ferrate is highly variable, pH and temperature are key factors, but light does not affect the stability of ferrate solutions.5 In dilute solution, the lowest rate of reduction of ferrate by water occurs between pH 9.4 and 9.7.6

In strong alkali (3 M or above), ferrate solutions reach another region of stability, thus allowing the preparation and purification of potassium ferrate by the wet method. Main problem with sodium or potassium ferrates is their separation, which requires tedious processes. Probably iron(VI) boosts the oxidizing ability of iron(III), while the presence of a microporous adsorbent of the clay helps the high selectivities. Oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds using potassium ferrate at room temperature in benzene and aqueous sodium hydroxide in the presence of benzyltriethylammonium chloride has been reported.7 Another approach involved the recourse to a solid mixture of K2FeO4, basic alumina, and a hydrated inorganic salt such as CuSO4.5H2O for oxidizing allylic and benzylic alcohols dissolved in benzene.8 Oxidative cleavage of propargyl alcohol derivatives using K2FeO4-Al2O39 has been reported. Conversion of aliphatic and aromatic alcohols including benzyl alcohol to carbonyl compounds by K2FeO4 with K10/Cu10 has also been reported with 62 % GC yield in 24 hours. Indication of the role of the solid support and of the metallic salt within this heterogeneous system came from the study of the oxidation of alcohols by a mixture of KMnO4 and CuSO4.5H2O, in which it was assumed that the salt acts as a source of humidity.10 Many transition metal ions are known to act as efficient oxidizing agents and a few as catalysts. Potassium ferrate, (iron VI) is known to be a powerful two electron oxidation with an oxidation potential of +2.2 V in acid and 0.72 V in base.11

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2. MATERIAL AND METHODS

For this purpose sodium ferrate was prepared by taking ferric nitrate (Fe(NO\textsubscript{3})\textsubscript{3}, 9H\textsubscript{2}O) 2.0 g (4.49 mmol) in a 50 ml flask and the required amount (1-3.5 ml; 14.7 – 51.4 mmol) of sodium hypochlorite solution was added drop-wise with constant stirring. Formation of a clear dark purple-red coloured solution indicates formation of ferrate anions. Cu NPs were prepared by borohydride reduction method by adding 10 ml sodium borohydride solution (2.0 mmol) to a solution of CuSO\textsubscript{4}, SH\textsubscript{2}O (1.0 mmol) with the help of a syringe with constant stirring. Appearance of very fine dark black coloured precipitate indicates formation of Cu NPs in the solution. In a typical oxidation procedure required quantity of Al\textsubscript{2}O\textsubscript{3} (4.0 gm) was added to CuSO\textsubscript{4} solution and to the vigorously stirred solution; required quantity of sodium borohydride (2.0 mmol) was added drop-wise with the help of a syringe. After completion of the reaction precipitate was filtered under suction and was left overnight at room temperature. Required quantity of organic substrate was adsorbed on the partially dried clay containing Cu NPs. After mixing with freshly prepared sodium ferrate (Na\textsubscript{3}FeO\textsubscript{4}) solution, the whole mass was then irradiated in a microwave synthesizer for the required time. After exposure, solid mass acidify with 2N H\textsubscript{2}SO\textsubscript{4} solution, then extracted with diethyl ether (3 x 30 ml). Extract was evaporated under reduced pressure to afford the product. IR spectra were taken with a Bruker Vector-22 IR spectrophotometer and 'H NMR spectra with a Xeol 400 MHz spectrophotometer in CDCl\textsubscript{3} with TMS as internal standard. Purity and identification of products were confirmed by taking m.p. of the product or its 2,4-dinitrophenyl hydrazone derivatives, by running TLC plates with authentic samples and spectral studies.

Identification of organic compounds:
Cyclopentanone (a') was weighed and analyzed in the form of its 2,4-dinitrophenyl hydrazone. Mp. of hydrazone 142 °C (reported 146 °C), 'H NMR δ 11.08 (1Hs), δ 8.43 (1Hs), δ 7.05-8.46 (2Hm), δ 1.07-3.34(4Hq), δ 1.16-1.68 (4Hq). 2-Methylocyclohexanone (b') was prepared from O-methylocyclohexanol (b) (2.0 mmol) as above. Mp. of hydrazone 136 °C (reported 137 °C); 1H NMR, δ 10.04 (1Hs), δ 9.54 (1Hs), δ 7.65-8.54 (2Hm), δ 1.35-2.85 (9Hm), δ 1.3 0-1.76 (3Hq). Cyclohexanone (e') was prepared from Cyclohexane (e) (2.0 mmol) as above. Mp. of hydrazone 162 °C (reported 162 °C), 1H NMR, δ 11.10 (1Hs), δ 8.13 (1Hs), δ 7.56-8.41 (2Hm), δ 2.55-2.50 (4Hq), δ 1.78-1.90 (6Hq), Acetophenone (d') was prepared from Ethylbenzene (d) (2.0 mmol) as above. The Mp. of hydrazone 249 °C (reported 250 °C), 1H NMR, δ 11.87 (1Hs), δ 9.66 (1Hs), δ 7.86-8.95 (7Hm), δ 1.75 (3Hs), 9,10-Anthraquinone (e') was prepared from Anthracene (e) (1.0mmol) as above. The Mp. of product was 285 °C (reported 286 °C), IR \textsubscript{max} 1678 cm\textsuperscript{-1}(\nu_{c=c}), 3070 cm\textsuperscript{-1}(\nu_{c-H, str., arom.}), 697 cm\textsuperscript{-1},725 cm\textsuperscript{-1},872 cm\textsuperscript{-1}(\nu_{C-H, bend., arom.}), 9-Fluorenone (f') was prepared from Phenanthrene (f) (1.0mmol) as above. The Mp. of product was 84 °C (reported 82-85 °C), 1H NMR, δ 7.84-8.70 (8Hm); IR \textsubscript{max} 1676 cm\textsuperscript{-1}(\nu_{c=c}), 3047 cm\textsuperscript{-1}(\nu_{C-H, str., arom.}), 756 cm\textsuperscript{-1},866 cm\textsuperscript{-1},881 cm\textsuperscript{-1}(\nu_{C-H, bend., arom.}), 1601 cm\textsuperscript{-1}(\nu_{C=C, str., arom.}).

3. RESULTS AND DISCUSSION

Oxidation of various organic substrates is summarized in Table 1. For getting the maximum yield 5 to 8 sets were performed by changing the concentration or conditions of each component, which can affect the yield. Control experiments were performed by adding organic substrate, pre-adsorbed on Al\textsubscript{2}O\textsubscript{3}, to the aqueous solution of ferric nitrate (entry 1, Table2) and sodium hypochlorite solution (entry 2, Table2) separately under similar conditions and the paste thus formed was irradiated in microwave oven. Yield increases with increasing power of microwaves (entries 3 and 4, Table 2) apparently due to the availability of more energy required to facilitate the reaction. While increase in time of exposure increases the yield in the beginning reaches to a maximum and beyond which, further increase in time decreases the yield (entries 4, 5 and 6, Table 2). This was probably due to the evaporation of product due to excess heating under prolonged exposure. Yield reaches to a
maximum and then starts decreasing with further increase in the amount of ferric nitrate (entries 7, 4 and 8, Table 2) while yield decreases with increasing amount of sodium hypochlorite (entries 4 and 9, Table 2). Probable reason for this appears to be the decomposition of ferrate ions. It is well known that the decomposition of high-valent oxyanions is catalyzed by traces of impurities like the reducing organic materials or metal traces, which may be present in these reactants. This also indicates that optimum conditions are necessary for getting the maximum yield. The charged layered structure of the aluminosilicate solid may provide, a suitable, highly polar environment to adsorb organic substrate and to favour its encounter with ferrate ions in the hydrated interlamellar spaces. It has been suggested that aluminosilicate solid acts as a source of humidity and also displays an intrinsic catalytic activity which is not due to the intervention of strong Brønsted or Lewis acidic centers present within the aluminosilicate structure. Presence of electron donating (-CH3, -OCH3) or abstracting (-OH) groups decreased or increased the yields respectively, in the usual manner (entries a,b,g &h, Table 1). Interestingly, more probably similar yields were obtained when the reaction was carried out in a water bath under reflux conditions in the absence of Cu NPs and under microwave irradiation in the presence of Cu NPs, the only difference was that in the later method reported yield was obtained in 1.5 to 3.0 min. Solid support, after removing the product formed, can be recycled 2 to 4 time with approximately 5 to 10 % decrease in efficiency in each cycle.

Table 1. Oxidation of various organic compounds (2.0 m mol) with Na2FeO4 adsorbed on Al2O3 in presence of Cu NPs under microwave irradiation A Oxidation at room temp.(~25 °C) in 48 h;

<table>
<thead>
<tr>
<th>Organic substrate (mmol)</th>
<th>Product</th>
<th>Al2O3</th>
<th>Fe(NO3)3.9 H2O(m.mol)</th>
<th>NaClO (mmol)</th>
<th>MW(% power)</th>
<th>Time (sec.)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentanol(a)</td>
<td>Cyclopentanone (a’c)</td>
<td>4.0</td>
<td>4.95</td>
<td>30.0</td>
<td>100</td>
<td>100</td>
<td>7.8a;29.5b;50.0c;32.1d; 35.0e.</td>
</tr>
<tr>
<td>O-Methyl cyclohexanol(b)</td>
<td>O-Methyl cyclohexanone (b')</td>
<td>4.0</td>
<td>4.95</td>
<td>25.4</td>
<td>100</td>
<td>100</td>
<td>15.2a;37.8b;34.2c;44.2d; 38.9e.</td>
</tr>
<tr>
<td>Cyclohexane(c)</td>
<td>Cyclohexanone (c')</td>
<td>4.0</td>
<td>7.42</td>
<td>45.0</td>
<td>80</td>
<td>120</td>
<td>9.9a;19.9b;21.8c;19.8d; 21.9e.</td>
</tr>
<tr>
<td>Ethylbenzene(d)</td>
<td>Acetophenone (d')</td>
<td>4.0</td>
<td>7.42</td>
<td>35.7</td>
<td>80</td>
<td>120</td>
<td>10.0a;38.3b;39.0c;39.6d; 49.0e.</td>
</tr>
<tr>
<td>Anthracene(e)</td>
<td>9,10-Anthra quinone(e')</td>
<td>4.0</td>
<td>7.42</td>
<td>35.7</td>
<td>60</td>
<td>120</td>
<td>27.0a;62.5b;76.1c;99.1d; 96.9e.</td>
</tr>
<tr>
<td>Phenanthrene(f)</td>
<td>9-Flourenone (f')</td>
<td>4.0</td>
<td>7.42</td>
<td>35.7</td>
<td>60</td>
<td>160</td>
<td>49.4a;69.4b;87.5c;88.1d; 94.4e.</td>
</tr>
<tr>
<td>p-methoxy benzoaldehyde(g)</td>
<td>p-methoxy benzoic acid(g')</td>
<td>4.0</td>
<td>4.95</td>
<td>30.4</td>
<td>100</td>
<td>130</td>
<td>5.0a;18.1b;17.7c;19.6d3e; 21.9e.</td>
</tr>
<tr>
<td>p-hydroxy benzaldehyde(h)</td>
<td>4-hydroxy benzoic acid(h')</td>
<td>4.0</td>
<td>4.95</td>
<td>30.4</td>
<td>100</td>
<td>120</td>
<td>8.0a;75.4b;85.9c;88.9d;94.2e.</td>
</tr>
</tbody>
</table>

b Oxidation in presence of Al2O3 under MW only; c Oxidation in presence of Cu NPs and Al2O3 under MW condition; d Oxidation in water bath with Al2O3 only in 3 h(a-f),1h(g&h); e Oxidation in water bath with Cu NPs and Al2O3 in 3h(a-f),1h(g&h)

Table 2: Effect of various factors on yield in the formation of Cyclopentanone from Cyclopentanol (2.0 mmol) in the absence of Cu NPs

<table>
<thead>
<tr>
<th>Entry nos.</th>
<th>Fe(NO3)3.9 H2O (m.mol.)</th>
<th>NaClO (m.mol.)</th>
<th>Al2O3</th>
<th>MW(% Power)</th>
<th>Time (sec.)</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.49</td>
<td>-</td>
<td>4.0</td>
<td>20</td>
<td>120</td>
<td>negligible</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>26.4</td>
<td>4.0</td>
<td>60</td>
<td>120</td>
<td>negligible</td>
</tr>
<tr>
<td>3</td>
<td>4.95</td>
<td>26.4</td>
<td>4.0</td>
<td>80</td>
<td>120</td>
<td>13.7</td>
</tr>
<tr>
<td>4</td>
<td>4.95</td>
<td>26.4</td>
<td>4.0</td>
<td>80</td>
<td>120</td>
<td>29.9</td>
</tr>
<tr>
<td>5</td>
<td>4.95</td>
<td>30.0</td>
<td>4.0</td>
<td>100</td>
<td>90</td>
<td>18.8</td>
</tr>
<tr>
<td>6</td>
<td>4.95</td>
<td>30.0</td>
<td>4.0</td>
<td>100</td>
<td>100</td>
<td>29.5</td>
</tr>
<tr>
<td>7</td>
<td>4.45</td>
<td>26.4</td>
<td>4.0</td>
<td>80</td>
<td>120</td>
<td>25.7</td>
</tr>
<tr>
<td>8</td>
<td>5.44</td>
<td>26.4</td>
<td>4.0</td>
<td>80</td>
<td>120</td>
<td>27.4</td>
</tr>
<tr>
<td>9</td>
<td>4.95</td>
<td>32.3</td>
<td>4.0</td>
<td>80</td>
<td>120</td>
<td>23.9</td>
</tr>
</tbody>
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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

REFERENCE


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Dr. Manish Shrivastava is Assistant Professor (Chemistry), Department of Chemistry Banasthali University, Rajasthan. He obtained his Graduation, Post graduation and D. Phill (PhD) degree from University of Allahabad, Allahabad. He has published over 20 research paper in International Journals, eight proceedings in national conference. At present time it is work in field of nanocatalyst, catalyzed organic synthesis and water treatment. At present time six students going to research work under the supervision and two students awarded the PhD degree under the supervision. Dr. Shrivastava presented research paper in numerous International and National conferences.