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Synthesis of some aromatic aldehydes and acids by sodium ferrate in presence of copper nano-particles adsorbed on K 10 montmorillonite using microwave irradiation

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Excellent yields were obtained in the oxidation of benzyl alcohol, benzaldehyde, 4-methoxy benzyl alcohol and 4-nitro benzaldehyde with sodium ferrate in the presence of copper nano particles adsorbed on montmorillonite K 10 under microwave irradiation. Aniline, *p*-toluidine, phenol, catechol, resorcinol and *p*-cresol polymerize under these conditions without exposing the mixture to microwaves. The one-pot system does not require tedious separation of ferrate and is quick and environmentally benign. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: microwave; sodium ferrate; oxidation; copper nano-particles; montmorillonite K10

INTRODUCTION

Classic reagents used for the oxidation of organic functionalities generally require rigorous control of the experimental conditions because of their lack of selectivity.[1–4] Oxidants based on chromium[5] and on manganese[6] are corrosive, and are irritants for the skin and sensitive body parts such as the eyes. They are toxic to man and to the environment. Derivatives of chromium(VI) in particular are well-known carcinogens.[7] 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 to +0.7 V vs 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 $FeO_4{}^{2-}$, remains monomeric.[8] 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.[9] In dilute solution, the lowest rate of reduction of ferrate by water occurs between pH 9.4 and 9.7.[10] 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. The 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.[11] Another approach involves recourse to a solid mixture of K_2FeO_4, basic alumina and a hydrated inorganic salt such as $CuSO_4 \cdot 5H_2O$ for oxidizing allylic and benzylic alcohols dissolved in benzene.[12] Oxidative cleavage of propargyl alcohol derivatives using $K_2FeO_4–Al_2O_3$[13] has been reported. Conversion of aliphatic and aromatic alcohols including benzyl alcohol to carbonyl compounds by K_2FeO_4 with $K10/Cu^{2+}$[14] has also been reported with 62% GC yield in 24 h. An 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 $KMnO_4$ and $CuSO_4.5H_2O$, in which it was assumed that the salt acts as a source of humidity.[15] Our approach to clean and selective

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oxidations is to make use of Fe(VI) as the oxidant in combination with montmorillonite, without separating Fe(VI) in the solid state. For this purpose our attention was directed to sodium ferrate (Na_2FeO_4), which has a different behaviour from other ferrates and remains soluble in an aqueous solution saturated in sodium hydroxide. Its preparation from an aqueous medium is thus made difficult and leads to rather impure samples. In the absence of solvent, conversely, it is possible to form Na_4FeO_3 salt by heating to 370 °C a mixture of Fe_2O_3 and Na_2O_2 under an atmosphere of dioxygen. Rigorous control of experimental conditions is required in order to minimize the amount of iron(III) and iron(IV) derivatives formed as byproducts contaminating the desired Fe(VI) salt.[16,17] Association of a ferric salt with a clay support has also been reported previously,[18–20] which prompted us to think in the direction of finding a way for sodium ferrate to be used in solution itself. To the best of our knowledge, without following the tedious and lengthy process of separation of Fe(VI), oxidation of organic substrates with *in-situ* prepared Fe(VI) in combination of montmorillonite K10 and metallic copper nano-particles has not been reported.

EXPERIMENTAL

A study was performed to determine the efficiency of economical and environmentally friendly oxidations of organic compounds by iron (VI) in combination with montmorillonite K10, without following the tedious and lengthy process of separating and purifying iron ferrate first in the solid state. For this purpose sodium ferrate was prepared by taking ferric nitrate $[Fe(NO_3)_3^{\bullet}9H_2O]$ 2.0 g (4.49 mmol) in a 50 ml flask and the required amount (1–3 ml; 14.7–44.1 mmol) of sodium hypochlorite solution was added drop-wise with constant stirring. Formation of a clear dark purple-red coloured solution indicates the formation of ferrate dianions.[21] Copper nano-particles were prepared by borohydride reduction by adding 10 ml sodium borohydride solution (1.0 mmol) to a solution of $CuSO_4^{\bullet}5H_2O$ (1.0 mmol) with the help of a syringe with constant stirring. The appearance of very fine dark black coloured precipitate indicates formation of copper nano-particles in the solution. In a typical oxidation procedure the required quantity of montmorillonite (2.0 g) was added to copper sulfate solution and, to the vigorously stirred solution, the required quantity of sodium borohydride (1.0 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 copper nano-particles. After mixing with freshly prepared sodium ferrate (Na_2FeO_4) solution, the whole mass was then irradiated in a domestic microwave oven for the required time. After exposure, solid mass was extracted with diethyl ether (3 × 20 ml). The extract was evaporated under reduced pressure to afford the product. A Kenstar (model OM-20 ESP, 800 W, Aurangabad, India) domestic microwave oven was used for studying the reactions under microwave irradiations. IR spectra were taken with a Bruker Vector-22 IR spectrophotometer and ^1H NMR spectra with a Xeol 400 MHz spectrophotometer in $CDCl_3$ with TMS as internal standard. Commercially obtained reagents were used without further purification. Merck GF254 silica gel coated plates were used to monitor reactions with TLC. In all the cases by running the TLC plate no product other than that reported could be found. The 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. A 2.0 g aliquot of montmorillonite was added to 1.0 mmol copper sulfate solution (10.0 ml) in a 50 ml flask with constant stirring with magnetic stirrer. To this, 1.0 mmol sodium borohydride solution (10.0 ml) was added drop-wise using a syringe. Precipitate was washed with distilled water and was left overnight at room temperature. Benzyl alcohol (**a**), 1.0 mmol, was adsorbed on the partially dried clay containing copper nano-particles and then the mass was well mixed with freshly prepared solution of sodium ferrate. After irradiating in microwave oven, the total mass was extracted with diethyl ether (3 × 20 ml). Benzaldehyde (**a′**) was weighed and analyzed in the form of its 2,4-dinitrophenyl hydrazone. The melting point of hydrazone was 231 °C (reported 237 °C), ^1H NMR δ 11.3 (1 Hs), δ 11.0 (1Hs), δ 9.2 (1Hs), δ 7.2–8.3 (7 Hm). Anisaldehyde (**b′**) was prepared from 4-methoxybenzyl alcohol (**b**) (1.0 mmol) as above. The melting point of hydrazone 253 °C (reported 254 °C); 1H NMR, δ 11.3 (1Hs), δ 11.0 (1Hs), δ 9.1 (1Hs), δ 4.0 (3Hs), δ 7.1–8.3 (6Hm). Benzoic acid (**c′**) was prepared from benzaldehyde (**c**) (1.0 mmol) as above. The melting point was 120 °C (reported 122 °C), IR ν_{max}. 2561–3069 cm^{-1} (ν_{-OH} and $\nu_{C-H\ stretch}$), 1687 cm^{-1} ($\nu_{C=O}$). 4-Nitrobenzoic acid (**d′**) was prepared from 4-nitro benzaldehyde (**d**; 1.0 mmol) as above; m.p. 238 °C (reported 241 °C), IR ν_{max} 2548–3115 cm^{-1} (broad ν_{-OH} and $\nu_{C-H\ stretch}$), 1690 cm^{-1} ($\nu_{C=O}$), 1581 and 1351 cm^{-1} ($\nu_{N=O}$).

RESULTS AND DISCUSSION

Oxidation of various organic substrates is summarized in Table 1. The reactions are complete within a few minutes in microwave oven. To obtain the maximum yield, four to six 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 montmorillonite, to the aqueous solution of ferric nitrate (entry 1, Table 2) and sodium hypochlorite solution (entry 2, Table 2) separately under similar conditions and the paste thus formed was irradiated in a microwave oven. Negligible amount of product formed, showing that ferric nitrate and sodium hypochlorite individually were not responsible for oxidation and the system functions properly only under optimum conditions.

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Table 1. Oxidation of various organic compounds (1.0 mmol) with Na_2FeO_4 adsorbed on montmorillonite (K10) in presence of Cu-nano particles under microwave irradiation

Organic substrate (mmol)	Product	K10 (g)	$Fe(NO_3)_3^{\bullet}$ $9H_2O$ (mmol)	NaClO (mmol)	MW (% power)	Time (s)	Yield, % (isolated yield in mg)
Benzyl alcohol (**a**)	Benzaldehyde (**a′**)	2.0	4.95	44.1	100	120	87.4(250)[a]; 83.9(240)[b]; 69.9(200)[c]; 87.4(250)[d]
4-Methoxybenzyl alcohol (**b**)	Anisaldehyde (**b′**)	2.0	4.95	36.8	80	120	72.8(230)[a]; 69.6(220)[b]; 53.8(170)[c]; 72.8(230)[d]
Benzaldehyde (**c**)	Benzoic acid (**c′**)	2.0	4.95	22.05	80	90	70.4 (86)[a]; 67.3(82)[b]; 32.8(40)[c]; 70.4(86)[d]
p-Nitro-benzaldehyde (**d**)	*p*-Nitrobenzoic acid (**d′**)	2.0	4.95	22.05	80	90	89.8 (150)[a]; 83.8(140)[b]; 47.9(80)[c]; 89.8(150)[d]
Aniline (**e**)	Polyaniline (**e′**)	—	4.95	22.05	—	—	polymerized
p-Toluidine (**f**)	Polytoluidine (**f′**)	—	4.95	22.05	—	—	Polymerized
Phenol (**g**)	Polyphenol (**g′**)	—	4.45	22.05	—	—	Polymerized
Catechol (**h**)	Polycatechol (**h′**)	—	4.45	22.05	—	—	Polymerized
Resorcinol (**i**)	Polyresorcinol (**i′**)	—	4.45	22.05	—	—	Polymerized
Cresol (**j**)	Polycresol (**j′**)	—	4.45	22.05	—	—	Polymerized

[a] Oxidation in presence of Cu nano-particles and K10; [b] oxidation in presence of K10 only; [c] oxidation at room temperature (~30 °C) in 48 h; [d] oxidation in water bath under similar conditions in 3 h (**a** and **b**); 1 h (**c** and **d**).

Table 2. Effect of various factors on yield in the formation of anisaldehyde from 4-methoxy benzyl alcohol (1.0 m mol) in the absence of Cu-nanoparticles

Entry nos	Fe $(NO_3)_3^{\bullet}$ $9H_2O$ (mmol)	NaClO (mmol)	Mont-morillonite K10 (g)	MW(% power)	Time (s)	Yield, %
1	4.49	—	2.0	80	120	15
2	—	36.7	2.0	80	120	10
3	4.95	36.8	2.0	20	120	47.2
4	4.95	36.8	2.0	80	120	69.6
5	4.95	36.8	2.0	80	60	31.6
6	4.95	36.8	2.0	80	150	53.7
7	3.71	36.8	2.0	80	120	50.6
8	5.94	36.8	2.0	80	120	53.7
9	4.95	51.34	2.0	80	120	50.6

The yield increased with increasing power of the microwave (entries 3 and 4, Table 2), apparently due to the availability of more energy to facilitate the reaction. While the increase in time of exposure increased the yield in the beginning, it reached a maximum beyond which further increase in time decreased the yield (entries 4–6, Table 2). This was probably due to the evaporation of product due to excess heating under prolonged exposure. The yield reached a maximum and then started to decrease with further increase in the amount of ferric nitrate (entries 7, 4 and 8, Table 2), while the yield decreased with increasing amount of sodium hypochlorite (entries 4 and 9, Table 2). The probable reason for this appears to be the decomposition of ferrate ions. It is well known that the decomposition of high-valency oxyanions is catalyzed by traces of impurities[22,23] like reducing organic materials or metal traces, which may be present in these reactants. This also indicates that optimum conditions are necessary to obtain the maximum yield. The charged layered structure of the aluminosilicate solid may provide a suitable highly polar environment to adsorb organic substrate and to favor its encounter with ferrate ions in the hydrated interlamellar spaces. It has been suggested[14] that aluminosilicate solid acts as a source of humidity and also displays an intrinsic catalytic activity (entries 'b' in Table 1), which is not due to the intervention of strong Brønsted or Lewis acidic centers present within the aluminosilicate structure. The presence of electron donating ($-OCH_3$) or abstracting ($-NO_2$) groups decreased or increased the yields, respectively, in the usual manner (entries 1–4, Table 1). It was also observed that polymerization took place if an amino or hydroxy group was present in the benzene ring (entries **e**–**j**, Table 1). Interestingly, similar yields were obtained when the reaction was carried out in a water bath under reflux conditions in the absence of copper nano-particles and under microwave irradiation in the presence of copper nano-particles, the only difference being that in the latter method the reported yield was obtained in 1.5–2.0 min. The solid support, after removing the product formed, can be recycled two to four times with approximately 5–10% decrease in efficiency in each cycle.

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REFERENCES

1. Trakanovsky WS (ed.). *Oxidation in Organic Chemistry, Part B*. Academic Press: New York, 1973.
2. Trost BM (ed.). *Comprehensive Organic Synthesis (Oxidation)*, Vol. 7. Pergamon Press: New York, 1991.
3. Page BJ, Loar GW. *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn, Vol. 6. Wiley: New York, 1988; 263–311.
4. Reidies AH. *Kirk–Othmer Encyclopedia of Chemical Technology*, 3rd edn, Vol. 14. Wiley: New York, 1981; 844–895.
5. Nriagu JO, Nieboer E. (eds). *Chromium in the Natural and Human Environments*. Wiley: New York, 1988.
6. Gritter RJ, Dupre GD, Wallace TJ. *Nature* 1964; **202**: 179.
7. House HO. *Modern Synthetic Reactions*, 2nd edn. W.A. Benjamin: Menlo Park, CA, 1972; 257–291.
8. Goff H, Murmann RK. *J. Am. Chem. Soc.* 1971; **93**: 6058.
9. Wagner WF, Gump JR, Hart EN. *Anal. Chem.* 1952; **24**: 1497.
10. Lee DG, Gai H. *Can. J. Chem.* 1993; **71**: 1394.
11. Kim KS, Chang YK, Bae SK, Hahn CS. *Synthesis* 1984; 866.
12. Kim KS, Song YH, Lee NH, Hahn CS. *Tetrahedon Lett.* 1986; **27**: 2875.
13. Caddick S, Murtagh L, Weaving R. *Tetrahedron Lett.* 1999; **40**: 3655.
14. Delaude L, Laszlo P. *J. Org. Chem.* 1996; **61**: 6360.
15. Menger FM, Lee C. *J. Org. Chem.* 1979; **44**: 3446.
16. Kiselev YM, Kopelev NS, Zavyalova NA, Perfiliev YD, Kazin PF. *Russ. J. Inorg. Chem. (Transl. Of Zh.Neorg. Khim.)* 1989; **34**: 1250.
17. Kopelev NS, Perfiliev YD, Kiselev YM. *J. Radioanal. Nucl. Chem.* 1992; **162**: 239.
18. Fieser M. *Fieser and Fieser's Reagents for Organic Synthesis*. Wiley: New York, 1984; Vol. 11, 237; Vol.12, 231.
19. Cornelis A, Laszlo P. *Synthesis* 1985; 909.
20. Cornelis A, Laszlo P. *Synthesis* 1980; 849.
21. Delaude L, Laszlo P, Lehance P. *Terahedron Lett.* 1995; **36**: 8505.
22. Veprek-Siska J, Ettel V. *Chem. Ind. (Lond.)* 1967; 548.
23. Ettel V, Veprek-Siska J. *Collect. Czech. Chem. Commun.* 1969; **34**: 2182.

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