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ANODIC OXIDATION OF ISOALKYLETHERS IN AQUEOUS ELECTROLYTES

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Abstract – Three isoalkylethers, di–sec–butylether (DSBE), di–i–propylether (DIPE) and t–butylmethylether (TBME) were oxidized in 1 M H_2SO_4 (mostly as emulsions) at Pt anodes. Solubility was improved by cosolvents, e.g. CH_3CN. The standard current density was 750 A m^{-2}. Methylethylketone MEK was the main product, obtained with c.e. of 50 % (yield 70 %), for the cleavage of DSBE. Acetone was found with 68 % c.e. and 66 % yield for the decomposition of DIPE. Acetic acid was the main side product in both cases. TBME was anodically cleaved into t–butanol with 83 % c.e. In case of DSBE, the reaction has some industrial interest, for it transforms a useless side product of butene hydration to a valuable product MEK.

1. Introduction

Aromatic ethers have been frequently oxidized at the Pt–anode in methanolic electrolytes with KOH. Arylalkylethers, e.g. anisole, yielded the dimethylketale of p–benzoquinone in good yields /1–4/. However, in order to obtain the quinone itself, saponification as a chemical follow up step must be performed. Benzylalkylethers lead under the same conditions to methoxylation at the benzyl–CH_2–group /5–9/. Again, the real oxidation product, namely the benzaldehyde, is only obtained after saponification of the acetale.

Aliphatic ethers are considered to be difficult to oxidize at the anode. Such compounds are therefore only rarely employed as starting materials. Anodic oxidation of tetrahydrofuran at platinum in methanol/$NaOCH_3$ yields the α–methoxylation product /10,11/. Once more, the corresponding hydroxylated compound, which is the preparative interesting cyclic semiacetale of the ω–hydroxy butyraldehyde, can only obtained in a second step of acid hydrolysis. However, we could directly synthesize the THF–OH at Pt in 1 M H_2SO_4 /12/:

At very high current densities, 4000 A m^{-2}, the current efficiency was 70 % and the selectivity 95 %. PbO_2 gave inferior results. The results at Pt were even better for this one step electrosynthesis with respect to the two step process in methanol /10,11/.

We have shown, that n–aliphatic /13/ and cycloaliphatic /12,14/ ethers are efficiently oxidized at conventional anodes in 1 M H_2SO_4. We have complemented this work by the anodic oxidation of cycloaliphatic ketones and diketones under the same conditions /15,16/. In parallel to this, we are looking for new anodes with surface redox systems since a couple of years. An important example is Ti/TiO_2, Sb_2O_4,

Cr_2O_3, an activated titanium anode with a ceramic oxide layer /17–20/. In this case, we characterize the new anode with simple model reactions such as isopropanol ⟶ acetone. Our ultimate scope is the replacement of the chemical chromic acid oxidation under retention of selectivity, well known in literature /21/.

We are also investigating in detail mechanistic and electrochemical aspects of the filmforming anodic electropolymerization of heterocycles as pyrrole in aqueous and nonaqueous systems at various substrates, commodity metals included. A review /22/ and two recent articles /23,24/ may document this.

In the following, we extend our work on the anodic oxidation of aliphatic ethers to isoalkylethers. No previous experience exists. The starting point in this case was some industrial interest, as outlined at the end of section 4.

2. Experimental

2.1 Feedstocks and preparative electrolysis

Three different isoalkylethers were employed:

1) Di–sec–butylether (DSBE), 95 – 98 %, distilled.
   Density (20 °C): 0.756 g cm^{-3}.
2) Di–iso–propylether (DIPE), 98 – 99 %, distilled.
   Density (20 °C): 0.724 g cm^{-3}.
3) t–butylmethylether (TBME), > 99 %, distilled.
   Density (20 °C): 0.741 g cm^{-3}.

DSBE and DIPE were obtained from Deutsche Texaco AG, Moers; Hüls AG, Marl, provided TBME.
The electrolyte was 1 M H_2SO_4, made from AnalaR grade 97 % H_2SO_4 (Merck) and bidistilled water, if not stated otherwise. Acetonitrile (Merck), "zur Synthese", was used as a cosolvent in most of the cases. Standard current density was 750 A m^{-2}. The temperature was hold at 35 °C to simulate industrial conditions. The direct current sources were galvanostates of Philips (PE 1512) and of Hewlett Packard (6269 B) for $I = 0 - 3$ A and $0 - 50$ A, respectively.

Anode materials were conventional: Smooth platinum sheet, 0.1 mm and Pb/PbO_2–anode with 1 – 2 mm lead sheet. Pt was cleaned with chromic acid, 110 °C and successive treatment in boiling 20 % HCl /25/. Pb sheet was subjected to fresh galvanostatic formation in 5 % H_2SO_4. The dimensions of the electrodes were 2 x 50 x 50 mm^2 = 50 cm^2 for the cell QDCC and 100 cm^2, onesided, for the plate and frame cell MPC.

The quasidivided cyclindric cell QDCC was made of glass (250 ml), with cooling jacket and planar ground cover. The anode was placed in the center, and two small area counter electrodes, stainless steel wires, each 0.3 cm^2, were located symmetrically to it at a distance of 1.5 cm /13,25/. Thus current density at the cathode was high, $j = 750 \cdot (25/0.3) \simeq 75000$ A m^{-2}, avoiding practically cathodic attack to the products /25/. The plate & frame cell (home made construction) was divided by a cation exchange membrane from the Nafion type. The free electrode and membrane surface areas were 100 cm^2, respectively. The anolyte was circulated by an IWAKI pump through an external cooler. The catholyte, 1 M H_2SO_4, slowly circulated via gas lift.
The following representative electrolysis is described in detail, cf. No. 6 in Table 2:

The quasidivided cell QDCC was filled with a mixture of 100 ml 1 M H_2SO_4 and 150 ml acetonitrile. 50 ml (0.29 mole) DSBE was added. After vigorous stirring with a magnetic stirrer ("cross" magnetic bar), two phases remained on standing and an emulsion under continuous stirring. The anode was a Pt sheet, dipping into the stirred electrolyte. A current of 3.75 A, corresponding to a current density of 750 A m^{-2}, was used for electrolysis. The temperature was adjusted to 35 °C. After about 5 hours, the electrolyte became homogeneous. After 5 hours and 34 minutes, the electrolysis was interupted. This corresponds to a theoretical DSBE conversion (4 F mole^{-1}, 100 % c.e.) of $\beta = 67$ %. As nonconverted DSBE 83.5 mmole (HPLC) were found, the effective conversion is $\beta_{eff} = 71$ %.

The electrolyte at the end of the electrolysis was slightly brown coloured and homogeneous. The 282 ml (249 g) were analyzed via HPLC. 201 mmole methylethylketone MEK and 89 mmole sec–butanol were identified. Yields and current efficiencies derived from this are included in Table 2, No. 6.

2.2 Product analysis

Product analysis was performed via HPLC. The instrumental part is described elsewhere /13,25/. A column with Nu 5 C 18, 8 x 250 mm, was used at a flow rate of 2 ml min^{-1}. Table 1 compiles the conditions for the HPLC analysis. The sample was diluted 1 : 5 V/V with the eluent. Refraction index R_i was used for indication, with one exception: formic acid HCOOH was determind by UV/VIS–absorption at 220 nm. Acetic acid was determined in parallel by potentiometric titration with 1 M NaOH.

Table 1 HPLC conditions

Group	Compound	Eluent vol / vol	t_R / min
Starting materials	DIPE	1 H_2O / 10 MeOH	6.0
	DSBE	"	7.6
Products	HCOOH	3 H_2O / 1 MeOH	5.3
	acetone	"	7.3
	CH_3COOH	"	8.4
	i–PrOH	"	8.5
	MEK	"	11.0
	t–butanol	"	11.6
	sec–butanol	"	14.6

2.3 Voltammetric measurements

For working electrodes, a Pt rotating disc electrode (Pine), A = 0.5 cm^2 and a leadstrip, partially coated with a PTFE tape, were employed. The Pt was pretreated by polishing with diamond spray (1 μm) at a rotating textile disc.

A galvanostatic formation was made for the lead (10 mA cm^{-2}, 1 h, 5 % H_2SO_4) in analogy to the macroelektrode.

The electrolytes were slightly different to the preparative runs, their compositions are indicated in the legends of Figs. 1 – 4 in section 3.4. The instrumental part is conventional. The usual three electrode configuration was used. The reference electrode was $Hg/Hg_2SO_4/1$ M H_2SO_4, which is +674 mV vs. SHE. Potentials measured against this reference are named U_s. The voltage scan rate was 5 mV s^{-1}. 3 cycles in the range of rest potential to the exponential rise of the current were measured to check steady state. The measurements at the emulsions were performed in strongly stirred electrolyte at 23 ^{0}C.

3. Results

3.1 Preparative anodic oxidation of di–sec–butylether (DSBE)

The results of our preparative batch runs with DSBE are compiled in Table 2. The quasidivided glass cell was employed for entries 1 – 9, while for the rest, 10 – 13, the divided plate and frame cell was used. The first group shows two runs without any cosolvent, while for all other electrolyses a cosolvent was added, in most of the cases acetonitrile. The DSBE concentration was between 7 and 33 vol %. All systems were heterogeneous at the beginning, but two, Nos 6 and 10, became homogeneous in the course of the electrolysis due to the accumulation of methylethylketone MEK, which acts by itself as a cosolvent.

Two types of conversion β of the starting material are shown in Table 2, namely the theoretical current conversion for 4 F/mole (β) and the effective conversion β_{eff}, cf. section 2.1.

β_{eff} is low in the case of Pt in the absence of a cosolvent and at PbO_2 under all conditions. The best

Table 2

Preparative Results for the anodic Oxidation of DSBE. j = 750 A m^{-2}, T = 35 °C.
Cells: QDCC (300 ml, Nos 1 – 9) and MPC (1250 ml, Nos 10 – 13)

Group	No	Anode	Cosolv.	Vol %			State	β/% (4 F)	β_{eff} %	MEK		CH_3COOH		HCN
				1M H_2SO_4	Cosolv.	DSBE				ce(%)	y(%)	ce(%)	y(%)	ce(%)
1	1	Pt	–	67	–	33	het.	35	2.6	2.3	35	14	44	–
	2	PbO_2	–	67	–	33	het.	35	2.6	1.2	10	14	24	–
2	3	Pt	MeCN	60	10	30	het.	62	15	0.3	1	51	50	2
	4	Pt	MeCN	47	30	23	het.	64	49	41	68	47	15	3.5
	5[1]	Pt	MeCN	28	39	33	het.	45	43	54	64	19	4	3
	6	Pt	MeCN	33	50	17	het→hom	67	71	52	70	41	10	4
	7	PbO_2	MeCN	60	10	30	het.	116	5	2	48	21	50	1
	8	PbO_2	MeCN	28	39	33	het.	110	7	4	30	19	60	3
	9	PbO_2	MeCN	33	50	17	het.	60	12	2.5	53	10	10	4
3	10	Pt	MeCN	55	38	7	het→hom	60	74	48	39	32	7	3
	11	Pt	Me_2CO	66	24	10	het.	71	70	54	60	37	15	–
	12	Pt	HOAc	33	50	17	het.	58	72	53	42	(–)	(–)	–
	13	Pt	MeOH	62	28	10	het.	70	56	9	11	8	2	–

Group 1 : Systems without cosolvent
Group 2 : Systems with MeCN as a cosolvent, QDCC–cell
Group 3 : Systems with MeCN and other cosolvents, MPC–cell

[1] j = 300 A m^{-2}

results are found for Pt in the presence of MeCN as cosolvent. The current efficiencies for MEK are above 50 %, and the yields (with respect to the converted DSBE) up to 70 %. It should be noted, that the c.e. calculation is based on the MEK alone, while the yields are evaluated on the basis of both products, MEK and sec–butanol, for it can be dehydrogenated to the ketone. MEK is accompanied by 10 – 50 mole % sec–butanol, not shown in the table. The occurrence of acetic acid up to nearly 50 % c.e. and HCN up to 4 % c.e. show, however, that neither the product MEK nor the cosolvent are stable against further oxidation. The other cosolvents, tested in addition, are inferior, especially methanol, which seems to be strongly oxidized under the electrolysis conditions.

Lower current densities, 10 and 30 mA cm^{-2}, do not significantly alter the picture. The addition of a surfactant of the arylalkylsulphonic acid type instead of a cosolvent does not improve the efficiency of DSBE converison. It must be emphasized, that a starting material containing only 85 % DSBE led to much lower c.e.'s and yields for MEK.

We were able to measure quantitatively the rate of anodic gas evolution $\dot{V}$ in the plate and frame cell experiments. A small gas burette was connected to the highest part of the anolyte loop. The $\dot{V}$–data were in good agreement with that values, which were calculated for oxygen from the current efficiency deficit to 100 %. Accordingly the anode gas contained nearly no CO_2.

Platinum losses were determined gravimetrically. They were 0.04 mg/Ah in the average, which is the same value as that found for the oxidation of THF /12/.

3.2 Preparative anodic oxidation of di–isopropylether (DIPE)

We have investigated this type of electrolysis with smaller intensity due to the inferior practical importance, cf. 4.2. Table 3 shows the preparative results. Again, Pt is more efficient than PbO_2 as anode material, but the differences are not so big. Acetone is formed with c.e.'s and yields up to 68 and 66 %, in the presence of 30 vol % MeCN. But even without any cosolvents, these data are distinctly higher than in the case of DSBE due to the tenfold higher solubility of DIPE in 1 M H_2SO_4, cf. section 4. The same electrolysis in the MPC cell gave lower c.e.'s and yields in comparison to the QDCC. To our surprise, only minor overoxidation to CH_3COOH and no HCN (in the presence of MeCN) was found. Platinum losses in the average were found to be 0.05 mg/Ah.

3.3 Preparative anodic oxidation of t–butylmethylether (TBME)

A third starting material, TBME, with t–alkylgroup was explored. Table 4 shows t–butanol to be the main product, which is relatively stable against further oxidation:

$$(CH_3)_3C\text{-}O\text{-}CH_3 \xrightarrow[H_2O]{-2e^-,\,-2H^+} (CH_3)_3C\text{-}OH + CH_2{=}O$$

Pt again is identified as the better anode material, but the differences to PbO_2 are relatively small. No cosolvent is needed due to the relatively high solubility of TBME in water (4.9 % at 20 °C /26/), cf. section 4.1. Formaldehyde is the second product. It was not determined quantitatively, but the product of follow up oxidation, formic acid. For the PbO_2 anode, only small quantities of HCOOH were found due to its rapid oxidation to CO_2. Both current efficiencies in Table 4 are calculated with respect to a theoretical

Table 3

Preparative Results for the anodic Oxidation of DIPE. j = 750 A m^{-2}, T = 35 ^{0}C.
Cells: QDCC (300 ml,) Nos 1 – 6, and MPC (1250 ml), Nos 7,8

Group	No	Anode	Cosolv.	Vol %			State	β/% (4 F)	β_{eff} %	Acetone		CH_3COOH		HCN
				1M H_2SO_4	Cosolv.	DIPE				ce(%)	y(%)	ce(%)	y(%)	ce(%)
1	1	Pt	–	67	–	33	het.	53	70	32	20	8	1	–
	2	PbO_2	–	67	–	33	het.	51	42	17	20	7	1	–
2	3	Pt	MeCN	47	30	23	het→hom	50	84	68	66	9	1	0
	4	PbO_2	MeCN	47	30	23	het.	50	66	34	34	5	1	0
	5	Pt	HOAc	47	30	23	het→hom	50	77	46	45	(–)	(–)	–
	6	PbO_2	HOAc	47	30	23	het.	50	72	10	8	(–)	(–)	–
3	7	Pt	–	81	–	19	het.	61	48	10	13	–	–	–
	8	PbO_2	–	79	–	21	het.	39	48	12	11	4	1	–

Group 1,3 : Systems without cosolvent in the QDCC and MPC cell, respectively
Group 2 : Systems with cosolvents.

amount of 2 F/mole product.

Table 4
Preparative results for the anodic oxidation of TBME. j = 750 A m^{-2}, T = 5 and 35 °C. Electrolyte composition: 66 vol% 1 M H_2SO_4, 33 vol% TBME. β (%) for 2 F/mole was 48 %.

No	Anode	T / °C	Current efficiencies c.e. (%)	
			t–butanol	formic acid
1	Pt	5	83	8
2	Pt	35	75	8
3	PbO_2	5	50	0.5
4	PbO_2	35	53	2.5

Table 4 shows in addition, that the electrolyte temperature has no significant influence to the results.

3.4 Voltammetric measurements

Figs. 1 – 3 display the result of voltammetric measurements at the rotating platinum disc electrode at 1200 rpm. The voltage scan rate was 5 mV s^{-1}. The third cycle is shown for each case, which is about steady state.

Fig. 1 shows the results in the systems without a cosolvent. A pronounced anodic peak is found prior to the final anodic rise, but only for the forward direction in the order of 1 and 10 mA cm^{-2}. The peak current density is roughly larger by an order of magnitude for DIPE in comparison to DSBE. This resembles the ratio of solubilities, cf. section 4. It should be mentioned, however, that the current density for the preparative run was at 75 mA cm^{-2}, and the anode potential will be in the exponentially rising part of the current voltage curve.

This could eventually explain the low current efficiencies for the organic anodic process in the absence of any cosolvent. As a matter of fact, the ratio of peak current density to the working current density, 75 mA cm^{-2}, corresponds roughly to the current efficiencies found via product analysis, cf. Tables 2 and 3.

However, this interpretation has to be modified due to the experimental findings shown in Fig. 2, which represents the result for the systems with 60 vol % acetonitrile as a cosolvent. In spite of the dramatically improved solubility of both ethers, DSBE and DIPE, the anodic peak current densities are very similar to those in Fig. 1. Clearly, the peaks are kinetically controlled and not by the transport of the ether to the anode. Both starting materials, DSBE and DIPE are not 100 % pure, but do contain a few % impurities. If these impurities would be the corresponding secondary alcohols, then the question arises, if the anodic peaks are due to the alcohol oxidation. But this must be excluded, for the concentrations are as 1 : 3 (in Figs. 1 and 2), and this is not reflected in the peak current densities. This argument, however, is not valid for a limitation due to adsorption. We prefer an interpretation on the basis of an initial chemical attack of the ethers by the PtO_x, which is generated at the potential of first current rise /12–14/. A self inhibition of the anodic processes by the anodic products seems to occur, thereafter.

It can be noted, that the acetonitrile shifts the curves in the positive direction, and this is indicative for a strong adsorption of MeCN itself. It is anodically attacked to some extent, and HCN is split off via the

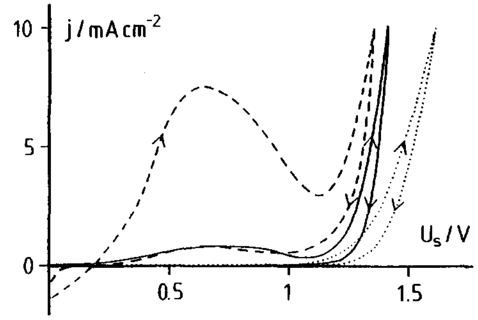


Fig. 1: Slow cyclovoltammetric curves for the anodic oxidation of 0.1 M DSBE (———) and 0.1 M DIPE (– – –) at the rotating Pt disc electrode in 1 H_2SO_4. Basic curve (······). The ethers form emulsions.

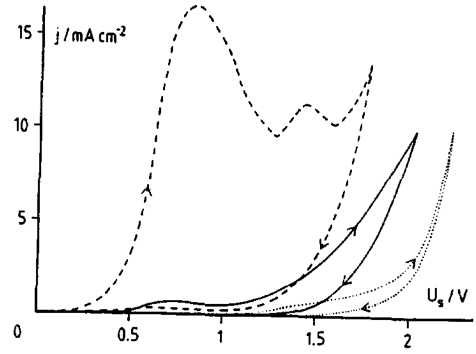


Fig. 2: Slow cyclovoltammetric curves for the anodic oxidation of 0.3 M DSBE (———) and DIPE (– – –) at the rotating Pt disc electrode in 1 M H_2SO_4 in 60 vol % MeCN. Basic curve (·····). DIPE is dissolved while DSBE forms an emulsion.

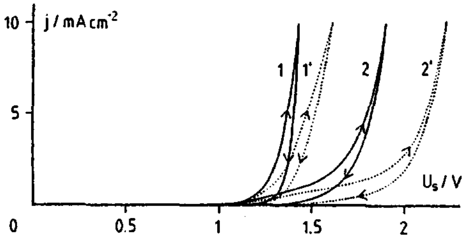


Fig. 3: Slow cyclovoltammetric curves for the anodic oxidation of 0.1 M TBME in 1 M H_2SO_4 (1) and of 0.3 M TBME in 1 M H_2SO_4/60 vol % MeCN (2). (1') and (2') are the corresponding basic curves. The ether dissolves in both electrolytes clearly.

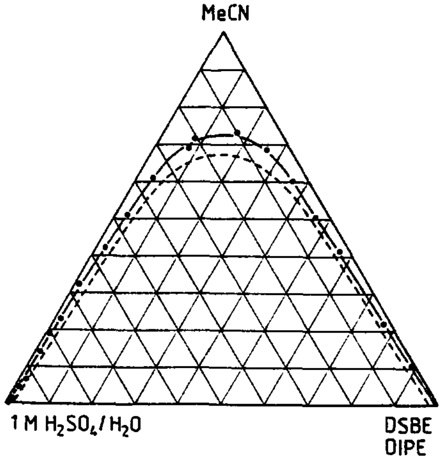


Fig. 4: Ternary diagram for 1 M H_2SO_4, MeCN and DSBE (———) and DIPE (– – –), respectively.

cyanohydrine, cf. Tables 2 and 3:

$$CH_3CN \xrightarrow[H_2O]{-2e^-,-2H^+} CH_2(OH)CN \xrightarrow{H^+} CH_2{=}O + HCN$$

Fig. 3 represents the current voltage behaviour in the presence of TBME; no anodic peak at negative potentials is observed, but only a negative shift of the exponentially rising curves with respect to the corresponding basic curves.

Lead dioxide as the alternative anode material was also characterized by slow cyclic voltammetry for DSBE. An amplification of the PbO_2 formation peak was observed. PbO_2 seems to react chemically with DSBE. Both features are indicative for a mechanism of heterogeneous redox catalysis in this case /17–20/.

4. Discussion

It is for the first time, that we oxidize aliphatic ethers with a relatively low solubility in 1 M H_2SO_4. Fig. 4 shows the diagram of the ternary systems with CH_3CN as a cosolvent. The solubility gap is only closed by the addition of about 70 % cosolvent. The solubilities in water are derived to be 0.13 % (DSBE) and 1.0 % (DIPE), which is close to the 0.88 % at 20 °C for H_2O /27/. Thus, solubilities are in the order of 1 – 10 mM. Without a cosolvent, emulsions are obtained, and transport limitation through diffusion layers at the oil droplets and at the electrode surface must be a consequence. If the convection is strong enough, thickness of diffusion layer is minimized, and medium current densities are possible /28/.

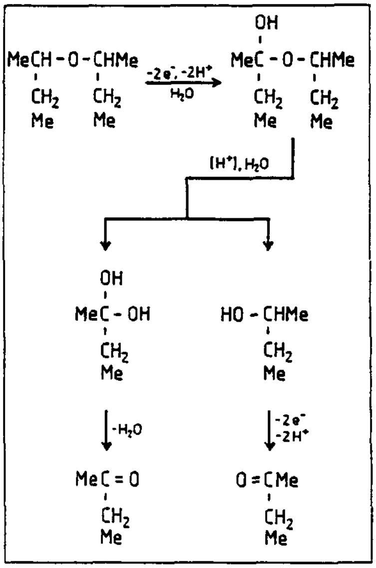
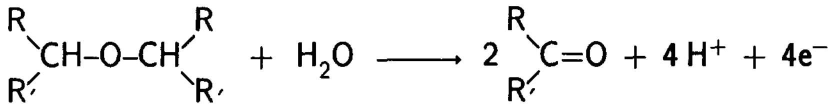


Fig. 5: Reaction mechanism for the anodic oxidation of DSBE.

From the product analysis in Tables 2 and 3, an oxidation mechanism according to Fig. 5 follows immediately. The initial step is the anodic formation of a semiketale, as it was the formation of a semiacetale in our previous work /12,13/. A rapid /29,30/ follow up reaction in terms of an acid catalyzed cleavage to yield the ketone and the secondary alcohol occurs thereafter. The alcohol can be further oxidized to the ketone, and an overall reaction can be defined:



$$(R)(R')CH{-}O{-}CH(R)(R') + H_2O \longrightarrow 2\,(R)(R')C{=}O + 4H^+ + 4e^-$$

n–alkyl ethers are cleaved at the anode into two molecules carboxylic acid under the consumption of the twofold number of Faradays /13/.

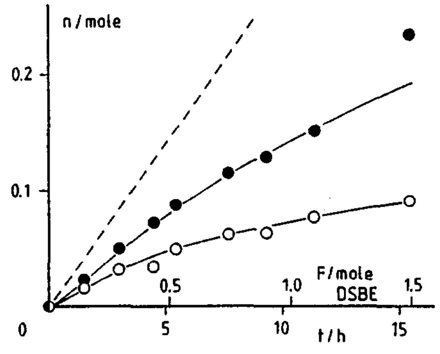


Fig. 6: Kinetic curves for the anodic oxidation of DSBE at Pt. n_0 = 0.577 mole, I = 3.75 A, cf. No 6 in Table 2. ●—● = MEK, o—o = i–BuOH. The dashed line is for 100 % c.e.

Fig. 6 shows kinetic curves for the anodic oxidation of DSBE. MEK and sec–butanol are generated in parallel. From this we conclude, that chemical cleavage of the semiketale does not occur in the adsorbed state, but after diffusion into the bulk of the electrolyte. Only a part of the alcohol diffuses back to the anode, where it is further oxidized. Both curves are below the theoretical line (100 % c.e.) due to the nonquantitative current efficiencies, cf. Table 2.

One of the reasons for this is the overoxidation of MEK. The molecule is attacked at the activated CH_2–group. According to the scheme Fig. 7, diacetyl is formed as an intermediate, which is easily cleaved to two molecules acetic acid /16/. This is relatively stable under these conditions. In case of DIPE, acetone is the primary product, which is much more stable against overoxidation. Tables 2 and 3 show indeed, that acetic acid is a large byproduct in case of DSBE oxidation, but only a minor byproduct for the oxidation of DIPE.

We have used aqueous electrolytes throughout. A low pH is necessary for an efficient anodic ether cleavage /13/. For the anodic oxidation of DIPE in phosphate buffer, current efficiency was only 1.5 % in comparison to 31 % in 1 M H_2SO_4. Water is a nonexpensive solvent, which allows for a high conductivity of the electrolyte solutions. It is a strong nucleophile, and interesting hydroxylic products are possible. In acid solutions, most positive potentials for oxide electrodes are possible. In accordance to our former work on the anodic oxidation of aliphatic ethers /12–14/, platinum was found to be optimum anode material.

DSBE oxidation is important from an industrial point of view. The petrochemical hydration of butenes leads to sec–butanol. DSBE is a useless byproduct /27,31/ cf. Fig. 8. In case of the hydration of propene , DIPE is a valuable side product, which is used for extractions. Acid catalysts are employed.

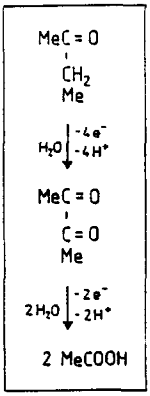


Fig. 7: Reaction mechanism for the anodic overoxidation of MEK.

TBME is a large scale product, which is obtained by the acid catalyzed addition of methanol to isobutene /27,31/.

For all three ethers, acid catalyzed decompositions into the starting materials can be performed. From this point of view, our anodic cleavage can be regarded as an interesting alternative, which leads in case of DSBE even to a valuable product, MEK.

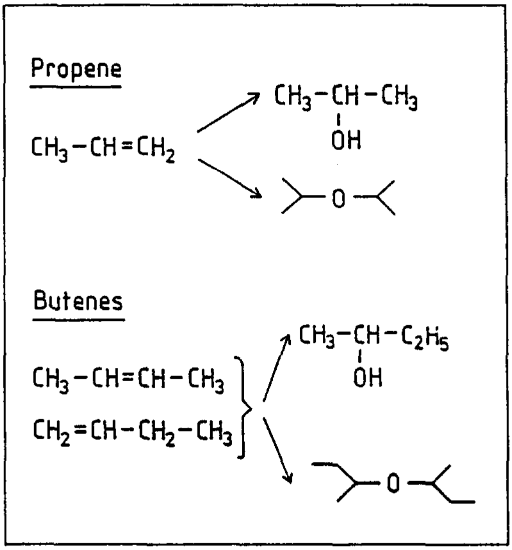


Fig. 8: Petrochemical hydration of olefins to form isoalcohols.

Acknowledgement

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References

/1/ Nilsson, A.; Palmquist, U.; Petterson, T.; Ronlan, A. J. Chem. Soc., Perkin Trans. I 1978, 708

/2/ Chenard, B.L.; Swenton, J.S. J. Chem. Soc., Chem. Commun. 1979, 1172

/3/ Chenard, B.L.; Mc Connell, J.R.; Swenton, J.S. J. Org. Chem. 1983, 48, 4312

/4/ Torii, S. "Electroorganic Synthesis", Part I: Oxidations.Verlag Chemie, Weinheim 1985

/5/ Wladislaw, B.; Viertler, H. Chemistry and Industry 1965, 1, 39

/6/ Wladislaw, B; Viertler, H. J. Chem. Soc. C 1968, p. 576

/7/ Miller, L.L.; Wolf, J.F.; Mayeda, E.A. J. Am. Chem. Soc. 1971, 93, 3306

/8/ Mageda, E.; Miller, L.L.; Wolf, J.F. J. Am. Chem. Soc. 1972, 94, 6812

/9/ Lines, R.; Utley, J.H.P. J. Chem. Soc., Perkin Trans. II 1977, p. 803

/10/ Shono, T.; Matsumura, Y. J. Am. Chem. Soc. 1969, 91, 2803

/11/ Germ. Pat. 3 000 243 (Hoechst AG, J. Cramer, 1979) cf. CA 95: 140 904 j

/12/ Wermeckes, B.; Beck, F.; Schulz, H. Tetrahedron 1987, 43, 577

/13/ Wermeckes, B.; Beck, F. Electrochim. Acta 1985, 30, 1491

/14/ Wermeckes, B.; Beck F. Chem. Ber. 1987, 120, 1679

/15/ Wermeckes, B.; Beck, F. DECHEMA Monographs 1988, 112, p. 1

/16/ Ye, S.; Beck, F. Electrochim. Acta 1990, 35, in press

/17/ Beck, F.; Schulz, H. Electrochim. Acta 1984. 29, 1569

/18/ Beck, F.; Schulz, H. J. Appl. Electrochem. 1987, 17, 914

/19/ Beck, F.; Wermeckes, B.; Zimmer, E. DECHEMA Monographs 1988, 112, 257

/20/ Beck, F. Chemische Industrie 1990, in press

/21/ Fieser, L.; Fieser, M. "Reagents for Organic Synthesis", 1967–1989 (14 volumes), John Wiley, New York

/22/ Beck, F. Electrochim. Acta 1988, 33, 839

/23/ Beck, F.; Hülser, P. J. Electroanal. Chem. 1990, 280, 159

/24/ Beck, F.; Oberst, M. J. Electroanal. Chem. 1990, 285, 177

/25/ Wermeckes, B.; Beck, F. Chem. Ber. 1985, 118, 3771

/26/ Mc Bain, J.W.; Richards, P.H. Ind. Eng. Chem. 1946, 38, 643

/27/ Strehlke, G. in Ullmanns Ecycl. Ind. Chem., VCH, Weinheim, 1987, Vol. A 10, p. 28

/28/ Feess, H.; Wendt, H. in "Technique of Electroorganic Synthesis", Part III, N.L. Weinberg and B.V. Tilak, Eds, John Wiley, New York, 1982, p. 81 – 179

/29/ Leininger, P.M.; Kilpatrick, M. J. Am. Chem. Soc. 1939, 61, 2510

/30/ Barker, S.A.; Bourne, E.J. J. Chem. Soc. 1952, 905

/31/ Weissermel, K.; Arpe, H.–J. "Industrial Organic Chemistry", 3rd ed., VCH Weinheim, 1988