

ANODIC OXIDATION OF 2,4,6-TRI-TERT-BUTYLPHENOL

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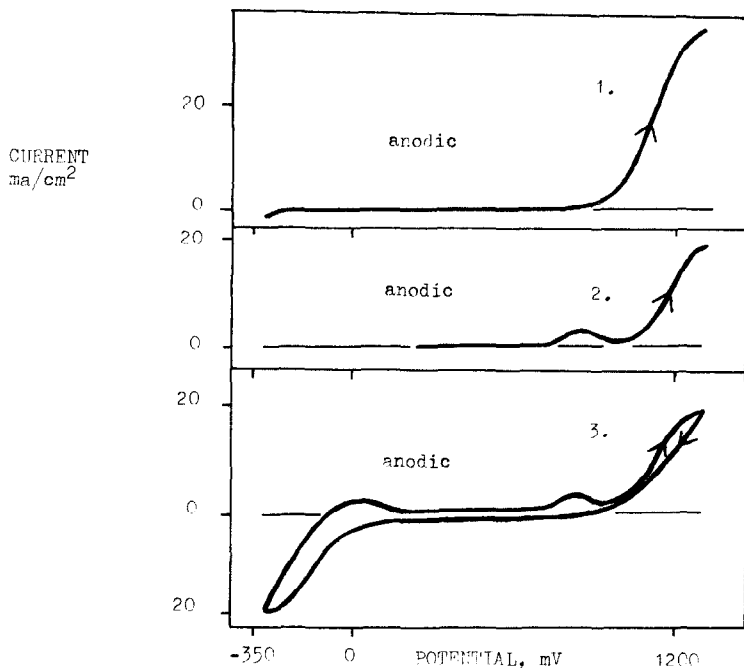
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The anodic oxidation of 2,6-di-tert-butyl-4-methylphenol has been reported (1); the main products were dimeric and a methylene quinone intermediate was proposed. Similar oxidation of 2,4,6-triphenylphenol in acetic acid solution was reported (2) to produce ortho and para quinol-acetates, while in basic solution phenoxy radical dimers were obtained. This report concerns 2,4,6-tri-tert-butylphenol, (I), which cannot form a methylene quinone and was expected to yield simple products.

Fast-response potentiostats were used in all electrochemical experiments including cyclic sweep measurements and voltammetry at rotating disc electrodes of both platinum and vitreous carbon. Preparative scale and coulometric electrolyses were conducted using platinum electrodes in glass cells divided by fine porosity glass frits. Products were analysed using g.l.c. equipment including a Pye 105 chromatograph for macro scale separations.

Oxidation of I at a vitreous carbon electrode in acetonitrile, containing 10% water and 0.1M tetraethylammonium hydroxide support electrolyte, was a reversible 1 electron transfer yielding the blue radical II. Voltammetric measurements indicated a Tafel slope of  $60 \pm 5$  mV/decade. Exhaustive electrolyses showed  $1.08 \pm 0.1$  electrons transferred per molecule oxidized, and the product after reaction with oxygen was III, di-1,3,5-tri-tert-butyl-4-oxocyclohexa-2,5-dienyl peroxide, m.p.  $144-145^\circ$ , reported  $147-148^\circ$  (3). The i.r. spectrum agreed with that published (3). In an ethanolic solution containing acetate buffer, a Tafel slope of approximately 300 mV/decade was observed for oxidation of I. Again the deep blue colour of II was generated and exhaustive electrolysis indicated  $n = 1.20 \pm 0.1$ . Some details of the electrolytic behaviour of II have

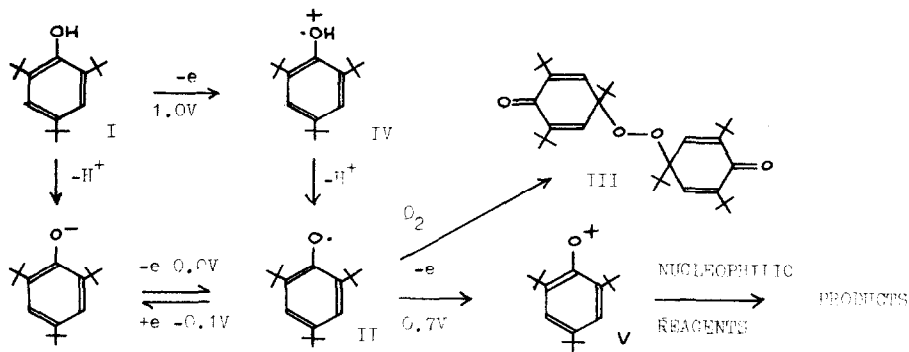
FIG. 1. POTENTIAL SWEEP MEASUREMENTS FOR ACETONITRILE CONTAINING 20mM OF 2,4,6-TRI-TERT-BUTYLPHENOL



1. First anodic sweep, -350 to +1300 mV at 300 mV/sec
2. Anodic sweep, at 300 mV/sec, +200 to +1300 mV after 10 cycles
3. Cyclic sweep at 300 mV/sec, -350 to +1300 mV, after 10 cycles.

FIG. 2

PROPOSED REACTION SCHEME



already been reported (2,4). It was not possible to attempt to oxidize II further because of the anodic limits of basic ethanol and acetonitrile solutions.

In unbuffered acetonitrile solution, with 0.5M sodium perchlorate support electrolyte, the primary process was irreversible, and occurred at a much higher anodic potential. The Tafel slope for platinum and vitreous carbon electrodes was  $116 \pm 10$  mV/decade and the reaction order  $0.9 \pm 0.1$ . Cyclic sweep measurements showed that a second anodic wave at lower potential was established after several cycles, illustrated in fig. 1. This behaviour suggested an ECE mechanism.

If the cyclic sweep range was extended from -350 mV to +1300 mV, (all potentials with respect to Ag/0.01M AgClO<sub>4</sub> in acetonitrile with 0.5M NaClO<sub>4</sub>), two waves were seen at lower potentials, probably due to the phenolate/phenoxy radical couple. The anodic section was less prominent since phenolate ions could react with protons generated in the chemical step C of the proposed ECE oxidation mechanism. The proposed reaction scheme is shown in fig. 2.

It has been recognized for some time (1,2) that the oxidation of phenols in alkaline solutions is a 1 electron transfer and in acidic or unbuffered solutions a 2 electron transfer. In this instance, however, 2 well-defined anodic waves have been observed. A two-stage oxidation mechanism has also been proposed (5) for the oxidation of p-dimethylaminophenol in aqueous solution at pH 8 and pH 9, where 2 anodic waves are observed. The proposed radical cation IV is similar to that indicated by e.s.r. and other methods in the anodic oxidation of substituted anilines (6,7).

Detailed kinetic analysis was not possible because the solutions were not buffered. If exhaustive electrolysis at 1.0 V were interrupted, cyclic sweep measurements showed that the wave at 0.7 V was very large. Exhaustive electrolysis at 1.0 V indicated  $2.3 \pm 0.1$  electrons transferred per molecule oxidized. In the presence of approximately 1M water, however, the anodic wave at 0.7 V was not observed, as if proton transfer was much faster, and exhaustive electrolysis showed  $4.2 \pm 0.2$  electrons transferred per molecule oxidized.

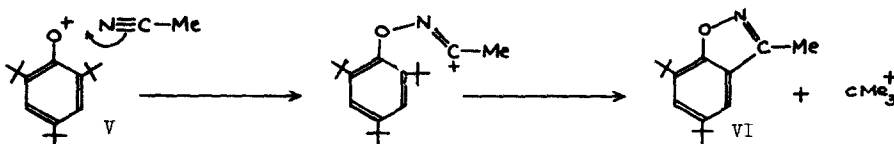
#### Products of electrolyses in acetonitrile

(i) The main anodic product from electrolysis of I in acetonitrile at 1.0 V consisted of pale yellow platelets, m.p. 55-56°. The molecular weight of the compound was 245, measured by mass spectrometry. Elemental analysis suggested a formula C<sub>16</sub>H<sub>25</sub>NO; (calc; C 78.30, H 9.44, N 5.70, found; C 77.80, H 9.20, N 5.94). The n.m.r. spectrum,  $\tau$  2.6(1H), 2.8(1H), 7.4(3H), 8.5(9H) and 8.6(9H), indicated 2 non-equivalent benzenoid hydrogen atoms, 1 methyl group and 2 non-equivalent tert-butyl groups. The compound was not hydrolysed by sulphuric acid or strong bases. This apparently new

compound was tentatively assigned the structure VI, 3-methyl-5,7-di-tert-butyl-1,2-benzisoxazole.

This compound may have been produced by attack of the nitrile N atom at the oxygen atom of V, followed by cyclization with loss of a tert-butyl cation. This is considered more likely than attack at the ortho or para C atoms of V. The overall yield =  $69 \pm 10\%$ , and the current efficiency  $68\% \pm 10\%$ .

FIG. 3. REACTION OF V WITH ACETONITRILE



(ii) When the electrolysis was conducted in acetonitrile containing approximately 1M water, the product was 2,6-di-tert-butyl-1,4-benzoquinone, m.p.  $66.5-67^{\circ}$ , reported  $68-69^{\circ}$ . The i.r. spectrum agreed with that published (8), as did the elemental analysis, (calc; C 76.32, H 9.17, found; C 76.70, H 9.27). The overall yield =  $85 \pm 10\%$ , and the current efficiency =  $95 \pm 10\%$ .

The high yield of paraquinone suggests direct attack by the oxygen atom of water on the para C atom of V. This leads to an overall 4 electron oxidation; preparation of quinones has already been described for the oxidation of related compounds in the presence of water (1,6).

Further work on phenol oxidations is in progress and will be reported.

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