feel, however, on the basis of our results, that the large difference in the coupling constants for the phenyl-
glyoxal semidione radical in DMF solution as compared with
DMSO solution is not simply due to a normal sol-
vent effect but to the presence of a large excess of the
trans form in the first solvent and of the cis form in
DMSO containing alkali metal ions.

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Theoretical Chemistry) for financial support, and
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maintenance grant.

(7) Now on leave at the Department of Chemistry, Illinois Institute
of Technology, Chicago, Ill.

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The Electrochemical Oxidation of Aromatic
Hydrocarbons in Methylene Chloride

Sir:

The electrochemical reduction and oxidation of aro-
matic hydrocarbons in nonaqueous solutions have been
reviewed recently. While the electroreductions are
characterized by the formation of stable anion radicals,
much of the past work suggests that the electro-
chemical oxidations occur by the abstraction of two
or more electrons. The successful use of methylene
chloride as a solvent in electron spin resonance (esr)
studies of hydrocarbon oxidation suggested that elec-
trochemistry in this solvent might provide evidence of
the initial formation of cation radicals on electrooxid-
ization. We report here some preliminary cyclic volt-
ammetric and coulometric studies. Recent work by
Poveer and Adams and co-workers has also pro-
ine evidence of an initial one-electron abstraction
during electrochemical oxidations in acetonitrile and
nitrobenzene.

The results of cyclic voltammetric oxidation of 9,10-
diphenylanthracene (DPA), rubrene, 1,3,6,8-tetra-
phenylpyrene (TPP), and tetracene are given in Table
I. The general behavior of DPA, rubrene, and TPP
was similar and was characterized by independence of
anodic peak potential, \( E_{pa} \), with scan rate, \( v \), and equal anodic \( i_{pa} \) and reversal cathodic \( i_{pc} \) peak cur-
rents, an independence of \( i_{pa}/v^{1/2} \) with \( v \), and a separation of \( E_{pa} \) and \( E_{pc} \) of 60–80 mV. These results suggest a
reversible one-electron abstraction from the parent
hydrocarbon to form a cation radical which is stable
during the time necessary for sweep reversal. For
tetracene, however, \( E_{pa} \) and \( i_{pa}/v^{1/2} \) change with scan
rate, and cathodic waves on reversal are either absent
or very small. Results similar to these are obtained
with anthracene. The evidence here indicates a fast
carbon reaction following the electron transfer.

Unequivocal evidence for a one-electron oxidation
was obtained by coulometric oxidations with esr ob-
servation of the resulting solutions. For the oxida-
tion of DPA and rubrene 1 faraday per mole of hydro-
carbon was consumed when oxidation was carried out
at controlled potentials about 0.15 V more positive
than \( E_{pa} \). Examination of the oxidized solution by
cyclic voltammetry showed a cathodic peak at the same
potentials as the cathodic peak obtained on reversal in
the unoxidized solution.

The esr spectra of the oxidized solutions, transferred
to 3-mm Pyrex tubing without exposure to air, were
especially identical with those obtained by chemical
oxidation of the hydrocarbons. The electrogenerated
radicals appeared to be stable for days in the sealed
tubes at liquid-nitrogen temperature. Tetracene and
anthracene when subjected to controlled potential
coulometric oxidation showed a current which decayed
to steady-state values appreciably higher than the back-
ground current; this is further evidence of instability of
these cation radicals.

The results suggest that the behavior of the aromatic
hydrocarbons depends upon whether or not they are
substituted in the positions of high electron density.
Cation radicals of substituted hydrocarbons (DPA,
rubrene, TPP) are stable, whereas unsubstituted ones
(anthracene, tetracene) react rapidly. Adams and co-
workers have reached a similar conclusion based on
results obtained in nitrobenzene. The cation radicals

Table I. Cyclic Voltammetric Data for the Oxidation of Several Hydrocarbons in Methylene Chloride

<table>
<thead>
<tr>
<th>Sweep rate, ( \text{mv/sec} )</th>
<th>( i_{pa} ) ( \mu \text{A} ), ( E_{pa} ) ( \text{V} )</th>
<th>( i_{pa}/v^{1/2} ) ( \mu \text{A} ), ( E_{pc} ) ( \text{V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>6.2</td>
<td>4.1</td>
</tr>
<tr>
<td>153</td>
<td>8.8</td>
<td>7.8</td>
</tr>
<tr>
<td>222</td>
<td>11.2</td>
<td>11.3</td>
</tr>
<tr>
<td>312</td>
<td>13.7</td>
<td>13.7</td>
</tr>
<tr>
<td>476</td>
<td>16.9</td>
<td>16.8</td>
</tr>
<tr>
<td>714</td>
<td>20.0</td>
<td>21.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sweep rate, ( \text{mv/sec} )</th>
<th>( i_{pa} ) ( \mu \text{A} ), ( E_{pa} ) ( \text{V} )</th>
<th>( i_{pa}/v^{1/2} ) ( \mu \text{A} ), ( E_{pc} ) ( \text{V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>153</td>
<td>2.2</td>
<td>2.5</td>
</tr>
<tr>
<td>222</td>
<td>2.6</td>
<td>2.8</td>
</tr>
<tr>
<td>312</td>
<td>3.0</td>
<td>3.4</td>
</tr>
</tbody>
</table>

- The solution was 0.2 M tetra-n-butylammonium perchlorate. The electrode was a platinum disk, 0.031 cm\(^2\) (except for TPP, where the area was 0.021 cm\(^2\)).
- Small cathodic current on reversal.

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A Radical-Induced γ Elimination

Sir:

We wish to report the observation of a radical-induced γ elimination from a carbon skeleton. The reaction involves treatment of 1,3-diiodopropane with a peroxide and results in formation of cyclopropane in high yield. The highest conversions to cyclopropane obtained with benzyloxyl peroxide and t-butyl peroxide were 100% and 90%, respectively. Results are summarized in Tables I and II.

Table I. Reaction of 1,3-Diiodopropane with Benzoyl Peroxide

<table>
<thead>
<tr>
<th>Reactants, mmole</th>
<th>79°</th>
<th>98°</th>
<th>116°</th>
<th>116°</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3I CH2CH2I</td>
<td>0.342</td>
<td>0.435</td>
<td>0.361</td>
<td>0.310</td>
</tr>
<tr>
<td>(PhCO)3</td>
<td>0.343</td>
<td>0.365</td>
<td>0.368</td>
<td>0.448</td>
</tr>
<tr>
<td>Products, mmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>0.32</td>
<td>0.36</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>CH3CH2CH2I</td>
<td>0.003</td>
<td>0.003</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>PhCH3CH2CH2I</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>Trace</td>
</tr>
<tr>
<td>CH3CH2CH2I</td>
<td>0.12</td>
<td>0.08</td>
<td>0.07</td>
<td>....</td>
</tr>
<tr>
<td>PhI</td>
<td>0.68</td>
<td>0.74</td>
<td>0.62</td>
<td>0.62</td>
</tr>
</tbody>
</table>

a No significance should be attached to the reaction time with the exception that it is long enough so that no detectable reaction occurred on further heating. In benzene as solvent. No reaction occurred in the absence of peroxide. Yields were estimated by use of nmr spectroscopy and gas chromatographic analysis. In addition, we observed a very small amount of a material which had the same retention time as 3-iodopropyl benzoate.

Although the mechanism of the reaction has not been established, the possibilities which one may envision are all such that our observation is likely to provide the opportunity to study one or more previously unreported free-radical processes such as carbon radical

(1) For the synthesis of cyclohexyl radical and its decomposition to iodine and norcarane is involved in the photolytic reaction of methylene iodide and cyclohexene, Simmons has reported some unsuccessful attempts to observe such a displacement. (2) D. C. Blomstrom, K. Herbig, and H. E. Simmons, J. Org. Chem., 30, 959 (1965).
(3) S. W. Benson, J. Chem. Phys., 34, 521 (1961). It was assumed that D(CH2CH2CH2I = D(CH2CH2CH2I), i.e., that the γ-iodopropyl radical is not appreciably stabilized by iodine bridging. (4) We have also found that cyclopentane can be produced by reaction of 1,3-diodopentane with a peroxide and that 1,1-diphenyleicyclopentane is produced when methylene iodide, 1,1-diphenylethylene, and a peroxide are allowed to react. Details will be reported later.

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Received January 11, 1967

Stereospecific Conversion of cis-trans Isomeric Aziridines to Open-Chain Azomethine Ylides

Sir:

Woodward and Hoffmann predicted for the thermal isomerization of cyclopropyl anion to allyl anion a conrotatory ring opening, while the photochemical ring cleavage should take a disrotatory course. Our results with the isoelectronic aziridine system offer the first verification of this prediction.

We reported recently that dimethyl 1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (I) is in equilibrium above 100° with a small concentration of the azomethine


Communications to the Editor