Evidence for Formation of 9-Anthrone and Bianthron-9-ylidene in the Controlled-potential Electrochemical Oxidation of Anthracene in Acetonitrile

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Summary Formation of 9-anthrone and small amounts of bianthron-9-ylidene in the controlled potential oxidation of anthracene in acetonitrile and the air oxidation of 9-anthrone are indicated by g.l.c. and by fluorescence data.

IN a recent communication[1] it was concluded that the results of an earlier report from our laboratories[2] that cited formation of 9-anthrone as the major primary product of the controlled-potential electrochemical oxidation of anthracene in rather dry acetonitrile solution at *ca.* + 1·0 v (*vs.* Ag^+/Ag) were in error. However, these experiments were performed under conditions that differed from ours in that a different supporting electrolyte was used, detection of 9-anthrone by g.l.c. was not attempted, and the electrolysis cell was not described. Some of the discrepancies may be due to the differences in experimental conditions. We now report additional detail and data in support of the reaction sequence previously suggested that involves 9-anthrone as the primary electrolysis product under the conditions we used.

Acetonitrile solutions 5·0 mM in anthracene, 0·5 M in $NaClO_4$, and 0·45 M in EtOH (initially 9 mM in water) were analysed by g.l.c. for anthracene, 9-anthrone, bianthron-9-yl, and anthraquinone.[2] These compounds have sufficiently high vapour pressure for g.l.c. detection although the high column temperatures required made detection of bianthron-9-yl and anthraquinone less than optimum. 9-Anthrone, however, was easily detected by this method.

Evidence for the presence of 9-anthrone in acetonitrile solution is also conveniently obtained by measuring the intensity of the blue fluorescence (450 nm) of its enol form, 9-anthranol, excited by 365 nm radiation (a Farrand model 104 242 spectrofluorometer with a mercury arc line source was used).

A solution of anthracene electrolysed at +1·0 v showed no 9-anthrone, bianthron-9-yl, or anthraquinone before the electrolysis was started. Near the end of the electrolysis large amounts of 9-anthrone (several mM) were detected. There was no g.l.c. indication of bianthron-9-yl during or at the end of the electrolysis. However, there was indication of small amounts of anthraquinone at the end of the electrolysis. The electrolysis solution was then carried through our usual procedure for isolating the electrolysis products.[2] Infrared spectra of the crude CCl_4 extract indicated the presence of anthraquinone and bianthron-9-yl in large quantities and possibly also traces of 9-anthrone.

Loosely-stoppered solutions of 9-anthrone in acetonitrile show approximately constant luminescence intensity at 450 nm for at least 2 days. However, if these solutions remain exposed to air, the intensity of the blue luminescence decreases gradually and has disappeared after *ca.* 4 hours. These observations are unaffected by adding sodium perchlorate to the test solutions. Furthermore, when acetonitrile solutions of 9-anthrone were carried through the work-up procedure[2] (the CCl_4 was allowed to stand for *ca.* 1 hr.), there was no fluorescence observed upon irradiation (365 nm) of the acetonitrile solution obtained by dissolving the residue after removing (Roto-vap) the CCl_4. Thus, 9-anthrone is converted in this work-up procedure to another, non-fluorescent, compound.

9-Anthrone (1 mM to 5 mM) in acetonitrile (0·5M in sodium perchlorate) was electrolysed at +1·0 v.; currents at background (residual) levels only were observed. Large quantities of 9-anthrone (several mM) were detected by g.l.c. during and at the end of the attempted electrolysis; no bianthron-9-yl was detected, although there were indications of small amounts of anthraquinone. When these solutions of 9-anthrone were carried through the usual procedure for isolating the electrolysis products, bianthron-9-yl and anthraquinone as well as variable amounts of 9-anthrone were again found by g.l.c.; characteristic i.r. peaks for 9-anthrone, bianthron-9-yl, and anthraquinone were also evident.

Two other reports have also indicated that 9-anthrones are formed in the electrochemical oxidation of anthracenes. Aikens *et al.* studied the cyclic voltammetry and the controlled potential oxidation of 1,5-dichloroanthracene.[3] They presented evidence for the formation of 1,5-dichloro-10-acetamido-9(10*H*)-anthracenone.

Bard[4] described the electrogenerated chemiluminescence of anthracene in dimethylformamide solution; it was characterized by emission of anthracene fluorescence along with two other bands at lower energies: 460 and 565 nm. The 460 nm band was attributed to the enol form, 9-anthranol; the origin of the 565 nm band was not given.

A very strong fluorescence emission band (480 nm excitation) with peaks at *ca.* 530 nm to 555 nm was also observed in our electrolysed anthracene solutions. This fluorescence was not present before or in samples taken during the early stages of the anthracene electrolysis. Comparison with authentic samples showed this fluorescence was due to very small amounts of bianthron-9-ylidene (9-anthrone, bianthron-9-yl, anthraquinone do not emit near 540 nm) which strongly suggests that the emission at 565 nm reported by Bard was also due to bianthron-9-ylidene.

Finally it should be recalled that our original report[5] also described the isolation of bianthron-9-yl as the apparent primary product from the controlled potential oxidation of acetonitrile solutions of anthracene in the presence of ethanol and of sodium and silver perchlorate salts. Experimental arrangements and techniques used in that work were slightly different from those in our later work. Moreover, coulometry indicated loss of 3 to 4 electrons per anthracene molecule in electrolyses performed in acetonitrile solutions containing more than *ca.* 70 mM water;[2] the solutions take up moisture from the atmosphere if they are not protected. Identification of 9-anthrone in the electrolysis solution resulted when g.l.c., as well as low anode potentials, and relatively anhydrous electrolysis solutions in cells with fairly tight-fitting covers were used. It seems very likely, therefore, that at least some of the difference between our observations and those recently reported[1] could be due to the different experimental conditions.

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