5. It is proposed that the ratio of pore radius to Debye length be used as a basic parameter for pore classification in electrochemical studies.

LITERATURE CITED


ELECTROCHEMICAL REDUCTION OF CYCLOHEXADIENONES (QUINOLIDE COMPOUNDS)

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Earlier polarographic studies have shown that the reactions of quinobromides with amines and Grignard reagents give rise to the formation of radical anions [1]. We have continued this work, studying the polarographic behavior of p-quinolide compounds with geminal substituents and identifying the products resulting from their electrochemical reduction. Polarograms were obtained in DMFA solution (revers. cal. elec.), using 0.1 M tetrabutylammonium (TBA) perchlorate as supporting electrolyte. The number of electrons involved in the reduction reaction was determined coulometrically through exhaustive electrolysis.

Study was first made of the polarographic reduction of the quinolides (I)-(IV) (Table 1), one of the geminal substituents of each of these compounds being a tert-butyl group capable of conversion to the stable 2,4,6-tri-tert-butylphenoxyl which undergoes reversible polarographic reduction at $E_{1/2} = -0.38$ V (acetonitrile) [2]. In fact, the polarogram of 2,4,6-tri-tert-butyl-4-bromocyclohexadien-2,5-one (I) shows two reversible waves, the first, at $E_{1/2} = -0.19$ V, resulting from the reduction of the quinobromide (I) to a radical anion which, in turn, breaks down into a bromide ion and 2,4,6-tri-tert-butylphenoxyl, according to ESR data (triplet, $a_H = 1.8$ Oe).

Polarography of the individual "blue aroxyl" under similar conditions showed the second wave at $E_{1/2} = -0.25$ V to have arisen from reduction of the 2,4,6-tri-tert-butylphenoxyl. Polarographic reduction of 2,4,6-tri-tert-butyl-4-chlorocyclohexadien-2,5-one (II) gave rise to a single pseudo-reversible wave (Kalousek commutator, $f = 12.5$ Hz) the wave height being that corresponding to a two-electron process. Two-electron electrochemical reduction leads to the formation of 2,4,6-tri-tert-butylphenol (Table 2). This same alkylyphenol appears as the sole product from the preparative electrolysis of 4-nitro- (III) and 4-methoxy-2,4,6-tri-tert-butylcyclohexadien-2,5-one (IV). Coulometric data indicate that each of these two-electron electrochemical
TABLE 1. Half-wave Potentials, Saturation Currents, and Number of Electrons* for the Polarographic Reduction of Quinolide Compounds (DMFA with 0.1 M TBA perchlorate as supporting electrolyte, 25°C, C = 5 • 10⁻⁴ mole/liter)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>R'</th>
<th>$-E_{1/2}$ V (s.c.e)</th>
<th>$I_{0}$ μA</th>
<th>$-E_{1/2}$ V (s.c.e)</th>
<th>$I_{0}$ μA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>C(CH₃)₃</td>
<td>Br</td>
<td>0.19</td>
<td>1.3</td>
<td>0.25</td>
<td>1.3</td>
</tr>
<tr>
<td>(II)</td>
<td>C(CH₃)₃</td>
<td>Cl</td>
<td>0.22</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(III)</td>
<td>C(CH₃)₃</td>
<td>NO₂</td>
<td>1.25</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(IV)</td>
<td>C(CH₃)₃</td>
<td>OCH₃</td>
<td>1.71</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(V)</td>
<td>C(CH₃)₃</td>
<td>OH</td>
<td>1.77</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(VI)</td>
<td>C(CH₃)₃</td>
<td>CH₃</td>
<td>2.07</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(VII)</td>
<td>CH₃</td>
<td>Br</td>
<td>0.17</td>
<td>1.6</td>
<td>1.20</td>
<td>0.8</td>
</tr>
<tr>
<td>(VIII)</td>
<td>CH₃</td>
<td>NO₂</td>
<td>1.19</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(IX)</td>
<td>CH₃</td>
<td>OCH₃</td>
<td>1.65</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(X)</td>
<td>CH₃</td>
<td>CH₃</td>
<td>2.15</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Calculated from the II'kovich equation.
† Polarogram developed 2 h after preparing the solution.

The electrochemical reduction of 4-methyl-2,4,6-tri-tert-butylcyclohexadien-2,5-one (VI) is a single-electron process leading to the formation of a radical anion (1:2:1 triplet, $\delta_H = 6.9$ Oe) which breaks down into a phenolate ion and an alkyl radical. Thus there is a second path, differing from that considered above, for radical anion decomposition, namely

\[
\begin{align*}
\text{(I) -- (V)} \\
\text{R = Br (I), Cl (II), NO₂ (III), OCH₃ (IV), OH (V);}
\end{align*}
\]

with $X = C(CH₃)_3$, here and in what follows.

The electrochemical reduction of 4-methyl-2,4,6-tri-tert-butylcyclohexadien-2,5-one (VI) is a single-electron process leading to the formation of a radical anion (1:2:1 triplet, $\delta_H = 6.9$ Oe) which breaks down into a phenolate ion and an alkyl radical. Thus there is a second path, differing from that considered above, for radical anion decomposition, namely

\[
\begin{align*}
\text{(VI) -- (VII)} \\
\text{CH₃}
\end{align*}
\]

Interest therefore attaches to data on the electrochemical reduction of 2,4,6-tri-tert-butyl-4-hydroxycyclohexadien-2,5-one (V). Preparative reduction of this compound ($E = 1.85$ V, relative to the saturated calomel electrode) leads to the formation of a mixture containing 32% 2,4,6-tri-tert-butylphenol, 33% 2,4,6-tri-tert-butylcyclohexene-3-one-1,5, and 35% 2,4,6-tri-tert-butylcyclohexanedione-1,5. Although the polarographic wave for the reduction is almost reversible ($n = 1$), the form of the anodic-cathodic wave was found to vary with the frequency of operation of the Kalousek commutator. While a smooth, reversible wave was obtained at