

## The Anodic Oxidation of Some Aliphatic Alcohols in Organic Solvents

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In a recent paper,<sup>1</sup> the anodic oxidation of absolute methanol and ethanol was discussed and the initial step in the electrochemical oxidation of these alcohols was proposed to be:



In this paper, the results of a study of the anodic oxidation of some aliphatic alcohols in acetonitrile, propylene carbonate, methylene chloride, and sulfolane are reported.

According to Mann and Barnes,<sup>2</sup> oxidation of methanol and ethanol cannot be observed in acetonitrile containing a perchlorate as supporting electrolyte and this is to be expected in view of the fairly high ionization potentials of aliphatic alcohols reported in the literature.<sup>3</sup>

The available potential range could, however, be extended by using a tetrafluoroborate as supporting electrolyte.<sup>4</sup> Comparison of the potential scales in the different solvents was done with the aid of the reversible ferrocene/ferrocinium redox couple as suggested by Strehlow.<sup>5</sup>

The results of the measurements on this couple in the solvents studied in this

Table 1. Anodic half-peak potentials for the ferrocene/ferrocinium system in different solvents vs. the Ag/0.01 M Ag<sup>+</sup> reference electrode. Supporting electrolyte: 0.15 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub>. Sweep rate 0.2 V/s.

Solvent	$E_{p/2}/V$	Peak separation/mV
CH <sub>3</sub> CN	0.04	56
C <sub>3</sub> H <sub>6</sub> CO <sub>3</sub>	-0.39	57
CH <sub>2</sub> Cl <sub>2</sub>	-0.45	57
C <sub>4</sub> H <sub>8</sub> SO <sub>2</sub>	-0.18	60

work are shown in Table 1. The anodic oxidation of the alcohols was measured by linear sweep cyclic voltammetry at a platinum wire electrode. The results of these measurements are shown in Table 2. It may be pointed out that all the alcohols studied gave a single well-distinguishable, irreversible oxidation peak in acetonitrile, propylene carbonate, and methylene chloride, whereas no proper oxidation peaks were detected in sulfolane, although the curves clearly indicated that oxidation of the alcohol was taking place. An explanation could be the very fast formation of a reaction product that blocks the electrode.

Coulometric measurements showed that the *n*-value is two, so that the first step in the oxidation reaction is probably reaction (1).

The half-peak potentials are about 100–150 mV less anodic in methylene chloride than in the other two solvents.

Table 2. Anodic oxidation of aliphatic alcohols. The potentials are reported vs. the ferrocene/ferrocinium system in each solvent. Supporting electrolyte: 0.15 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub>. Sweep rate 0.5 V/s.

Compound	$E_{p/2}/V$			$E_{sp/4} - E_{p/4}/V$			IP <sup>a</sup> /eV
	CH <sub>3</sub> CN	C <sub>3</sub> H <sub>6</sub> CO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN	C <sub>3</sub> H <sub>6</sub> CO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	
Methanol	2.73	2.64	2.5	0.19	0.44	—	10.8
Ethanol	2.61	2.59	2.43	0.19	0.45	0.17	10.5
1-Propanol	2.56	2.55	2.41	0.14	0.36	0.23	10.2
2-Propanol	2.50	2.58	2.39	0.16	0.37	0.16	10.2
1-Butanol	2.56	2.50	2.35	0.18	0.37	0.24	10
2-Butanol	2.55	2.49	2.34	0.11	0.36	0.27	10.2
1-Pentanol	2.46	2.45	2.31	0.14	0.38	0.25	9.9

<sup>a</sup> IP = ionization potential; values taken from Ref. 3.

This difference is significant even when one takes into account the uncertainty involved in using the ferrocene/ferrocinium couple to compare the potential scales.

It has been suggested<sup>6</sup> that correlations between anodic oxidation potentials and gas phase ionization potentials of organic compounds could be used for the prediction of oxidation potentials for electrochemical syntheses of organic compounds. An inspection of Table 2 shows that, indeed, the oxidation potentials follow the ionization potentials (1-propanol, 2-propanol, 1-butanol, and 2-butanol have approximately equal ionization potentials).

However, comparison with the data reported for some aliphatic hydrocarbons<sup>4</sup> and the information given by Miller<sup>6</sup> indicate that the oxidation potentials of aliphatic alcohols are about 200–400 mV less anodic than the IP values would suggest. Thus solution phase ionization requires less energy than gas phase ionization in the case of these alcohols. The reasons for such a difference require further investigation.

*Experimental.* The solvents were purified by standard methods.<sup>7</sup> The aliphatic alcohols were analytical grade products, which were dried with anhydrous potassium carbonate. Tetrabutylammonium tetrafluoroborate was prepared by neutralizing the commercially available tetrabutylammonium hydroxide with tetrafluoroboric acid and recrystallizing the product from methanol.

The linear sweep experiments were performed with a Chemical Electronics potentiostat and sweep generator using a *x/y*-recorder for registering the voltammograms. A three-compartment glass cell equipped with an adjustable Luggin capillary was used in the experiments. The working electrode was made from 0.5 mm platinum wire, a platinum disc served as the counter electrode and the reference electrode consisted of a silver wire dipping into a solution containing 0.01 M silver perchlorate.

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Received October 5, 1971.

## On the Crystal Structure of a Complex between Potassium *p*-Toluenesulfonate and 1,4,7,10,13,16-Hexaoxa-cyclooctadecane

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The conformation of cyclic oligo-ethers related to ethylene oxide has recently been studied by Dale and Kristiansen by infrared spectroscopy.<sup>1</sup> It is concluded that the 18-ring hexa-ether adopts a  $D_{3d}$  conformation when complexing alkali cations, but an entirely different one when crystallizing alone. To obtain more detailed information about the conformation of the complex, an X-ray analysis has been carried out on the complex between potassium tosylate and 1,4,7,10,13,16-hexaoxacyclooctadecane.

The crystals are orthorhombic ( $a=8.17$ ,  $\text{\AA}$ ,  $b=11.73$ ,  $\text{\AA}$ ,  $c=24.19$ ,  $\text{\AA}$ ) with space group  $P2_12_12_1$  and four formula units in the cell ( $\rho_{\text{calc}}=1.34$  g  $\text{cm}^{-3}$ ,  $\rho_{\text{obs}}=1.35$  g  $\text{cm}^{-3}$ ). About 3000 reflections were registered on an automatic four-circle diffractometer with a highly orientated graphite crystal monochromator and