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A SURVEY OF NONAQUEOUS CONDITIONS FOR THE ANODIC OXIDATION OF N-BUTYL ALCOHOL

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Abstract—A survey of nonaqueous conditions for the oxidation of n-butyl alcohol is reported. Oxidation may be effected in the neat alcohol or in moderately dilute solution in acetonitrile. High current yields of butyraldehyde are obtained in the neat alcohol, but in dilute solution n-butyl butyrate is the major product. Lithium fluoborate is superior to lithium nitrate or perchlorate as the supporting electrolyte.

We have been interested in the anodic oxidation of saturated aliphatic alcohols. Much of the previous work in this area has been carried out in aqueous solution, often aqueous sulfuric acid,[1-4] and the lower alcohol homologs have been oxidized as the neat liquids.[5,6] We were interested in developing conditions which could be applied to the higher alcohols, which exhibit only limited water solubility, and whose dielectric constants are too low to permit electrolysis of the neat liquids. An electrochemically inert solvent-supporting electrolyte combination was thus sought.

Mann has recently reviewed a variety of non-aqueous solvents for electrochemical use.[7] Compatibility with alcohol oxidation was not considered explicitly, but the high anodic potentials available in acetonitrile and sulfolane make these solvents particularly attractive for electrochemical oxidation of alcohols.

Lund oxidized benzylic alcohols in acetonitrile,[8] but early attempts to study saturated aliphatic alcohol oxidation voltammetrically led to the conclusion that hydrogen evolution, the expected cathode reaction in alcohol oxidation, does not occur in acetonitrile.[9] More recently, however, Sundholm has reported both voltammetric data for alcohol oxidation and successful preparative electrolyses effected at platinum in acetonitrile.[10,11] Sundholm's preparative data, however, appears inconsistent and raises many questions. Oxidation of n-propyl alcohol is reported to afford propionaldehyde in 57% yield while n-butyl alcohol is reported to give 6% of butyraldehyde, 8% of butyric acid, and 49% of n-butyl butyrate under what must be presumed to be identical conditions. A rationale for this disparity was not attempted.

We undertook a survey of solvents and supporting electrolytes to determine those most applicable to alcohol oxidaltion. n-Butyl alcohol was chosen as the substrate. Initially the alcohol was in large excess of the amount of charge passed, so it was anticipated that the major product would be butyraldehyde or its acetal. Precipitation of butyraldehyde 2,4-dinitrophenylhydrazone permitted gravimetric determination of the aldehyde current yield. This analytical method provided a rapid survey of conditions and additionally served to determine the total product in the aldehyde oxidation state, whether it was actually present as the free aldehyde or as its acetal (*vide infra*).

Insofar as possible, it was desired to carry out the study under conditions which would be available to the average organic chemist. Thus the controlled potential conditions with periodic cathodic pulsing of the anode and the multicompartment cell described by Sundholm were not used. Instead, a one compartment cell and a simple D.C. power supply were employed. A platinum anode was employed.

Results of the survey are given in Table 1. It should be noted that approximately the same amount of charge was passed for each reaction except where specified otherwise. The charge passed was about 0·67 F per mole of alcohol in those reactions where the alcohol concentration was 10% (solvent concentration = 90%). This ratio was of course smaller in reactions having higher alcohol concentrations.

Electrolysis of the neat, dry alcohol (**1–3**) demonstrated a clear superiority of lithium fluoborate over nitrate and perchlorate. It was found from electrolysis of stock (undried) alcohol and from a sample containing 10% water (**4**, **5**), that a small amount of water does not adversely affect the current yield of aldehyde. This finding is perhaps not surprising since alcohols have been successfully oxidized in aqueous solution, solubility permitting.†

A study of organic solvents was next undertaken. Initially, the solvent concentration was kept low (10% by volume), but easily oxidized solvents, tetrahydrofuran, dimethylsulfoxide, and dimethylformamide, suppressed aldehyde formation completely (**20–26**). In sulfolane (**15**) and nitromethane (**18**) modest yields of aldehyde were obtained, but in acetonitrile (**6**) the aldehyde yield was as high as that obtained in the neat alcohol.

When the concentration of solvent was increased to 50%, the aldehyde current yield suffered. Using fluoborate, a good yield was still obtained in acetonitrile (**7**) and a moderate yield in sulfolane (**16**), but only a trace was observed in nitromethane (**19**).

Finally, in dilute solution (90% solvent by volume), a trace of aldehyde was obtained in sulfolane (**17**), and only a 9% yield was observed in acetonitrile (**8**). When perchlorate or nitrate was substituted for fluoborate in 90% acetonitrile (**9**, **10**), only traces of aldehyde were obtained.

†However, caution is advised in interpretation of voltammetric data obtained in the presence of water. In a study of the oxidation of *tert*-benzylic alcohols to arylalkyl ketones, well defined voltammetric waves for alcohol oxidation could only be obtained in anhydrous acetonitrile. Controlled potential preparative electrolyses, however, proceeded readily in 10% water–90% acetonitrile and afforded ketone current yields which were comparable or (usually) superior to those obtained in the anhydrous system. Voltammetric data alone would have lead to the totally erroneous conclusion that the only reaction taking place is electrolysis of water.

Table 1. Survey of reactions for anodic oxidation of n-butyl alcohol at platinum

Reaction No.	Solvent[a]	Solvent conc. (% by volume)	Supporting[b] Electrolyte	Current Yield of Aldehyde
1	None[c]	-	N	43
2	None	-	P	38
3	None	-	F	77
4	None[d]	-	N	41
5	Water	10	N	47
6	AN	10	F	77,77[e]
7	AN	50	F	64
8	AN	90	F	9
9	AN	90	N	trace[f]
10	AN	90	P	trace
11	AN[g]	90	F	10
12	AN[h]	90	F	22
13	AN[i]	90	F	9
14	AN[h]	90	$(CH_3)_4NBF_4$	19
15	SFL	10	F	57
16	SFL	50	F	53
17	SFL	90	F	trace
18	NM	10	F	22
19	NM	50	F	trace
20	THF	10	P	0[j]
21	THF	10	F	0
22	DMSO	10	N	0
23	DMSO	10	F	0
24	DMF	10	N	0
25	DMF	10	P	0
26	DMF	10	F	0

[a] AN, acetonitrile; SFL, sulfolane; NM, nitromethane; THF, tetrahydrofuran; DMSO, dimethyl sulfoxide; DMF, dimethyl formamide.

[b] N, lithium nitrate; P, lithium perchlorate; F, Lithium fluoborate.

[c] Except where noted, dry alcohol, distilled from calcium metal, was employed. Solvents were dried by standard methods.

[d] Here reagent grade alcohol was used as obtained.

[e] Results of two independent electrolyses.

[f] A trace of aldehyde means that cloudiness appeared when 2,4-dinitrophenyl-hydrazine was added to the electrolyzed solution, but that the precipitate could not be collected for weighing. In a control, it was determined that a 0·5% yield of aldehyde would give a definite, weighable, precipitate.

[g] Controlled potential reaction.

[h] One half as much total charge passed as usual.

[i] A two compartment cell was employed.

[j] A yield of 0 means that the cloudiness noted in footnote *f* was not observed.

Attempts to increase the aldehyde yield in the 90% acetonitrile—10% alcohol-fluoborate system were unsuccessful. Controlled potential electrolysis was carried out using as a reference electrode a silver wire immersed in 0·1M silver nitrate in acetonitrile. This reference is reported to exhibit a potential of +0·36V vs the saturated calomel electrode.[12] Contact with the alcohol cell was effected with a Luggin capillary. At 2·4 V vs the reference (11), the aldehyde current yield was about the same as in non-controlled potential reactions, and the current dropped off at lower potentials. The current yield was improved to 22% by passing half as much total charge as usual (12) but this of course was at the expense of the conversion of alcohol.

Reduction of aldehyde at the cathode was conceivable since this electrode was sufficiently cathodic that lithium metal was deposited on it, and reduction of aldehydes by lithium, albeit under somewhat different conditions (liquid NH_3) is well known. Cathodic reduction was eliminated by carrying out the electrolysis in a two compartment cell. the aldehyde current yield remained at 9% (13).

Metal separation could be eliminated by using tetramethylammonium fluoborate as the electrolyte (14). With this salt the only visible cathode reaction was gas evolution (hydrogen?). Again in this reaction, only half as much charge was passed as usual, and the 19% yield of aldehyde is comparable to the corresponding lithium salt electrolysis (12).

Gas chromatographic analysis of the 90% acetonitrile electrolyses was next carried out. Prior to analysis samples were distilled on a vacuum line. Care was taken that higher boiling components (such as acetals and esters) present in small quantities would not remain undistilled. In this study all cells were connected in series so that the same amount of charge would be passed. Analyses of all reactions were performed in triplicate and were carried out at one time under identical conditions. Also. the electrolysis study, heretofore performed only at platinum, was extended to graphite anodes. Results are given in Table 2.

It is disturbing that the current yields are less than quantitative. We considered it important to determine the fate of the entire reaction mixture insofar as possible, including noting of volatile by-products and distillation residues, even if unidentified.

In the reactions employing nitrate as the supporting electrolyte (27 and 29), volatile by-products were not in fact observed, but large quantities of undistilled residue

Table 2. Product distributions[a] from oxidation of n-butyl alcohol in 10% alcohol—90% acetonitrile mixtures

Anode-Electrolyte	Pt-$LiNO_3$	Pt-$LiBF_4$	C-$LiNO_3$	C-$LiBF_4$
Reaction No.	27	28	29	30
Butyraldehyde	0	8.1	5.2	35.1
Butyraldehyde di-n-Butyl Acetal	0	0	0	0
n-Butyl Butyrate	0	51.4	14.4	15.1

[a]Numbers are current yields.

were obtained in each case, and the low current yield of volatile products in the nitrate runs has a likely explanation here.

When fluoborate was employed on the other hand (**28**, **30**, **31** and **32**) there was no residue in excess of the weight of supporting electrolyte. Reactions were open to the air to permit escape of gas formed at the cathode, but evaporation losses were too small to explain the low current yields observed.

Reactions **28** and **30** indicate that carbon favors oxidation of alcohol to aldehyde while platinum promotes further oxidation of the aldehyde to form ester. This trend is also seen in reactions **31** and **32**, although here acetal formation tends to protect the aldehyde from further oxidation (*vide infra*). Comparison of reactions **29** and **30** indicates that oxidation of aldehyde to ester is also favored with a nitrate supporting electrolyte.

Tomilov has recently discussed several mechanisms for the oxidation of primary and secondary alcohols.[13] These may be grouped into two categories depending upon whether the first step is removal of an electron from the alcohol (Scheme 1A) or abstraction of an α-H atom (Scheme 2A).

Two similar mechanisms may be written for aldehyde oxidation. In Scheme IB, removal of an n-electron† affords a radical cation in a manner similar to a pathway recently demonstrated for ketone oxidation.[14] Formation of an acyl radical by abstraction of the aldehyde hydrogen (Scheme 2B) is the other mechanism.

The observed data are for the most part consistent with the following propositions: (1) Abstraction mechanisms (Scheme 2) are favored by the presence of nitrate, presumably due to intermediacy of the nitrate radical. (2) Fluoborate is an inert electrolyte. In its presence, alcohol oxidation occurs at the anode surface, resulting in a dependence of product distribution on that surface, with platinum favoring the hydrogen abstraction mechanism. (3) Conditions most conducive to hydrogen abstraction favor oxidation of the aldehyde.‡

Nitrate is known to undergo a one-electron oxidation to a radical at a potential well below that required for alcohol oxidation,[15] and the resulting radical is known to be a hydrogen abstractor,[16] while fluoborate only oxidizes at higher potentials than alcohols. With fluoborate, then oxidation of alcohols occurs at the anode, and platinum would be expected to be the better hydrogen abstractor on the basis of its known ability to form strong bonds to hydrogen (hence its use as a hydrogenation catalyst). These propositions are clearly borne out in a study of secondary alcohols,[17] but the present data include a serious anomaly, Reaction **27**, in which no alcohol oxidation products could be discerned.

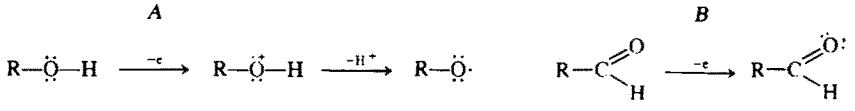
The relative rates oxidation of aldehyde and alcohol are reflected in the ester:aldehyde ratio which increases as aldehyde oxidation becomes more favored. In general, the ratio was higher in reactions thought to be more conducive to hydrogen abstraction. Thus the aldehyde appeared to oxidize more efficiently, relative to the alcohol, at platinum than at carbon, and with nitrate as compared with fluoborate. Failure to obtain any products in Reaction **27** is completely anomalous. It should be noted that this result was confirmed by four repetitions.

Alcohol oxidations proceeding via the Scheme 1 mechanism might be expected to afford formaldehyde by radical fragmentation, although the amount is not likely to be very large.[18] Sundholm observed di-n-propoxymethane, a formaldehyde derivative, in the anodic oxidation of n-propyl alcohol,[5] but we could detect no formaldehyde or derivatives thereof in our reactions.

Formation of acetals in Reactions **31** and **32**, in contrast

†"n-Electron" here refers to one of the unshared electrons on oxygen, in the same sense photochemists use the term.

‡Put another way, of the Scheme 2 mechanisms, B is easier than A, aldehyde oxidation is favored, and its concentration does not get very high before it successfully competes with the alcohol. Of the Scheme 1 mechanisms, A is favored over B and aldehyde concentration builds up.



Scheme 1.

Scheme 2.

to formation of free aldehydes in Reactions 28–30 also deserves comment. Some workers have reported acetal formation in oxidation of neat alcohols while others have observed formation of free aldehydes in acetonitrile. A systematic study of a single alcohol oxidation, effected under identical conditions except for the presence of acetonitrile has not hitherto been reported, however. Our study indicates that the major portion of product in the aldehyde oxidation state is indeed present as the acetal when oxidation of the neat alcohol is carried out. In dilute solution in acetonitrile, on the other hand, the free aldehyde is formed and the acetal is not present. Sundholm has proposed a mechanism for acetal formation which does not involve the free aldehyde. Miller has shown, however, that non-electrochemical reactions normally considered to be acid catalyzed may be observed in anodic oxidations.[19] Thus dibenzyl ether was converted in part to N-benzylacetamide upon anodic oxidation and it was shown that the amide could arise from a reaction between benzyl alcohol and acetonitrile, catalyzed by anodically generated acid. We have observed a reaction similar to Miller's with tertiary aliphatic alcohols in acetonitrile. In addition, Sundholm reports isobutylene as a by-product in the oxidation of t-butyl alcohol, a product clearly resulting from acid catalyzed dehydration.† Thus acetal formation, when it occurs in the anodic oxidation of primary alcohols, is very likely the expected acid-catalyzed reaction of an aldehyde in alcohol solution having a low water activity.

Acetal formation occurs most readily when a large excess of alcohol is present; that is, in those reactions run in the neat alcohol. Oxidation of the acetal is more difficult than the aldehyde, so further oxidation to the ester takes place less readily when the acetal, rather than the free aldehyde, is present. The acetal was shown not to oxidize with the platinum-fluoborate system, so the ester formed under these conditions must come from oxidation of the aldehyde.

Table 3 describes oxidations carried out in the neat alcohol. Here the majority of product in the aldehyde oxidation state is actually present as the acetal. A small amount of ester is found when a platinum anode is used, but no ester is formed at carbon.‡ It should be noted that the ortho ester α,α,α-tri-n-butoxybutane, is a possible product having the same oxidation state as the n-butyl butyrate. The ortho ester was prepared and was shown to be absent.

In conclusion, the anodic oxidation of primary alcohols to aldehydes is best effected in the neat liquid substrate. If a solvent must be used, acetonitrile is superior to others surveyed.§ A fluoborate supporting electrolyte is advised. Carbon anodes favor aldehyde production whereas platinum (smooth) appears best for the four electron oxidation to ester. Controlled potential offers no apparent advantage.[21,22]

Table 3. Product distributions[a] from oxidation of n-butyl alcohol as the neat liquid

Anode–Electrolyte	Pt-$LiBF_4$	C-$LiBF_4$
Reaction No.	31	32
Butyraldehyde	8.4	7.8
Butyraldehyde di-n-Butyl Acetal	38.6	30.8
n-Butyl Butyrate	3.1	0.0

[a]Numbers are current yields.

EXPERIMENTAL

Electrolyses were performed with 50 ml of soln containing 0·4 g of electrolyte. Non-controlled potential experiments employed a power supply capable of 200 mA and 500 V. Controlled potential runs were effected with a Wenking potentiostat model 70HV1 from Brinkmann Instruments, Inc. A copper plating cell placed in series with the alcohol cell served as coulombmeter. The platinum anode was a wire mesh electrode from E. H. Sergent and Company (Cat. No. S-29632). The carbon anodes were $\frac{1}{4}$" diameter U7 density grade carbon rods available from Ultra Carbon Corporation (Cat. No. U50–7).

For analysis by the derivative method, excess of the usual solution of 2,4-dinitrophenylhydrazine[20] was added to a portion of the electrolysis soln. After 15–30 min, 5 volumes of water was added and after another 15 min, the ppt was filtered (suction), washed with water, and dried to constant weight in a vacuum dessicator over $CaCl_2$. The filtrate was checked for completion of precipitation by adding water and cooling in ice, and for the presence of excess reagent by adding acetone. Purity of the derivative was checked by TLC.

Gas chromatography employed a Hewlett-Packard Model 700 instrument using $\frac{1}{8}$" × 6' columns packed with 10% Carbowax 20M or with UCC-W982 on Chromosorb W-AW-DMCS and operated at 110°. Samples were distilled by being placed first in one arm of an inverted U-tube, cooling in dry ice, evacuating and sealing the system, and warming the sample to room temperature while the second arm of the U-tube was placed in dry ice.

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†Sundholm even reports a current yield for isobutylene, but the term cannot have its usual meaning since the alkene and starting alcohol are in the same oxidation state.

‡The current yield of aldehyde plus acetal obtained by gas chromatography in Reaction **31** is lower than that obtained as a 2,4-dinitrophenylhydrazone in Reaction **3** as a result of twice as much charge being passed in Reaction **31** as in Reaction **3**. Decreased current yield upon passage of more charge was seen in the 10% alcohol-90% acetonitrile runs also (Reactions **8**, **12**), but it is surprising to observe this difference in the neat alcohol reactions where the charge was only sufficient to oxidize 3·3% (**3**) or 6·7% (**31**), of the alcohol.

§Solvents not surveyed in the present study but which appear favorable include propylene carbonate (see Ref. 10) and methylene chloride.

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