

Preparation of dihydroxyviolanthrone with electrogenerated Mn^{+3}

CH. COMNINELLIS, E. PLATTNER

Institut de génie chimique, Ecole Polytechnique Fédérale de Lausanne, CH 1015 Lausanne, Switzerland

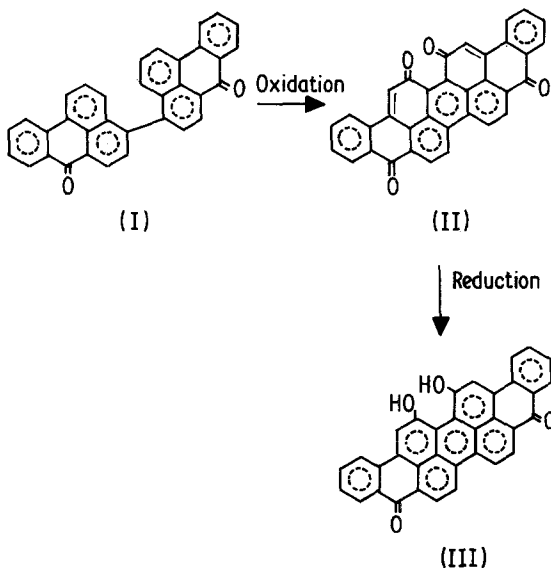
Received 2 September 1983; revised 21 November 1983

Dihydroxyviolanthrone (III) has been prepared by oxidation of 4,4'-bibenzanthrone(I) to dioxoviolanthrone(II) with electrogenerated Mn^{+3} and reduction of (II) to (III) with SO_2 . A decrease in current efficiency was observed after each cycle due to organic material carried over with the electrolyte back to the electrochemical reactor.

A simple relation has been derived for the estimation of the loss in current efficiency due to the organics present in the electrolyte.

1. Introduction

Dihydroxyviolanthrone, a green vat dye, is prepared on the industrial scale by oxidation of 4,4'-bibenzanthrone(I) to dioxoviolanthrone(II) with MnO_2 in conc. H_2SO_4 ; reduction of (II) with $NaHSO_3$ gives dihydroxyviolanthrone (III) [1].



The main problem in this process is the formation of large amounts of waste water containing H_2SO_4 and $MnSO_4$ which must be treated before rejection.

To overcome this problem a new process has been developed in which the oxidation of (I) to (II) is effected using electrogenerated Mn^{+3} and

the reduction of (II) to (III) using SO_2 [2]. The flow sheet is given in Fig. 1.

2. Experimental details

2.1. Analysis

Product analysis was carried out by thin layer chromatography and the Mn^{+3} concentration in the reaction medium was determined by iodometric titration.

2.2. Electrolytic preparation of Mn^{+3}

The electrolytic preparation of Mn^{+3} was carried out in an electrolytic cell of 150 ml capacity. The anode was made of a platinum cylinder (28 cm² area) and the cathode was a platinum spiral enclosed in a 10 ml porous porcelain pot; stirring was provided by a magnetic bar.

2.3. Oxidation of (I) to (II)

The oxidation of (I) to (II) with Mn^{+3} was effected in thermostated reactor of 150 ml capacity stirred with a magnetic bar.

The $Mn_2(SO_4)_3$ slurry was placed in the reactor, the required amount of (I) was added in small portions and the reaction was allowed to go to completion (indicated by the disappearance of the cherry-red colour of the manganic ion).

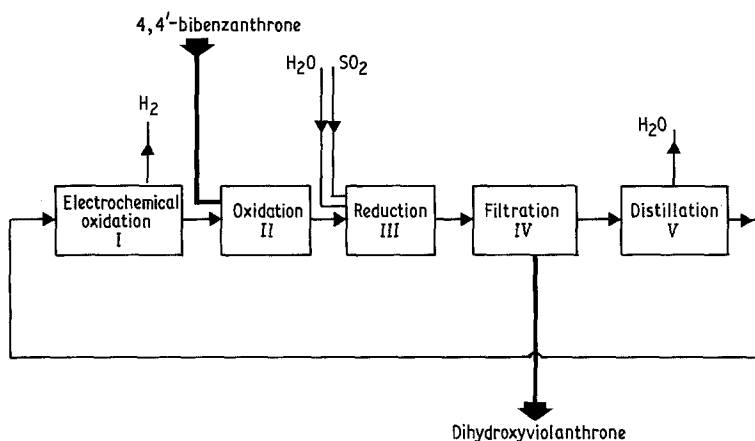


Fig. 1. Flow sheet of the process. I. Electrochemical oxidation of MnSO_4 to $\text{Mn}_2(\text{SO}_4)_3$. II. Oxidation of 4,4'-biphenanthrone to dioxoviolanthrone with $\text{Mn}_2(\text{SO}_4)_3$. III. Reduction of dioxoviolanthrone to dihydroxyviolanthrone with SO_2 . IV. Filtration of dihydroxyviolanthrone. V. Distillation to increase the H_2SO_4 concentration from 48 to 85 weight%.

2.4. Reduction of (II) to (III)

The reaction medium at the end of oxidation was placed in a three-necked flask and diluted with water (1 : 1 volume). Then an excess of SO_2 was passed through the solution and the reaction medium heated at 90°C and allowed to react for about 2 h. Dihydroxyviolanthrone was separated from the reaction medium by filtration.

2.5. Electrolytic regeneration of Mn^{+3}

If necessary, the electrolyte was treated with activated carbon to eliminate organic impurities present in the electrolyte, then water was distilled off under vacuum (1–3 mm Hg) to increase the H_2SO_4 concentration in the electrolyte from 48 to 85 (weight)% and, finally, electrolysis was carried out to prepare Mn^{+3} .

3. Results and discussion

3.1. Electrolytic preparation of Mn^{+3}

The electrolytic preparation of Mn^{+3} in concentrated H_2SO_4 has been studied in an earlier paper [3].

It has been found that Ag^+ has a catalytic effect on the oxidation of MnSO_4 . Thus, electrolysis of a slurry of MnSO_4 (105 g $\text{MnSO}_4 \cdot \text{H}_2\text{O dm}^{-3}$ of solution) in concentrated H_2SO_4 (85 weight%) containing 6×10^{-3} mol dm^{-3} Ag_2SO_4 as catalyst gives $\text{Mn}_2(\text{SO}_4)_3$ with 90% current efficiency for 90% conversion of MnSO_4 . The working current density was 50 mA cm^{-2} and the temperature 85°C .

3.2. Oxidation of (I) to (II)

The experimental conditions strongly influence the selectivity and the rate of the reaction. A series of experiments was conducted at different conditions and it was found that:

- (a) the reaction must be effected in 80–90 (weight)% H_2SO_4 , as below 80% H_2SO_4 the reaction is very slow and above 90% the selectivity of the reaction decreases considerably
- (b) the reaction temperature must lie between $25\text{--}35^\circ\text{C}$ as high temperature favours the formation of by-products
- (c) 4,4'-biphenanthrone (I) must be present in excess to avoid further oxidation of dioxoviolanthrone (II) to pyrene derivatives.

3.3. Reduction of (II) to (III) with SO_2

The reduction of (II) to (III) was effected in 48 weight% H_2SO_4 at $60\text{--}90^\circ\text{C}$ using a large excess of SO_2 (6 times the theoretical amount) to increase the rate of reaction.

3.4. Electrolytic regeneration of Mn^{+3}

It was found that the current efficiency for Mn^{+3} formation decreases after each cycle (Fig. 2). This is due to organic material being carried over with the spent liquor back to the cell [4].

Purification of the electrolyte by passage over activated carbon increased the current efficiency of Mn^{+2} oxidation (sixth cycle in Fig. 2).

To clarify this phenomenon the electrolytic preparation of Mn^{+3} was effected in the presence

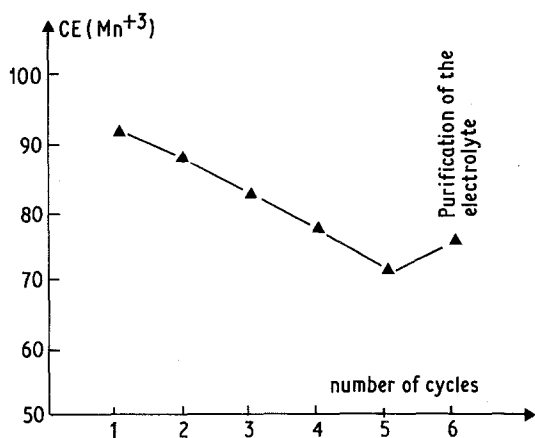


Fig. 2. Current efficiency of manganic sulphate formation as a function of number of cycles. The electrolyte was purified (by passage over activated carbon) before the sixth cycle.

of some organic compounds. Depending on their action on the selectivity of Mn^{+3} formation, organics can be divided into two main groups (Table 1).

Group A: Compounds which do not influence (or influence only to a small extent) the selectivity of Mn^{+3} formation

Group B: Compounds which strongly decrease the current efficiency (CE) for Mn^{+3} formation.

The decrease in CE for Mn^{+3} formation in the presence of Group B compounds depends on the concentration of the organic compound and on its molecular formula.

Table 1. Classification of organic compounds according to their action on the selectivity of Mn^{+3} formation

Group A	Group B
(a) Paraffins octane	I. Aliphatic (a) Dibasic acids oxalic malonic
(b) Cycloparaffins cyclohexane	(b) Hydroxy dibasic acids tartaric
(c) Fatty acids acetic acid	II. Aromatic benzoic acid 4,4'-bibenzanthrone

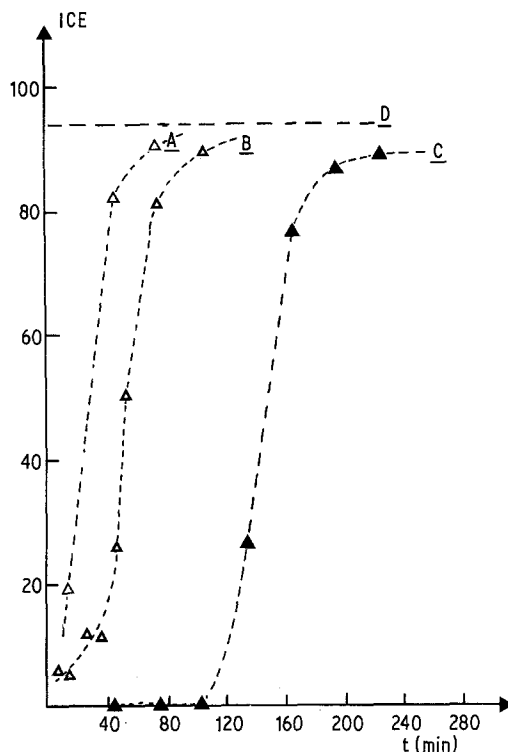


Fig. 3. Instantaneous current efficiency (ICE) for Mn^{+2} oxidation as a function of time. A. $1.4 \times 10^{-3} \text{ mol dm}^{-3}$ bibenzanthrone; B. $2.7 \times 10^{-3} \text{ mol dm}^{-3}$ bibenzanthrone; C. $7.0 \times 10^{-3} \text{ mol dm}^{-3}$ bibenzanthrone; D. in absence of any organics.

3.4.1. Influence of organic concentration. The instantaneous current efficiency (the CE at a given instant) for Mn^{+2} oxidation as a function of time in the presence of different concentrations of

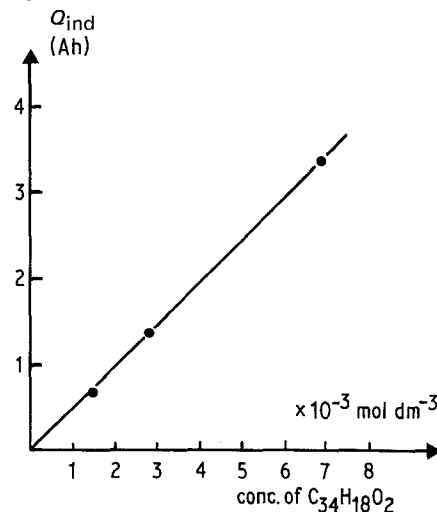


Fig. 4. Charge of induction period (Q_{ind}) as a function of organic concentration (bibenzanthrone).

Table 2. Dependence of the constant K of Equation 1 on the organic compound present in the electrolyte

Organic compound	Oxalic acid $C_2H_2O_4$	Malonic acid $C_3H_4O_4$	Tartaric acid $C_4H_6O_6$	Benzoic acid $C_7H_6O_2$	4,4'-bibenzanthrone $C_{34}H_{18}O_2$
K	1.4	1.5	1.25	0.83	0.80

organics (4,4'-bibenzanthrone) is shown in Fig. 3. Some time is required before the oxidation of Mn^{+2} occurs as in the absence of organics. The electrical charge passed in this period is defined as the charge of the induction period.

This charge is proportional to the concentration of the organic compounds in the electrolyte as is shown in Fig. 4.

3.4.2. *Influence of molecular formula.* The charge passed in the induction period (Q_{ind}) has been related to the charge needed for complete combustion of the organic compound (Q_{comb}) by the relation

$$[Q_{ind}] = K[Q_{comb}] \quad (1)$$

The constant, K , in this relation depends on the organic compound (Table 2); thus for aromatic compounds it is smaller than unity and for aliphatics greater than unity.

The fact that the constant, K , is smaller than unity for aromatic compounds indicates that these compounds are not completely oxidized to carbon dioxide. Formation of some other compounds, probably of Group A occurs.

4. Conclusion

In the indirect electrochemical process using Mn^{+2}/Mn^{+3} as carrier a loss in current efficiency has been observed in the working process due to organic material carried over with the electrolyte.

References

- [1] E. Clar, 'Polycyclic Hydrocarbons', Vol. 2, Academic Press, London (1964).
- [2] Ciba-Geigy, Swiss Patent No. 2996/81-9 (1982).
- [3] Ch. Comminellis and E. Plattner, *J. Electrochem. Soc.* **129** (1982) 749.
- [4] A. T. Kuhn and M. Birkett, *J. Appl. Electrochem.* **9** (1979) 777.