The Anodic Oxidation of Anthracene in the Presence of Ethanol in Acetonitrile

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Summary The anodic oxidation of anthracene in acetonitrile containing ethanol produces bianthrone as the primary product and is accompanied by the consumption of 3·0 Faradays per mole of substrate.

A RECENT investigation led to the conclusion that 9-anthrone (which is further oxidized to bianthrone during work-up) is the primary anodic oxidation product of anthracene in acetonitrile containing ethanol.[1] Precise coulometry was reported ($n = 2{\cdot}05 \pm 0{\cdot}06$ electrons) in support of this conclusion and the gas chromatographic detection of large amounts of 9-anthrone in the electrolytic solutions was cited in further support. Furthermore, the authors claim that 9-anthrone is converted into bianthrone when subjected to their workup conditions. The anodic oxidation of anthracene derivatives is of fundamental importance to the understanding of anodic oxidation mechanisms of aromatic hydrocarbons[2] and the report revealing the conversion of anthracene into 9-anthrone has been widely cited.[1]

We have re-investigated the controlled-potential oxidation of anthracene in acetonitrile containing ethanol and report that: (a) coulometry indicates that 3·0 Faradays per mole of anthracene are consumed; (b) bianthrone is the only product that can be detected; and (c) 9-anthrone *is not* converted into bianthrone when subjected to the electrolysis and work-up conditions.

The coulometric procedure was the same as in previous communications.[3,4] Acetonitrile was purified by two distillations from phosphorus pentoxide and had a water content of about 4—10 mM. The water content is not believed to be critical since bianthrone was reported to be the final product either in the presence of water or ethanol.[1] The results were independent of whether the coulometry was conducted in an open vessel or under an atmosphere of argon.

The coulometric procedure was calibrated using the pyridination of anthracene, a well established two-electron oxidation,[5,6] as the standard reaction (Table).

The standardization runs, 1—6, show that $2{\cdot}03 \pm 0{\cdot}05$ Faradays per mole of substrate were consumed during the standard two electron oxidation. An n-value of $3{\cdot}02 \pm 0{\cdot}08$ was observed for the oxidation of anthracene in the presence of ethanol.

Bianthrone was shown to be the primary oxidation product in the following manner: A suspension of anthracene in acetonitrile–acetic acid containing lithium perchlorate

Coulometry for the anodic oxidation of anthracene

Run	Anode potential*	Nucleophile	Nucleophile Concn.	n
1	+1·20	Pyridine	10 mM	2·07
2	+1·20	,,	,,	2·10
3	+1·20	,,	,,	1·97
4	+1·20	,,	,,	2·00
5	+1·20	,,	,,	1·97
6	+1·20	,,	,,	2·05
7	+1·20	Ethanol	20 mM	3·00
8	+1·20	,,	40 mM	3·15
9	+1·20	,,	200 mM	2·90

* Volts *versus* SCE: for comparison with the Ag/Ag$^+$ electrode, subtract about 0·3 v.

was exhaustively oxidized to yield a suspension of another solid. The solid was filtered and without any work-up procedure was shown to be identical to authentic bianthrone. 9-Anthrone could not be detected by i.r. or n.m.r. spectrometry.†

9-Anthrone was also subjected to the work-up procedure of ref. 1. 9-Anthrone was recovered unchanged. Furthermore, passing oxygen through a solution of 9-anthrone in acetonitrile for 0·5 hr (considerably longer than is required for the work-up) brought about a negligible if any conversion into bianthrone.

We therefore conclude that the results of the previous investigation are in error.[1]

I thank the Swedish Natural Science Research Council for support and Dr. Lennart Eberson for helpful discussions.

(*Received, June 26th* 1969; *Com.* 923.)

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† Similar results were obtained when the solvent was acetonitrile containing ethanol.

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