

ELECTROCHEMICAL OXIDATION OF MANGANOUS ACETATE TO MANGANIC ACETATE IN ACETIC ACID MEDIUM

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Manganic acetate has been widely used as a selective oxidant for the synthesis of organic compounds. Till recently manganic acetate has been prepared chemically by oxidising manganous acetate using potassium permanganate at higher temperature (> 373 K). A simple electrochemical method has been developed to prepare manganic acetate from manganous acetate at $308 - 313$ K. Various parameters like current density, concentration of acetic acid, temperature, stability of manganic acetate has been studied in detail. The current efficiency for the manganic acetate formation was found to be 82%.

Keywords: Manganous acetate, manganic acetate and electrochemical oxidation

INTRODUCTION

Manganic ion mediated anodic oxidation of alkyl aromatics and its derivatives in sulphuric acid medium has been investigated extensively [1-4]. In this process alkyl group has been converted predominantly into the carbonyl group. Few studies have been done regarding stability and uses of manganic ion in acetic acid medium [5]. Manganic acetate is a selective oxidant widely used in the synthesis of many organic compounds like lactones [6-9], polycyclic compounds [10-13], allylic acetate [14,15] and benzyl acetate [16,17] etc. Till recently manganic acetate was prepared chemically by oxidising manganous acetate in acetic acid using potassium permanganate at a temperature of > 373 K [8,9,14,16,17]. This method is expensive [9]. Very few have studied the electrochemical preparation of manganic acetate [18,19]. A simple electrochemical method for the oxidation of manganous acetate to manganic acetate in acetic acid medium is reported here.

EXPERIMENTAL

BDH manganous acetate (LR), acetic acid (AR) and sodium acetate (AR) were used in all the experiments. A platinum sheet as anode (area = 0.27 dm^2) and a graphite cathode were used. The electrodes were cleaned well before electrolysis. Temperature of the cell was maintained using a "JULABO" thermostat. A 250 ml glass beaker was used as an undivided

cell. 100 cm^3 of electrolyte was taken in each experiment. Manganic ion was estimated by adding an excess of 10% potassium iodide solution into a 5 cm^3 of oxidised electrolyte and then titrated against standard sodium thiosulphate solution.

RESULTS AND DISCUSSION

Influence of the concentration of acetic acid

The results obtained under different acetic acid concentrations are given in Table I. The strength of the acetic acid plays a crucial role in determining the stability of the manganic ion formed. Acetic acid concentration was varied from $5 - 17 \text{ M}$ for the oxidation of manganous acetate. At lower acetic acid concentration (5 M and 7 M) the electrolyte was brown in colour with suspended particles and a brown colour deposit was also formed on the platinum anode. A minimum concentration of 10 M acetic acid is necessary to produce stable manganic ion at least for 12 hrs. Afterwards its original dark pink colour changes to brown colour with suspended particles. Manganic acetate prepared in 14 M acetic acid is highly stable (more than 24 hrs) and gives higher yield and current efficiency (Table I). Formation of brown colour deposits and suspended particles at lower acetic acid concentration may be due to disproportionation of manganic ion to manganese dioxide and manganous ion.

TABLE I: Influence of the concentration of acetic acid on the manganic acetate formation $[\text{Mn}(\text{OAc})_2] = 0.2 \text{ M}$, $[\text{Na OAc}] = 1.2 \text{ M}$, C.d. = 2 A.dm^{-2}
Anode area = 0.27 dm^2 Temp = $308 \pm 2 \text{ K}$

Expt No	(HoAc) (M)	Cell voltage (V)	Manganic acetate obtained (gms)	Yield of manganic acetate (%)	Current efficiency (%)
1.	5	5	2.79	59	64
2.	7	5	2.77	59	64
*3.	10	6	2.83	60	65
4.	14	8	3.56	75	82
5.	17	10	2.68	57	62

* Minimum concentration of acetic acid necessary to produce stable manganic ion

Similar result was observed by several authors [20,21] in sulphate media.



Influence of current density

Oxidation of manganous acetate was carried out at various current density and the results are given in Table II. Maximum current efficiency of 82% was obtained at 2.0 A.dm^{-2} in 14 M acetic acid. At higher current densities ($> 2.0 \text{ A.dm}^{-2}$) suspended manganese dioxide in solution and brown colour deposit on the anode surface were formed.

Effect of temperature

Electrochemical oxidation of manganous acetate was carried out at various temperatures and the results are shown in Table III. Temperature (208 ± 2) favours higher yield (76%)

TABLE II: Influence of the current density (C.d) on manganic acetate formation
 $[\text{Mn}(\text{OAc})_2] = [\text{HoAc}] = 14 \text{ M}$, $[\text{Na OAc}] = 1.2 \text{ M}$,
Temperature $308 \pm 2 \text{ K}$

Expt No	Current density (A.dm^{-2})	Cell voltage (V)	Manganic acetate obtained (gms)	Yield of manganic acetate (%)	Current efficiency (%)
1.	1.0	6.0	1.83	39	43
2.	1.5	7.0	2.68	57	62
3.	2.0	8.0	3.56	75	82
4.	2.5	8.5	3.20	66	74

TABLE III: Effect of temperature on manganic acetate formation $[\text{Mn}(\text{OAc})_2] = 0.2 \text{ M}$, $[\text{NaOAc}] = 1.2 \text{ M}$
 $[\text{HOAc}] = 14 \text{ M}$, C.d. = 2 A.dm^{-2}

Expt No	Temperature K ± 2	Cell voltage (V)	Manganic acetate formed (gms)	Yield of manganic acetate (%)	Current efficiency (%)
1.	308	8.0	3.56	75	82
2.	313	7.5	3.25	68	75
3.	318	7.0	3.14	65	72

current efficiency (82%). At higher temperature (213 K) current efficiency decreases and also formation of manganese dioxide takes place. Experiments have also been carried out using porous pot as a separator. The current efficiency has not changed significantly with or without separator. This indicates that manganic ion formed at the anode does not undergo significant reduction at the cathode.

Stability of manganic ion

The stability of manganic ion was studied in 10 M and 14 M acetic acid. Manganic acetate was prepared in 10 M acetic acid with initial concentration of (Mn^{3+} ion) 0.122 M . It was kept at room temperature for 48 hrs. Manganic ion concentration was analysed at the end of 12, 24 and 48 hrs. The original concentration of manganic ion was reduced by 9%, 15% and 24% after 12, 24 and 48 hrs. respectively. This decrease may be due to disproportionation reaction of manganic ion mentioned in eqn (1). However manganic acetate prepared at 14 M acetic acid was stable for more than 24 hrs. without any decomposition.

CONCLUSION

Electrochemical oxidation of manganous acetate to manganic acetate was carried out in acetic acid medium. Lower acetic acid concentration, higher current density and temperature favours formation of manganese dioxide on the anode surface and in solution. A current density of 2 A.dm^{-2} and 14 M acetic acid at 218 K produce maximum yield and current efficiency. Manganic acetate was highly stable in 14 M acetic acid.

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