Tetrahedron Vol. 43, No 3, pp. 577 to 583, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00
Pergamon Journals Ltd.

SELECTIVE ANODIC OXIDATION OF TETRAHYDROFURAN

BERND WERMECKES, FRITZ BECK and HARRY SCHULZ

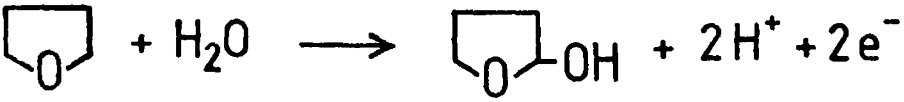
Universität-GH-Duisburg, FB6 - Elektrochemie,
D4100 Duisburg 1, F.R.G.

(*Received in Germany* 31 *July* 1986)

Abstract - The anodic oxidation of tetrahydrofuran in acid aqueous electrolytes has been investigated in detail. Selective oxidation to 2-hydroxy tetrahydrofuran has been found to proceed. Under optimum conditions (smooth platinum, high current densities, 200 - 400 mA/cm^2, 1 - 6 M THF, 1 M H_2SO_4, 35 °C, quasi divided cells), the product was obtained in batch type laboratory scale (60% of 2 F/mol conversion) with 70% current efficiency and 95% selectivity. Only traces of butyrolactone and succinic acid, the dominating products in the case of PbO_2 anodes, were found. Oxygen is the main side product.

INTRODUCTION

Aliphatic ethers have been regarded to be anodically stable[1]. Recently[2], their oxidation to semiacetals with a further conversion to aldehydes and carboxylic acids has been reported. In this paper we show that electrooxidation in aqueous electrolytes can be extended to cyclic ethers. As a starting material of industrial importance we used tetrahydrofuran (1) (THF) which was oxidized under appropriate conditions (see below) with excellent selectivity to the cyclic semiacetal THF-OH 2 :



1 2

Contrary to open chain semiacetals THF-OH is relatively stable with regard to cleavage in acid medium. Solutions of n-butyraldehyde (10 mM) and of THF-OH (up to 0.1 M) in 1 M H_2SO_4 were evaluated by UV spectroscopy (band at 279 nm). A degree of hydrolysis of about 20% was derived. γ-Hydroxy butyraldehyde, a bifunctional molecule of practical interest, has been synthesized formerly by chemical oxidation of tetrahydrofuran with aryldiazonium salts[3], by hydration of 2,3-dihydrofuran[4] and by hydroformylation of allylalcohol[5]. None of these alternatives is totally satisfying with regard to selectivity and simplicity.

RESULTS and DISCUSSION

Electrode material plays an important role in organic electrosynthesis. It controls selectivity of the overall electrode process. We have studied some conventional and some advanced anode materials in this connection. The results are compiled in Table 1. Optimal results for the desired product were obtained with bright platinum. Current efficiency (c.e.) reaches 70% at high current densities (c.d.). Yield (with respect to converted THF) is virtually quantitative($>$95%), the products of further oxidation are detectable only in traces. This means that anodic water decomposition to O_2, a "clean" side reaction, is the only competing electrode reaction. In undivided cells with carbon cathodes of equal size 1,4-butanediol has been detected as a side product, generated by cathodic hydrogenation of the anodic product γ-hydroxy butyraldehyde which is in equilibrium with THF-OH. The other anodes are less beneficial. Some of them retain selectivity for THF-OH but at a lower level of c.e., not larger than 25%. Acheson graphite Sigri MS® exhibits some swelling upon anodic polarization in sulfuric acid. Glassy carbon is unstable as well; a brittle surface layer is detected after electrolysis. Pb/PbO_2 and Ti/Cr_2O_3[7] are unselective and appreciable amounts of the 4 F/mol and 8 F/mol - products, butyrolactone (BL) and succinic acid (SA), have been found at the same degree of conversion.

Current efficiency for THF-OH increases appreciably with increasing current density in the case of bright Pt, cf. Table 1. This explains straightforwardly the low current efficiencies for platinized Ti where a large roughness factor is involved[8]. The low c.e. for Ti/RuO_2 can be rationalized in terms of the well-known low oxygen overvoltage at this anode material. In this case the predominating anode process is anodic oxygen evolution.

As bright platinum is an expensive electrode material the question arises for the quantity of anodic platinum losses Δm. The average amount of Δm was 0.04 mg Ah^{-1}, determined in 10 independent runs. No systematic alteration with c.d. was found. Δm is significantly above the value in pure diluted H_2SO_4[9], but it is not prohibitively high.

Table 1.
Preparative results for anodic oxidation of 1 M THF in 1 M H_2SO_4 at 35 °C

No.	Anode Material	Current Density j [mA cm^{-2}]	Current Efficiency [%]		
			THF-OH	BL	SA
1	bright Pt	10	41	3.7	0
		30	49	2	0.2
		75	59	2.3	0.8
		200	67	1.5	0.5
		400	70	6	1.1
2	Ti/PtO_x[6]	10	15	1.2	$<$0.1
	Ti/RuO_2[6]	30	4.5	0.1	0
	Ti/Cr_2O_3[7]	0.5	24	53	10
	Pb/PbO_2	10	16	49	18
	Graphite, Sigri MS	30	17	5	1
	Glassy Carbon	200	24.5	3	1

No 1: Pt at various current densities.
No 2: various anode materials.
The scale of electrolysis was 0.2 mol THF. Conversion was 60%
(2 F/mol) in all cases.

Selectivity is generally a matter of electrochemical conversion of the starting material. This is clearly demonstrated for Pt and PbO_2 in Fig. 1. While Pt retains its high selectivity for THF-OH up to 60 - 70% theoretical conversion β (Fig. 1 A), PbO_2 is a nonselective anode material even at very low conversions, cf. Fig. 1 B. THF-OH shows clearly the behaviour of an intermediate and the main product is butyrolactone BL. At even higher conversions the concentration of the product of further oxidation, succinic acid, begins to increase.

We have electrolyzed THF in aqueous sulfuric acid at even higher THF-concentrations. As it is shown in Table 2 the production of butyrolactone increases somewhat by this way. pH was varied in the range of 0 to 6. As it is shown in Table 2, c.e. decreases only slightly with increasing pH, quite contrary to our previous findings with open chain ethers[2]. The last three examples disclose that temperature in the range 20 - 50 °C has nearly no influence on the c.e. for THF-OH.

Our results show clearly that THF-OH can be obtained from THF in aqueous electrolytes at a platinum anode with excellent selectivety and good current efficiency. Previously, only the anodic oxidation of THF to SA[10,11] or BL[12] has been reported, mostly with PbO_2-anodes. Platinized Pt was used as well[13], but without product analysis. Anodic oxidation of THF in methanol/$NaOCH_3$ yields α-methoxy tetrahydrofuran, but the selectivity is unfavourable[14,15]. We have confirmed poor c.e. ($<$ 20%) and low selectivities for anodic methoxylation of THF. The product saponifies very slowly in 1 M H_2SO_4 to yield THF-OH. By this way the direct electrosynthesis of this product, disclosed by our work, seems most favourable.

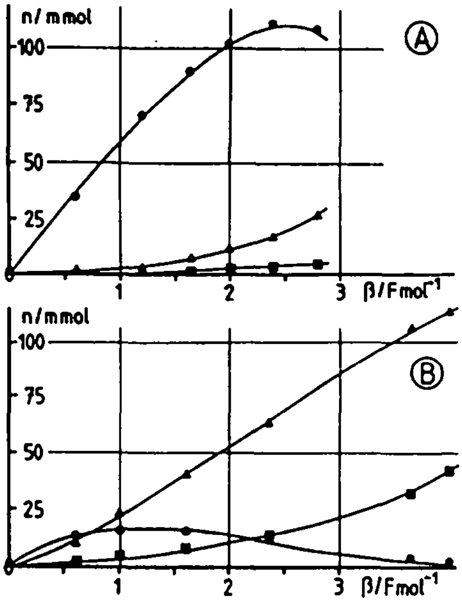


Fig. 1 Conversion/time curves for anodic oxidation of THF at 35 °C.
A) Pt, 75 mA/cm², n_0= 200 m mol THF.
B) PbO, 10 mA/cm², n_0=225 m mol THF.
Electrode area in both cases:
A = 50 cm²
●——● 2-hydroxy tetrahydrofuran (THF-OH)
▲——▲ γ-butyrolactone (BL)
■——■ succinic acid (SA)

Table 2.
Preparative results for anodic oxidation of THF in aqueous electrolytes, at 60% conversion with bright platinium as anode material

No.	c_{THF} M	Electrolyte	T [°C]	j [mA cm^{-2}]	Current Efficiency [%]		
					THF-OH	BL	SA
1	1	1 M H_2SO_4	35	75	59	2	0.8
	2	"	"	"	61	10	1.3
	4	"	"	"	66	13	1
	6	"	"	"	58	14	0.8
2	1	1 M H_2SO_4/pH0	35	200	67	1.5	0.5
	"	0.1 " /pH1	"	75	53	2	0.3
	"	0.01 " /pH2	"	75	40	1.1	0.6
	"	A) /pH3	"	200	49	3	1
	"	B) /pH6	"	200	48	3	1.1
3	1	1 M H_2SO_4	20	200	63	1.5	< 0.1
	"	"	35	"	67	1.5	0.5
	"	"	50	"	58	2	1

No 1: at higher THF-concentrations in 1 M H_2SO_4, 35 °C, 75 mA cm^{-2}
No 2: at various pH-values
No 3: at different temperatures
A) 1.5 M Na_2SO_4, addition of H_2SO_4
B) 1.5 M Na_2SO_4, 0.2 M KH_2PO_4, addition of NaOH

In order to be sure that the product of hydrolysis of THF is not oxidized in all of our runs, the following two experiments were undertaken with 1,4-butanediol (BD):

a) A solution 1 M THF/1 M H_2SO_4 was stored 24 hours at room temperature and then analysed via HPLC (H_2SO_4 pH 1.7 as an eluent). No butanediol was found.

b) A solution of 1 M BD in 1 M H_2SO_4 was electrolyzed under standard conditions (Pt, 35 °C, 75 mA cm^{-2}, 60% theoretical conversion). The result in terms of current efficiencies (c.e.) was: THF-OH: 12%, SA: 2%, BL: traces. With THF as starting material, c.e. was 59% under these conditions.

We have electrolyzed other cycloaliphatic monoethers, and our results with THF have been confirmed essentially. However, cycloaliphatic diethers led predominantly to fragmentation products. This will be reported elsewhere.

MECHANISTIC CONCLUSIONS

According to the reaction sequence given in Fig. 2, THF can be oxidized through the intermediates THF-OH and BL[12] up to succinic acid SA[10,11]. Hydrolysis to the open chain compounds 1,4 butanediol (BD), γ-hydroxy butyraldehyde (HBA), γ-hydroxy butyricacid (HBAc) and succinic acid (SA) must be regarded. The question arises why a selective anodic oxidation to THF-OH is possible with Pt at high current densities. It is the only reaction of high preparative interest in this sequence.

It is well known from cyclic voltammetry [16-18] and from direct XPS surface analysis[19-22], that platinum is covered with oxides PtO_x at electrode potentials more positive than 0.8 V vs. SHE. The steady potentials in the course of the electrooxidation of THF are as high as 2.5 V vs. SHE (at 100 mA cm^{-2}). It must be concluded that the electrode reaction occurs at an oxide modified surface. High valent oxides like PtOOH and PtO_2 should prevail. Oxygen evolution should be strongly competitive.

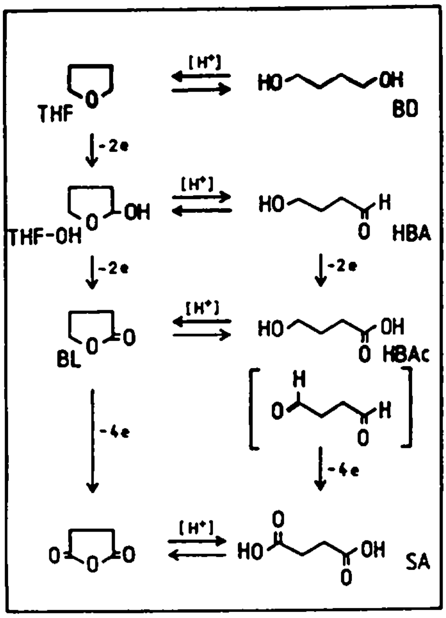


Fig. 2 Anodic oxidation of THF up to succinic acid SA.

It follows from our electrochemical measurements, which will be published elsewhere[23], that THF is entensively adsorbed at the oxidic surface, and that one electron is transferred in the rate determining electrochemical step. Let us assume that adsorption as well as further oxidation at the above mentioned very positive working potential starts from a PtO surface according to equation (1) and (2), respectively:

$$(PtO)_s + THF \longrightarrow (PtO - THF)_s \qquad (1)$$

$$(PtO)_s + H_2O \xrightarrow{slow} (PtOOH)_s + H^+ + e^- \qquad (2)$$

The index "s" means a surface bound, adsorbed state. It is then, that adsorbed THF may be chemically oxidized by PtOOH (adjacent to the adsorbed organic molecule):

$$(PtO - THF)_s + 2(PtOOH)_s \xrightarrow{k} THF\text{-}OH + 3PtO + H_2O \qquad (3)$$

However, PtOOH may be further oxidized to PtO_2, which decomposes to yield oxygen:

$$(PtOOH)_s \xrightarrow{fast} (PtO_2) + H^+ + e^- \qquad (4)$$

$$2(PtO_2)_s \xrightarrow{k'} O_2 + 2(PtO)_s \qquad (5)$$

Regeneration of new adsorption sites PtO is accomplished by the chemical reactions (3) and (5). At high anodic current densities, e.g. high degree of coverage θ for PtOOH, eqn. (3) is preferred over (4) + (5), for the rate of (3) increases with θ^2. High current efficiency for THF-OH at high c.d. is satisfactorily explained by this mechanism.

The sequence of heterogeneous chemical reaction (3) between oxidant and organic molecule and electrochemical regeneration of the oxidant in terms of heterogeneous redox catalysis is frequently observed[24]. The specific advantage of direct electrosynthesis is clearly demonstrated in so far as PtOOH (or PtO_2) as a chemical reactant should be very instable and expensive.

EXPERIMENTAL

Electrolytes were made from bidistilled water, anal. grad 96% H_2SO_4 (Merck) and freshly distilled THF (purum). The following anode materials, usually as a 5 x 5 cm sheet (A = 50 cm^2, both sides) were used:

a) Bright Pt-sheet, 0.1 mm thick
b) Ti/PtO_x: 1 mm Ti sheet, etched in hot 20% HCl, painted with H_2PtCl_6 in isopropanol, dried (80 °C) and fired at 550 °C. After three repetitions 2 g Pt m^{-2} were supplied.
c) Ti/RuO_2, as above, but painting with $RuCl_3$ and $Ti(OBu)_4$ in isopropanol[6].
d) Ti/Cr_2O_3, as above, but painting with $CrCl_3$ and $Ti(OBu)_4$ in isopropanol and fired at 650 °C[7].
e) Pb/PbO_2, by anodic formation of lead sheet, 1 mm in 5% H_2SO_4.
f) Graphite, Sigri MS, 5 mm plate.
g) Glassy carbon, 1 mm plate.

Platinum sheet and Pt-electrodes were conditioned prior to every run by a combined oxidation (warm chromic/sulfuric acid) and reduction (boiling 20% HCl) pretreatment[25]. - For preparative electrolysis a 250 ml cylindric glass cell with cooling jacket and planar ground cover was used throughout. Electrolysis was performed in stirred electrolytes at constant current density. Scale was 0.2 mol THF.

Work up was performed by ether extraction (24 h cont.), ether stripping and vacuum distillation of crude product in presence of an acid catalyst, see below. The electrolyte could be analyzed directly via HPLC under slightly modified conditions with regard to our former report[2]. H_2SO_4 (pH 1.7) was used as an eluent. 1 ml of the electrolyte was diluted 1:5 with H_2SO_4 (pH 1.7). From this 20 µl were injected and chromatographed at a flow rate of 2 ml min^{-1}. Typical retention times were:

BD, 1,4-butanediol	: 11.5 min;	HBA, γ-hydroxy butyric acid	: 12 min;
SA, succinic acid	: 14 min;	THF-OH, α-hydroxy-THF	: 16 min;
BL, butyrolacton	: 21 min;	THF, unreacted THF	: 17.5 min.

The eluent for THF was methanol/water 1/4 V/V. Peak with t_R= 16 min is correlated to THF-OH rather than to γ-hydroxy butyraldehyde due to the fact, that detection with UV/VIS - spectroscopy gave no signal with the above mentioned t_R.

Product characterization. A nearly colorless oil could be isolated from the electrolyte by exhaustive ether extraction. HPLC showed clearly that this product was nearly pure THF-OH. After addition of a trace phosphoric acid or some pieces of a cation exchange material in the H^+-form the crude product was distilled at 2 mm Hg. The main fraction boiled at 24 - 30 °C. GC showed five peaks due to oligomerization to polyacetals under these conditions. In the presence of traces of acid the first peak (monomer) intensified strongly. GC/MS-coupling revealed molecules $(88)_n$ with n = 1 - 5. ^1H-NMR of product was in good agreement with the ring structure according to the following data: 60 MHz ($CDCL_3$) (ppm) 1.9 (m, 4 βH; cf. 1.8 for THF[26]); 3.9 (m, 3αH; cf. 3.8 for THF[26]); 5.1 and 5.4 (m, one OH, semiacetal; cf. 5.0 - 6.5 for semiacetal[27]).

IR spectrum exhibited a weak carbonyl band (1720 cm^{-1}) according to the aldehyde in equilibrium. A second band at 1770 cm^{-1} corresponds to the C=O-group of BL which was present as an impurity.

A part of the crude product was reacted with a fivefold molar excess of 2,4-dinitrophenylhydrazine in 2 N HCL to give the 2,4-dinitrophenylhydrazone in 90% yield in reference to the THF-OH content. M.p. 117,6 °C in agreement with the values of Paul[28] and of Meerwein et al.[3]. Elemental analysis (theoretical figures in brackets): C: 44.97 (44.78%); H: 4.47 (4.48%); N: 20.95 (20.90%).

1 g (0.01 mol) of crude product gave with conc. aqueous $NH_2OH \cdot HCl$ and work up 0.61 g (0.006 mol; 60% yield) of a colorless oil, n_D(21.5 °C) = 1.461. The oxime has 1.473 as n_D(15 °C) according to [29].

Acknowledgement - Financial support for the HPLC equipment by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

REFERENCES

[1] O. Hammerich in Organic Electrochemistry (M.M. Baizer, H. Lund. Eds.) M. Dekker, New York (1983); V.D. Parker et al., in Encyclopedia of the Elements, Vol XI (A.J. Bard, H. Lund, Eds.) M. Dekker, New York (1978).

[2] B. Wermeckes, F. Beck, Electrochim. Acta 30, 1491 (1985)

[3] H. Meerwein, H. Allendörfer, P. Beekmann, F. Kunert, H. Morschel, F. Pawellek und K. Wunderlich, Angew. Chem. 70, 211 (1958).

[4] R. Paul, M. Fluchaire und G. Collardeau, Bull. Soc. Chim. Fr., Memoires Presentés à la Société Chimique 1950, p. 668

[5] Europ. Pat. Applic. EP 129 802 (1/1985, Kuraray Co, Ltd. and Daicel, Chem.Indust Ltd.).

[6] H.B. Beer, DDR-Pat. 55223 (Prior. 12.5.1965); Belgium Pat.710551 (2/67).

[7] F. Beck, H. Schulz, Ber. Bunsenges. Phys. Chem. 88, 155 (1984).

[8] A.T. Kuhn, P.M. Wright in A.T. Kuhn (Ed.), Industrial Electrochemical Processes, p. 555, Elsevier, Amsterdam (1971).

[9] F. Beck, Elektroorganische Chemie, Verlag Chemie, Weinheim (1974) p. 97.

[10] US-Pat. 2420954 (Oil § Refineries Inc, 1941).

[11] Brit. Pat. 590310 (British Celanese Ltd, 1947).

[12] M.G. Smirnowa, A. I. Kirsanowa, Izv. Sev. Kavk.Nauchn. Tsentra Vyssh. Shk. Ser. Tekh. Nauk. 1979, 7 (4), 27; C.A. 93, 56830 h (1980).

[13] G. Horanyi, E. M. Rizmayer, Electrochim. Acta 30, 767 (1985).

[14] T. Shono, Y. Matsumura, J. Am. Chem. Soc. 91, 2803 (1969).

[15] Hoechst A.G., 7/81, Erf. J. Cramer; cf. C.A. 95, 140904 j (1982).

[16] W. Vielstich: Fuel Cells, Wiley, New York (1970).

[17] R. N. Adams: Electrochemistry at Solid Electrodes, Marcel Dekker, New York (1969)

[18] S. Gilman in Electroanalytical Chemistry (Ed. by A.J. Bard), Vol. 2, pp 112 - 192, Marcel Dekker, New York (1967).

[19] K.S. Kim, N. Winograd, R.E. Davis, J. Am. Chem. Soc. 93, 6296 (1971).

[20] K.S. Kim, C.D. Sell, N. Winograd, Proc. Electrocatalysis (Ed. M.W. Breiter), p. 243, Electrochem. Soc. Princeton, New Jersey (1974).

[21] M. Peukert, F.P. Coenen, H.P. Bonzel, Electrochim. Acta 29, 1305 (1984).

[22] J. Heitbaum, E. Rach, J. Willson, M. Wohlfahrt-Mehrens, Dechema-Monograph. 102, 235 (1986).

[23] F. Beck, B. Wermeckes, to be published.

[24] F. Beck, H. Schulz, Electrochim. Acta 29, 1569 (1984).

[25] B. Wermeckes, F. Beck, Chem. Ber. 118, 3771 (1985).

[26] C.L. Habracken, H.J. Munter u. J.C.P. Westgeest, Rec. Trav. Chim. Pays-Bas 86, 56 (1967).

[27] O.L. Chapman u. R.W. King, J. Am. Chem. Soc. 86, 1256 (1964).

[28] R. Paul u. S. Tschelitcheff, Bull. Soc. Chim. Fr. 15, 197 (1948).

[29] DBP 817921 (Rhône Poulenc, 1950).