Influence of Anions on Anodic Oxidation of Hexamethylbenzene

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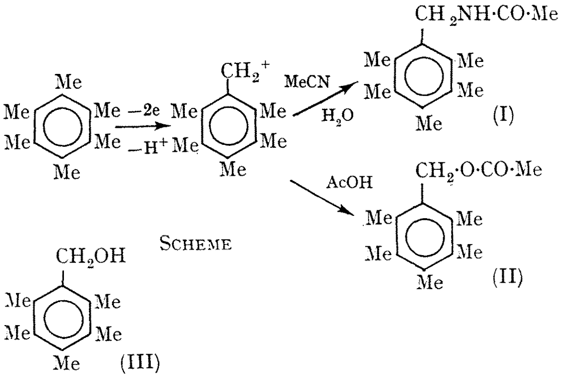
Summary Electroinactive anions of the supporting electrolyte have a large effect on the product distribution observed during anodic oxidation of hexamethylbenzene in mixtures of acetonitrile and acetic acid.

ANODIC oxidation of hexamethylbenzene (HMB) in acetonitrile–sodium perchlorate and acetic acid–sodium acetate gives pentamethylbenzylacetamide (I)[1,2] and pentamethylbenzyl acetate (II),[3] respectively, (I) and (II) being formed *via* the pentamethylbenzyl cation (see Scheme).

Eberson and Olafsson, in studying the mechanism of anodic acetamidation, found that the presence of water did not decrease the yield of the acetamide appreciably.[2] On anodic oxidation of HMB in acetonitrile–water (molar ratio 9 : 1) with sodium perchlorate as supporting electrolyte the ratio of (I) to pentamethylbenzyl alcohol (III) was 95 : 5. This result is surprising. Since water is a stronger nucleophile than acetonitrile one would expect the pentamethylbenzyl cation to react faster with water than with acetonitrile.



SCHEME

The use of tetrabutylammonium tetrafluoroborate rather than sodium perchlorate, with otherwise the same conditions, causes a change in the ratio of (I) to (III) from 95 : 5 to 5 : 95.

In order to study this effect further, HMB was oxidized in mixtures of acetonitrile and acetic acid. The oxidations were carried out at an anode potential of 1·05 v. (*vs.* Ag/0·1M Ag^+) between two Pt electrodes at 30°. The reactions were discontinued when 10% of the amount of charge calculated for a 2*e* process had passed. (I) and (II) were then analysed by g.l.c. The results are given in the Table.

Anodic oxidation of HMB (0·005 *mole*)

Supporting electrolyte		Molar ratio MeCN/AcOH[a]	Molar ratio (I) : (II)
$NaClO_4$ (0·025 mole)	..	50 : 50	53 : 47
,, ,,	..	95 : 5	76 : 24
,, ,,	..	99 : 1	84 : 16
Bu_4NClO_4 (0·01 mole)	..	,,	78 : 22
Bu_4NBF_4 (0·01 mole)	..	,,	19 : 81

[a] Total amount equal to 1·00 mole.

Equal amounts of acetonitrile and acetic acid give roughly the same amounts of (I) and (II). Intuitively, one would expect that on decreasing the amount of acetic acid a corresponding increase would be observed in the ratio of (I) to (II). However, this relationship is not observed. Even with 1% acetic acid, as much as 16% of (II) is formed. When tetrabutylammonium perchlorate is substituted for sodium perchlorate there is only a small change in the ratio. However, a drastic change occurs when tetrabutylammonium tetrafluoroborate is used as supporting electrolyte. Now (II) is the major product.

It has been shown[4] that the tetrafluoroborate anion is not oxidized until about 2·9 v. In this case the reactions were carried out at an anode potential of 1·05 v and discharge of the tetrafluoroborate anion was therefore avoided. Thus, the supporting electrolyte is not involved in the primary electrode process. The formation of the pentamethylbenzyl cation is therefore the primary step. The second step is the reaction of the cation with the nucleophile in the vicinity of the anode surface. Since tetrafluoroborate shows a preference for the formation of (II) over (I) compared with perchlorate, acetic acid is probably kept close to the anode surface by preferential solvation of the tetrafluoroborate anion. Thus, there will be a higher concentration of acetic acid in the vicinity of the anode than in the bulk of the solution.

In cathodic reduction it has been shown that the formation of adiponitrile as compared with propionitrile from acrylonitrile is strongly dependent on the cation of the supporting electrolyte.[5] In that case tetra-alkyl-ammonium salts give much higher yields of adiponitrile than alkali-metal salts. This has also been interpreted in terms of a solvation phenomenon.

I gratefully acknowledge valuable discussions with Dr. Lennart Eberson, University of Lund. This work was supported by a grant from the Swedish Natural Science Research Council.

(*Received, April* 28*th*, 1969; *Com.* 571.

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