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Controlled Oxidation of Benzyl Alcohol by *in situ* Prepared Sodium Ferrate in Organic and Aqueous Medium

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ABSTRACT

in situ prepared sodium ferrate oxidizes benzyl alcohol exclusively to benzaldehyde in acetonitrile medium. Under these conditions, addition of iridium(III) chloride as a homogeneous catalyst showed a negative affect on the yield. Change in the medium from organic to aqueous changes the product exclusively to benzoic acid and the addition of iridium(III) chloride increases the yield to a great extent. Thus only by changing the reaction conditions, product of oxidation can be monitored.

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INTRODUCTION

Oxidation of alcohols is of great significance in organic chemistry, both for fundamental research and industrial manufacturing [1]. Out of many oxidants potassium ferrate (K_2FeO_4) is the best known member among the family of iron(VI) derivatives. In basic solution the rate of decomposition of ferrate is highly variable. pH and temperature are the key factors, but light does not affect the stability of ferrate solution. Previously the stability of ferrate was reported [2] to be at pH 10 but later on kinetic measurements showed [3] that lowest rate of reduction of ferrate by water is between pH 9.4 to 9.7. The reduction potentials for Fe(VI) to Fe(III) have been estimated as 2.20 and 0.72 V for reactions in acidic and basic media, respectively [2] suggesting that K_2FeO_4 is potentially the stronger oxidant compared to other oxidants. Potassium ferrate has been reported to oxidize a variety of organic functional groups with or without solid support [3-10]. Studies involving K_2FeO_4 generally employ alkaline aqueous conditions [11-13] in which K_2FeO_4 is highly soluble but unstable. Potassium ferrate is insoluble in non-aqueous systems. Decomposition of ferrate can be observed by the colour change from deep purple to brown, indicating the reduction of Fe(VI) to Fe(III). There have been studies on K_2FeO_4 mediated oxidation of alcohols under phase-transfer conditions [5,14]. There are many reports on the oxidation of activated alcohols on solid supports in non-aqueous solvents also [6-8,15].

Poor solubility in most of the organic solvents, its instability in aqueous medium and high rate of decomposition in the presence of acids restricts the storage and use of potassium ferrate as an oxidant. Moreover, separation of potassium ferrate in the solid form before it can be used as an oxidant is a tedious and multi-step process. Sodium ferrate (Na_2FeO_4) remains soluble in aqueous solutions saturated with sodium hydroxide and thus its preparation from aqueous solutions is difficult and leads to impure samples. Use of *in situ* prepared sodium ferrate instead of potassium ferrate may minimize the problems to a great extent. In case of ferrate oxidations successful monitoring of the redox processes requires two opposite conditions to be tackled, poor solubility of ferrates in organic phase and many organic substrates are insoluble in aqueous phase. During the course of study we found that addition of small amounts of certain acids enhances the oxidizing capability of ferrate in oxidizing organic substrates dissolved in organic solvents. Oxidation of benzyl alcohol to benzaldehyde by potassium ferrate has been reported in non-aqueous medium [16]. However, to the best of our knowledge, no work has been reported on the influence of organic acids on the oxidative abilities of Na_2FeO_4. Selective oxidation of benzyl alcohol is an important oxidation process. From the synthetic point of view, catalysis by iridium(III) chloride in the oxidation of benzyl alcohol in aqueous acidic medium has been reported by us [17] in which cerium(IV) sulfate could oxidize benzyl alcohol with 23.7 % yield of benzaldehyde. Present study shows that five times less amount of same catalyst (6.68×10^{-5} mmol compared to 3.34×10^{-4} mmol) oxidizes benzyl alcohol exclusively into benzoic acid with much higher yield. Further, change of the medium from aqueous to organic results in selective oxidation of benzyl alcohol exclusively into benzaldehyde. We found that the oxidative ability of Na_2FeO_4 was significantly promoted by adding a small amount of acid. The present work provides a green method for getting the desired product by oxidizing benzyl alcohol with sodium ferrate (Na_2FeO_4) in aqueous or in non-aqueous medium.

EXPERIMENTAL

In the oxidation of benzyl alcohol by sodium ferrate in aqueous and in organic phase ferric nitrate and sodium hypochlorite (4 %) (Lancaster), benzyl alcohol, sulphuric acid, hydrochloric acid (E-Merck) 2, 4-dinitrophenylhydrazine (Loba Chemie Indaustranal Ltd.) were used as such without further purification. Ruthenium(III) chloride (Johnson-Matthay Chemicals Ltd.), was prepared by dissolving the sample ($RuCl_3 \cdot xH_2O$) in minimum amount of hydrochloric acid and the solution was diluted to 1000 mL with distilled water. The final strengths of hydrochloric acid and ruthenium(III) chloride were 10.91×10^{-3} and 4.0×10^{-3} M respectively. 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 derivative and by running TLC plates with authentic samples. Products were confirmed finally with the help of their spectral studies like FTIR spectra with Perkin Elmer spectrophotometer, ^{1}H NMR spectra were studied with a Xeol 400 MHz spectrophotometer in $CDCl_3$ with TMS as internal standard. All spectral studies were performed at Banaras Hindu University, Varanasi on the paid basis.

***in situ* preparation of sodium ferrate:** Sodium ferrate (Na_2FeO_4) solution was prepared by taking required quantity of ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] in a 50 mL beaker and then required amount of sodium hypochlorite solution was added drop-wise with constant stirring. Formation of clear dark purple red coloured solution indicated the formation of ferrate dianions in the solution [8].

As in the case of oxidation of ferric chloride by sodium hypochlorite, oxidation of ferric nitrate may be shown by eqn. 1:

$$2Fe(NO_3)_3 + 3NaClO + 10NaOH \longrightarrow 2Na_2FeO_4 + 6NaNO_3 + 3NaCl + 5H_2O \quad (1)$$

General procedure: In a round bottom flask calculated amount of organic compound was mixed with the solution containing fixed amounts of ferric nitrate and sodium hypochlorite. A water-cooled condenser was attached with the flask. The flask attached with condenser was heated in a water bath at the fixed temperature for the desired time (Macro Scientific Works Pvt. Ltd., Delhi, India). After completion of the reaction the contents were cooled and were extracted three times with diethyl ether (3 × 15 mL).

RESULTS AND DISCUSSION

Preparation of benzaldehyde from the oxidation of benzyl alcohol: It was observed that the oxidation of benzyl alcohol resulted exclusively in benzaldehyde without it's over oxidation to benzoic acid if the reactions were performed in organic phase. It was also observed that selection of solvent was important because yield of product strongly depended on the solvent. To find out in which solvent maximum yield of product may be obtained, the study was performed in the presence of various organic solvents. Table-1 shows that maximum yield of product was obtained when acetonitrile was used as a solvent. It was also observed that the presence of an organic acid enhances the oxidative property of sodium ferrate, thus, the study was performed in the presence of four acids *viz.* acetic acid, phosphomolybdic acid, phosphotungstic acid and oxalic acid separately to find out which acid catalyzes the oxidation of benzyl alcohol to the maximum extent (Table-2). It is clear from the table that the amount of acid and water also affected the yield. Maximum yield was obtained when 250 mg of oxalic acid was taken in 2.5 mL of water. Presence of water was necessary so that the acid may dissociate to give the hydrogen ions, which probably catalyze the oxidative capacity of sodium ferrate. Table-3 shows the effect of change of various parameters on the yield of benzaldehyde. Increase in time increases the yield in the beginning but after a certain point increase in duration of experiment starts decreasing the yield (Table-3, entries 1-5). This may be due to the decomposition of sodium ferrate initiated by longer durations at higher temperatures. Increase in the temperature increases the yield (Table-3, entries 6-10). However, reactions were not performed above 100 °C considering economy and practical difficulties in mind. It was also observed that increase in the amount of

TABLE-1
EFFECT OF VARIATION OF DIFFERENT SOLVENT ON THE YIELD OF BENZELDEHYDE
[Benzyl alcohol] = 1.0 mmol, [Sodium ferrate] = 4.95 mmol, Time = 180 min, Temperature = 100 °C

Solvent	Oxalic acid (mg)/Water (mL)	Yield (%)
–	–	6.7
CH_2Cl_2	250/2.5	29.9
$CHCl_3$	250/2.5	31.9
CS_2	250/2.5	18.1
CCl_4	250/2.5	23.8
C_6H_5Cl	250/2.5	9.3
CH_3CN	250/2.5	34.1

TABLE-2
EFFECT OF PRESENCE OF VARIOUS ORGANIC ACIDS ON THE YIELD OF BENZALDEHYDE
[Benzyl alcohol] = 1.0 mmol; [Acetonitrile] = 190.0 mmol; Time = 180 min; [Sodium ferrate] = 4.95 mmol; Temperature = 100 °C

Acid (mg)/Water (mL)	Yield (%)
0.25 mL Acetic acid/0.0 water	17.5
25.0 Phosphotungstic acid/0.25 water	18.8
250.0 Phosphotungstic acid/2.5 water	5.7
25.0 Phosphomolybdic acid/0.25 water	18.0
250.0 Phosphomolybdic acid/2.5 water	8.5
25.0 Oxalic acid/0.25 water	18.3
250.0 Oxalic acid/2.5 water	34.1
300.0 Oxalic acid/3.0 water	32.3
400.0 Oxalic acid/4.0 water	31.3
500.0 Oxalic acid/5.0 water	29.7

TABLE-3
EFFECT OF VARIATION OF DIFFERENT PARAMETERS ON THE YIELD OF BENZALDEHYDE IN ORGANIC PHASE
[Benzyl alcohol] = 1.0 mmol; [Oxalic acid/water] = 250.0/2.5 mg/mL; [Acetonitrile] = 190 mmol

S. No.	Sodium ferrate (mmol)	Time (min)	Temp. (°C)	Product	$[IrCl_3] \times 10^{-5}$ mmol	Yield (%)
1	4.95	120	100	Benzaldehyde	–	17.9
2	4.95	150	100	Benzaldehyde	–	21.0
3	4.95	180	100	Benzaldehyde	–	34.1
4	4.95	210	100	Benzaldehyde	–	30.7
5	4.95	240	100	Benzaldehyde	–	26.7
6	4.95	180	60	Benzaldehyde	–	11.6
7	4.95	180	70	Benzaldehyde	–	13.5
8	4.95	180	80	Benzaldehyde	–	16.8
9	4.95	180	90	Benzaldehyde	–	19.5
10	4.95	180	100	Benzaldehyde	–	34.1
11	2.48	180	100	Benzaldehyde	–	26.4
12	4.95	180	100	Benzaldehyde	–	34.1
13	9.90	180	100	Benzaldehyde	–	32.9
14	19.8	180	100	Benzaldehyde	–	18.0
15	4.95	180	100	Benzaldehyde	1.00	19.9
16	4.95	180	100	Benzaldehyde	3.34	18.0

sodium ferrate increases the amount of benzaldehyde in the beginning but after a certain stage increase in the amount of oxidant starts decreasing the yield (Table-3, entries 11-14). Reason for the dectrease in yield at higher concentrations of sodium ferrate may be due to the wasteful decomposition of ferrate at higher concentrations. It has been reported that the rate of decomposition of ferrate increases with increasing concentrations [18]. It was observed that maximum yield of benzaldehyde is obtained when amount of sodium ferrate is kept at 4.95 mmol in the reaction mixture. In organic phase it was observed that addition of iridium(III) chloride, under optimum conditions for getting benzaldehyde as the product of oxidation (Table-3, entry 12), decreased the yield (Table-3, entries 15-16). Presence of carbonyl group in the product was indicated by thin layer chromatography and the spot test methods. m.p. of the hydrazone of the product was found to be 235 °C (reported 237 °C). Finally the product was confirmed by its IR and NMR spectra. IR (KBr, ν_{max}, cm^{-1}): 3286 (N-H str.), 3101 (C-H str. Aromatic), 2853 (C-H str. aldehyde), 1621 (C=N str.), 1586 (N=O asym. str. aromatic nitro), 1335 (N=O sym. str. aromatic nitro), 1313 (C-N str.). NMR signals: δ 7.457-8.355 (5H, m), δ 3.634 (1H, s), δ 2.490 (1H, s), δ 11.626 (1H, s), δ 8.658 (1H, d), δ 8.823-8.814 (1H, d).

Synthesis of benzoic acid from the oxidation of benzyl alcohol: Contrary to the results obtained in organic phase, benzyl alcohol was oxidized exclusively to benzoic acid when the oxidation was performed in aqueous phase. It was also observed that in aqueous phase addition of traces of iridium(III) chloride increases the yield of benzoic acid to a great extent. In aqueous phase also increase in the amount of oxidant increases the yield of benzoic acid in the beginning but after reaching to a maximum yield starts decreasing with further increase in the oxidant (Table-4, entries 1-8), thus showing similar trend as was obtained in the organic phase. It was also observed that compared to the organic phase, quite high amount of sodium ferrate was needed to oxidize benzyl alcohol into benzoic acid. Surprisingly in aqueous phase addition of iridium(III) chloride increases the yield of benzoic acid to a

TABLE-4
EFFECT OF VARIATION OF DIFFERENT PARAMETERS ON THE YIELD OF BENZOIC ACID IN AQUEOUS PHASE (IN ALL THE CASES 1 mmol BENZYL ALCOHOL WAS OXIDIZED EXCLUSIVELY TO BENZOIC ACID)

S. No.	Sodium ferrate (mmol)	Time (min)	Temp. (°C)	$[IrCl_3] \times 10^{-5}$ mmol	Yield (%)
1	9.90	180	100	–	5.7
2	14.85	180	100	–	8.2
3	19.80	180	100	–	17.4
4	24.75	180	100	–	23.6
5	29.70	180	100	–	24.8
6	34.65	180	100	–	33.5
7	39.60	180	100	–	21.6
8	44.55	180	100	–	18.2
9	34.65	180	100	1.67	40.2
10	34.65	180	100	3.34	42.9
11	34.65	180	100	5.01	47.4
12	34.65	180	100	6.68	61.7
13	34.65	180	100	8.35	50.0
14	34.65	180	100	10.02	47.6
15	34.65	120	100	6.68	11.9
16	34.65	150	100	6.68	48.6
17	34.65	180	100	6.68	61.7
18	34.65	210	100	6.68	24.8
19	34.65	240	100	6.68	24.5
20	34.65	180	60	6.68	5.0
21	34.65	180	70	6.68	8.6
22	34.65	180	80	6.68	12.0
23	34.65	180	90	6.68	14.7
24	34.65	180	100	6.68	61.7

great extent in the beginning but after a certain period yield starts decreasing on increasing the amount of catalyst (Table-4, entries 9-14). The set giving the maximum yield in presence of iridium(III) chloride was selected to see the affect of change of duration of experiment on the yield. It was observed that the yield increases only up to a certain point and beyond which further increase in the duration of experiment decreases the yield (Table-4, entries 15-19). As observed in the case of reaction performed in organic phase in aqueous phase also increase in temperature increased the yield and the maximum yield was obtained at 100 °C (Table-4, entries 20-24). Presence of carboxylic group was identified by thin layer paper chromatography and spot tests methods. Melting point of the product was found to be 120 °C (reported mp. of benzoic acid is 122 °C) while neutralization equivalent of compound was found to be 120.5 °C (122 °C for pure compound). Similar spot at similar height on running TLC plate with authentic sample showed that only one product *i.e.* benzoic acid was obtained. Formation of benzoic acid was finally confirmed by taking its IR and NMR spectra. IR (KBr, ν_{max}, cm^{-1}): 2996-2500 (O-H & C-H broad peak), 1689 (C=O str. aromatic), 1590 (C=C str. aromatic), 1298 (C-O str.). NMR Signals: δ 7.256-8.187 (5H, m).

Conclusion

Present study shows that the product of oxidation of benzyl alcohol by sodium ferrate can be monitored only by changing medium from organic to aqueous. If the reactions are performed in acetonitrile medium in the presence of oxalic acid only benzaldehyde is obtained as the product of oxidation. On the other hand benzoic acid becomes the sole product if the oxidation is performed in aqueous medium. Further, the addition of traces of iridium(III) chloride in aqueous medium enhances the yield to a great extent while its addition in organic phase decreases the yield.

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