Anode Potential Controlled Mechanism of Oxidation of 9,10-Dimethylanthracene

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Summary Anodic acetoxylation of 9,10-dimethylanthracene produces a dimeric acetate derived from the cation-radical when conducted at $+1\cdot1$ v or the 9,10-diacetate derived from the dication at $+1\cdot8$ v.

IT has recently been shown that anodic substitution or addition reactions in which a nucleophilic moiety is incorporated into an aromatic hydrocarbon frequently occurs by an ECE mechanism involving interaction of a nucleophile with an anodically generated cation-radical.[1] I now present unequivocal evidence for another mechanism of anodic substitution or addition, that is, an EEC process:

Electron transfer: oxidation of hydrocarbon to cation-radical

Electron transfer: oxidation of cation-radical to dication

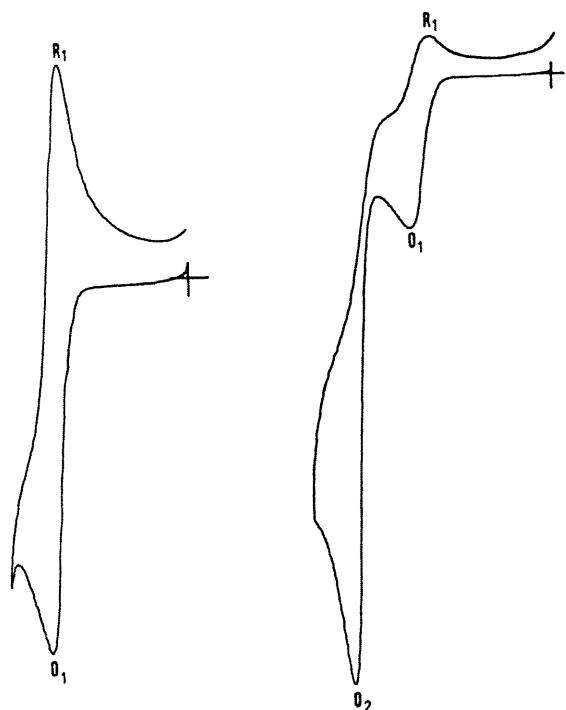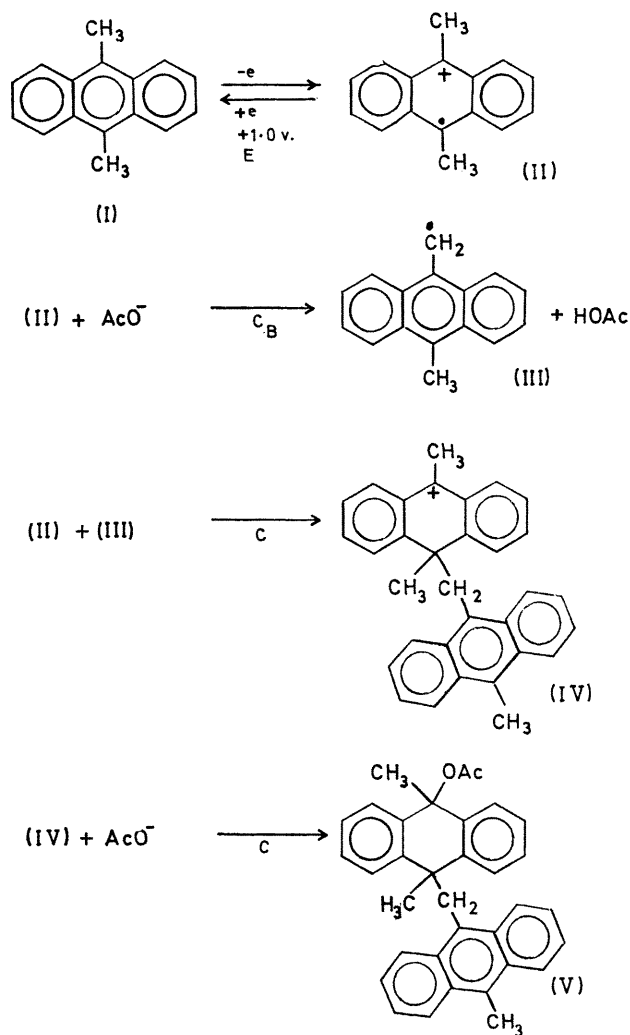*Chemical attack*: on dication by un-oxidized nucleophile

(0·1 M) is illustrated in the Figure. On the anodic going sweep, a one-electron oxidation peak† (O_1) is observed at $+1\cdot0$ v. If the direction of the voltage sweep is changed after O_1, a cathodic peak, R_1, is observed at $+0\cdot92$ v (Figure, a) corresponding to the reduction of the cation-radical. If the anodic sweep is continued beyond the first peak, a

SCHEME 1

FIGURE. *Cyclic voltammogram of 9,10-dimethylanthracene in acetonitrile containing lithium perchlorate* (0·1M) *at a sweep rate of* 10 v/min. (a) *potential switched after first oxidation peak.* (b) *Potential switched after second oxidation peak.*

The cyclic voltammogram of 9,10-dimethylanthracene (DMA) in acetonitrile containing lithium perchlorate

second oxidation peak, O_2, is observed at $+1\cdot58$ v.‡ Since the cation-radical is stable during the time-scale of cyclic voltammetry,[2] it follows that O_2 involves the oxidation of the cation-radical to the dication.

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† The e.s.r. spectrum of the cation-radical has been observed during anodic oxidation of DMA.[2]   All potentials refer to the saturated calomel electrode.

‡ In the absence of an added nucleophile this peak appears to involve the loss of three electrons.   This was verified by coulometry at $+1\cdot8$ v and a four electron oxidation product, which is believed to be the bisacetamide has been isolated.

The voltammetric arguments are verified by a coulometric study of the anodic acetoxylation of DMA. Anodic oxidation of DMA at $+1\cdot1$ v in acetonitrile–acetic acid $(3:1)$ containing sodium acetate $(0\cdot25$ M$)$ and lithium perchlorate $(0\cdot1$ M$)$ resulted in the consumption of $1\cdot2$ Faradays per mole of substrate. Coulometry of DMA in the same media at $+1\cdot8$ v was accompanied by the passage of $2\cdot0$ Faradays per mole of DMA.

TABLE

Dependence of ΔE *on structure for* 9,10-*disubstituted anthracenes*

Compound	ΔE (mv)[a]
9,10-Dimethylanthracene ..	580
9,10-Dichloroanthracene ..	390
9,10-Diphenylanthracene ..	370
9,10-Di-p-anisylanthracene ..	160

[a] Measured at a voltage sweep rate of 10 v/min. in acetonitrile containing lithium perchlorate $(0\cdot1$M$)$.

Exhaustive preparative electrolysis of DMA in the media mentioned above was conducted at $+1\cdot1$ v and $+1\cdot8$ v and the products were isolated and identified by i.r., n.m.r., and mass spectrometry. In both cases the reactions take place with high yield of a single major product. Structure (V) (Scheme 1) was assigned to the low potential oxidation product and structure (VII) (Scheme 2) to the product obtained at $+1\cdot8$ v.

We have recently shown that the anodic oxidation of DMA in the presence of pyridine nucleophiles is followed by attack on a methyl proton.[3] We designate this reaction as EC_B to distinguish from the case where the nucleophile reacts at a carbon centre. This mechanism is followed during the anodic oxidation of DMA in the presence of acetate ion at $+1\cdot1$ v (Scheme 1).

However, when the reaction is conducted at anode potentials greater than O_2 (Figure, b), the initially formed cation-radical is further oxidized before interaction with a nucleophile can occur. The dication (VI) then reacts with acetate ion to form the diacetate (VII) (Scheme 2).

We believe that this is the first unequivocal evidence for anodic addition to an aromatic hydrocarbon involving the dication. It has been shown that 9,10-diphenylanthracene is hydroxylated at potentials where the dication is formed,[4] but since the cation-radical gives the same product, the mechanism is open to question. Anodic addition to aryl-olefins, on the other hand, have been shown to involve reactions of the dications.[5,6]

The oxidation of DMA is unambiguous since ΔE is large§ (*ca.* 600 mv). Depending on the relative energies of

the two species (cation-radical and dication), the value of ΔE can conceivably vary over a wide range and be very small in some cases.¶ The degree of reaction involving the cation-radical and dication is thus highly dependent on the magnitude of ΔE. Although very important in anodic substitution and addition reactions, the ECE mechanism[1] must not be considered the exclusive reaction pathway and the mechanism for a given reaction must not be considered to occur by this mechanism until our ability to predict the value of ΔE becomes much better than the present state of knowledge allows or until experimental evidence for the particular reaction is available.
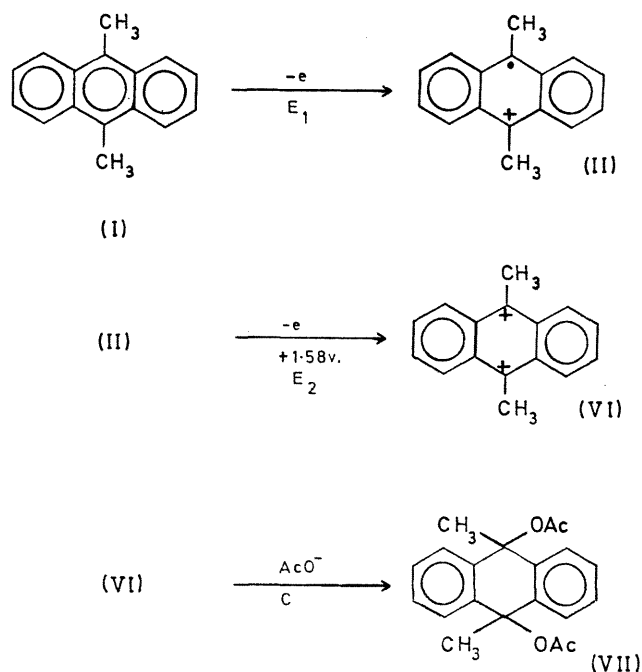
SCHEME 2

§ The potential difference for oxidation to the cation-radical and the dication.
¶ As is the case with the arylolefins.[5-7] The Table illustrates the dependence of ΔE on structure for a series of 9,10-disubstituted anthracenes.

[1] G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, in the press.
[2] L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *J. Amer. Chem. Soc.*, 1967, **89**, 5766.
[3] V. D. Parker and L. Eberson, *Tetrahedron Letters*, in the press.
[4] R. E. Sioda, *J. Phys. Chem.*, 1968, **72**, 2322.
[5] V. D. Parker and L. Eberson, *Chem. Comm.*, 1969, 340.
[6] V. D. Parker and L. Eberson, *Chem. Comm.*, 1969, 451.
[7] V. D. Parker, K. Nyberg, and L. Eberson, *J. Electroanalyt. Chem. Interfacial Electrochem.*, in the press.