

Oxidative Cleavage of 2,3-Butanediol to Acetaldehyde at Platinum Electrode in Acidic Solution

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Summary: It is shown that direct electrooxidation of 2,3- butanediol in sulfuric acid solution at platinum sheet anode yields cleaved products. However, current efficiency for the formation of acetaldehyde was not high.

Introduction

2,3-Butanediol is obtained as dilute aqueous solutions with concentrations below 10%, typically a few percent, by the fermentation of glucose and xylose [1-4]. There is much recent interest in the electrochemical conversion of biomass-derived materials [5] to fuels or fuel components [6] and/or commercial organic chemicals [7]. Some recent reports describe direct or indirect (mediated)

electrochemical oxidation of diols [8-12]. The electrochemical method for the oxidative cleavage of diols may be generally favourable from the point of view of avoiding the use of large amounts of expensive, poisonous and/or hazardous reagents. Therefore, direct electrochemical oxidation of 2,3-butanediol to acetaldehyde was attempted on a platinum sheet electrode.

Table 1: Conditions of gas chromatographic analysis.

Products	CH ₃ CHO	O ₂
Stationary phase (2m)	PEG*	M.S.**
Carrier gas	H ₂	H ₂
Flow rate (ml/min)	40	40
Temperature (°C)	80	40
Retention time (min)	1.68	0.5

*Polyethyleneglycol 20 M

**Molecular Sieve 5A; current 60 mA, T.C.D. Sensitivity 1 mV.

Experimental

2,3-Butanediol (dl, meso mixture, EP, Assay GC min. 99% obtained from Tokyo Kasei Kogyo Co. Ltd. was used without further purification.

Apparatus and cell used for measuring polarization curves, and controlled potential electrolyses are described elsewhere [8].

Yanaco G 800 gas-chromatograph was used for the analysis of products. Conditions of analysis are listed in Table 1. Silica gel column was also used at 40°C to confirm the absence of CO₂ and CO in the gas-product.

Results and Discussion

Polarization curve measurement

Plots of current density vs. anode potential were made using potentiostat to find out the desirable anode potential for controlled potential electrolysis. In 0.5 M sulfuric acid solution, positive shift in polarization curve was observed at platinum anode when 0.1 M 2,3-butanediol was added in the electrolyte. The magnitude of the shift was about 125 mV at 1.900 V and 150 mV at 1.950 V vs. SCE.

Controlled potential electrolysis

Electrolyses were carried out using a platinum electrode in 0.1 M 2,3-butanediol solution in 0.5 M sulfuric acid. The results are summarized

Table 2: Controlled potential electrolysis of 2,3-butanediol in sulfuric acid solution at platinum anode

	1.900	2.000	2.050	2.075
Anode potential (V vs. S.C.E.)	1.900	2.000	2.050	2.075
Anodic current density (average) (A/dm ²)	0.363	1.229	1.489	1.874
Current consumption (mF)	11.04	13.43	14.49	16.96
2,3-butanediol in electrolyte*(M)	0.10	0.10	0.10	0.10
Products (m. moles)				
CH ₃ CHO	0.13	0.28	0.45	0.58
O ₂	2.28	2.67	2.57	2.78

*0.5 M H₂SO₄ solution, 100 ml

in Table 2. The current efficiency for the cleavage of the diol to acetaldehyde shows a slight increase with the rising anode potential.

In contrast to an earlier report [13] using platinized platinum electrode in strongly acidic solution, our results establish that direct electrolytic oxidation of 2,3-butanediol at platinum in sulfuric acid solution does lead to cleavage of the C-C bond giving acetaldehyde as one of the products.

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References

1. G.A. Adams and R.Y. Stanier, *Can. J. Res.*, **23B**, 1 (1945).
2. A.C. Blackwood, A.C. Neish, W.E. Brown and G.A. Ledingham, *Can. J. Res.*, **25B**, 56 (1947).

3. A.C. Neish, A.C. Blackwood, F.M. Robertson and G.A. Ledingham, *Can. J. Res.*, **25B**, 85 (1947).
4. A.C. Neish, A.C. Blackwood, F.M. Robertson and G.A. Ledingham, *Can. J. Res.*, **26B**, 335 (1948).
5. H.L. Chum and M.M. Baizer, Eds., "The Electrochemistry of Biomass and Derived Materials", ACS Monograph Series No.183, American Chemical Society, Washington DC (1985).
6. T. Nonaka and M.M. Baizer, *Electrochim. Acta*, **28**, 661 (1983).
7. M.M. Baizer, T. Nonaka, K. Park, Y. Saito and K. Nobe, *J. Appl. Electrochem.*, **14**, 197 (1984).
8. (a) I.U. Haque, *J. Chem. Soc. Pak.*, **11**, (51) (1989).
(b) I.U. Haque, *J. Chem. Soc. Pak.*, **12**, (3/4), (1990).
9. A. Yoshiyama, T. Nonaka, M.M. Baizer and T-C. Chou, *Bull. Chem. Soc. Jpn.*, **58**, 201 (1985).
10. S. Torii, T. Inokuchi and T. Sugiura, *J. Org. Chem.*, **51**, 155 (1986).
11. M.F. Semmelhack, C.S. Chou and D.A. Cortes, *J. Am. Chem. Soc.*, **105**, 4492 (1983).
12. N. Botros and C.O. Huber, *Anal. Chim. Acta*, **208**, 247 (1988), and references therein.
13. G. Horanyi, G. Inzelt and K. Torkos, *J. Electroanal. Chem.*, **106**, 305 (1980).