The Polarographic Reduction of Diazoacetone

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The electrochemical reduction of diazoacetone in 10 % water: ethanol solution, between pH = 3 and pH = 9, has been studied. Two waves have been observed in acid solution: the first is attributed to the reduction of diazoacetone to aminoacetone and the second one to the reduction of 2,5-dimethylidihydropyrazine (formed by dimerization of the aminoacetone) to 2,5-dimethylpiperazine. In neutral and alkaline media the first wave splits into two waves corresponding to a reduction of diazoacetone to hydrazone and aminoacetone.

Introduction

Although the electrochemical behaviour of organic nitrogen compounds has been widely investigated, relatively few studies have been concerned with diazocarbonyl compounds1-3. However, the behaviour of diazoketones towards reducing agents has been studied in detail4-6 and mainly with the aim of obtaining aminoketones, aminoaicohols, hydrazones and ketones.

Following an investigation on the \( \alpha \)-diazoketones of the type \( \text{RCOCR'}N_2 \) (R and R' are H, alkyl, phenyl) by means of various techniques7-12, the present work reports polarographic results obtained for the first member, diazoacetone.

Experimental

Materials

Diazoacetone was prepared and purified by literature methods13. Since it is slightly soluble in water, the polarographic determinations were made in 10% (by vol.) ethanol solutions, maintaining the constant ionic strength of 0.2 by adding NaCl. Britton-Robinson buffers were employed.

Physical Measurements

A Sargent-Welch (model PBx) pH-meter was used for the pH measurements of solutions. Polarographic and coulometric measurements were carried out in an argon atmosphere on an AMEL mod. 462 apparatus with a three-electrode cell arrangement. Measurements were made at 20.0 \( \pm \) 0.2 °C. The dropping mercury electrode had the characteristic constant \( m^{3/2}H^{1/2} = 0.717 \text{ mg}^{3/2}\text{sec}^{1/2} \) for \( h = 55.0 \text{ cm} \), at \( -1.0 \text{ V} \) and with a drop time = 2 sec obtained with a mechanical device. All the reported potential values are referred to the saturated calomel electrode (SCE). Infrared spectra were recorded on a Perkin-Elmer mod. 521 spectrophotometer and UV spectra on an Optica CF4 DR spectrophotometer. Diazoacetone is sufficiently stable in the solvent used. Polarograms and UV spectra (characterized by two absorption bands at 244 (sh) and 275 nm) are practically unchanged even after three hours.

Results

Throughout the pH range examined, diazoacetone shows two irreversible reduction steps. They are generally well developed and show no maxima. In addition, they give limiting currents proportional to the concentration of depolarizer, for the molarity range, \( 2.10^{-4}-8.10^{-3} \text{m} \), investigated. Figs 1-3 and Tables I and II collect data showing the effect of pH on the reduction of diazoacetone. At pH > 5, the

![Fig. 1. Conventional polarograms of 2.0 \( \times \) 10^{-3}M diazoacetone at various pH values.](image-url)
Fig. 2. The pH-dependence of the limiting currents for the reduction waves of diazoacetone.

<table>
<thead>
<tr>
<th>pH</th>
<th>i_r (or i_r + i_r')/μA</th>
<th>i_r'/μA</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>10.93</td>
<td>3.22</td>
</tr>
<tr>
<td>4.2</td>
<td>10.39</td>
<td>3.21</td>
</tr>
<tr>
<td>5.2</td>
<td>9.98</td>
<td>3.20</td>
</tr>
<tr>
<td>6.2</td>
<td>9.39</td>
<td>3.07</td>
</tr>
<tr>
<td>7.2</td>
<td>8.97</td>
<td>3.06</td>
</tr>
<tr>
<td>8.2</td>
<td>8.69</td>
<td>2.94</td>
</tr>
<tr>
<td>9.2</td>
<td>7.90</td>
<td>2.93</td>
</tr>
</tbody>
</table>

Table I. Diffusion current constants for the first and second reduction waves of diazoacetone at different pH values.

Table II. Limiting current values and half-wave potentials for the reduction waves of 2.0 × 10^-3 M diazoacetone at different pH values.

<table>
<thead>
<tr>
<th>pH</th>
<th>i_r</th>
<th>i_r</th>
<th>i_r'</th>
<th>i_r'</th>
<th>(E_{1/2})_r</th>
<th>(E_{1/2})_{r'}</th>
<th>(E_{1/2})_{r''}</th>
<th>(E_{1/2})_{r'''}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>15.7</td>
<td>4.7</td>
<td>0.815</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>14.9</td>
<td>4.6</td>
<td>0.873</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>5.2</td>
<td>9.4</td>
<td>5.2</td>
<td>0.916</td>
<td>1.076</td>
<td>1.453</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>7.2</td>
<td>6.2</td>
<td>0.928</td>
<td>1.082</td>
<td>1.460</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>5.1</td>
<td>7.8</td>
<td>0.938</td>
<td>1.103</td>
<td>1.470</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.2</td>
<td>4.2</td>
<td>8.3</td>
<td>0.940</td>
<td>1.119</td>
<td>1.538</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>9.2</td>
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<td>7.5</td>
<td>0.948</td>
<td>1.144</td>
<td>1.687</td>
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</tr>
</tbody>
</table>

* Ill-defined wave; same experimental conditions as in Table I.
corresponding to the diffusion plateau of the various waves (I, I', I'', II), using a mercury pool electrode of approximate area 10 cm². The reductions were interrupted at intervals of time to allow polarographic and UV checks of the species present. The processes appeared to be independent of both pH and concentration of the solution. The reductions corresponding to the plateau of wave (I) at pH < 5 and of wave (I'') between pH 6 and 9, involve six electrons per diazoacetone molecule. The reduction product was obtained by extraction with ether followed by evaporation under reduced pressure. The UV spectrum in water of the resulting colourless liquid is identical with that of an authentic sample of 2,5-dimethylpyrazine (λ = 277, 295 (shoulder) nm). The reductions at the plateau of wave (I') correspond to an average n of 2 (between 1.7 and 2.5 in the various runs). The reduced solutions were examined spectrophotometrically and polarographically. The UV spectrum showed an absorption band at λ = 282 nm. Polarographically it is observed that, while wave (I') has disappeared, waves (I'') and (II) remain unchanged in both position and height. The product could not be separated. Coulometries on the plateau of wave (II) give n = 8. The final solution is transparent in the UV and gives an IR spectrum absent of significant features.

\[
\text{CH}_2\text{COCH}_2\text{N}_2 + 2e + 2\text{H}^+ \rightarrow \text{CH}_2\text{COCH} = \text{NNH}_2 \\
\text{CH}_2\text{COCH}_2\text{NNH}_2 + 4\text{H}^+ \rightarrow \text{CH}_2\text{COCH}_2\text{NH}_2 + \text{NH}_3
\]

Between pH = 5 and pH = 7 there is a gradual passage from Eqn (1) to (2). A similar mechanism has been proposed for the electrochemical reduction of 3-diazoacamphor.

Wave (II) has been previously explained as due to the reduction of the aminoketone to acetone, by analogy with the electrochemical reduction of diazoacetophenone. Unfortunately, we have been unable to isolate the product obtained by coulometric reduction. However, we can certainly eliminate acetone as the final product. In our opinion the process involved is the reduction of 2,5-dihydrodimethylpyrazine to 2,5-dimethylpiperazine.

\[
\text{C}_6\text{H}_{10}\text{N}_2 + 4e + 4\text{H}^+ \rightarrow \text{C}_6\text{H}_{14}\text{N}_2
\]

The authors wish to thank Dr. L. Sestili (University of Perugia) for the use of the Amel mod. 462 instrument.

4 L. Birkof er, Chem. Ber. 80, 83 [1947].
5 W. Gruuber and H. Renner, Mh. Chem. 81, 751 [1950].

Discussion

The results obtained suggest that under the experimental conditions used, diazoacetone, in buffered solution at pH < 5, is irreversibly reduced to aminoacetone in a single wave involving six electrons:

\[
\text{CH}_2\text{COCH}_2\text{N}_2 + 6e + 6\text{H}^+ \rightarrow \text{CH}_2\text{COCH}_2\text{NH}_2 + \text{NH}_3
\]

This suggestion is fully supported by the fact that the product isolated in coulometry is 2,5-dimethylpyrazine. It is known, in fact, that aminoacetone has a marked tendency to dimerize giving 2,5-dimethylidihydropyrazine, which is rapidly oxidised to 2,5-dimethylpyrazine by air. In addition, the dependence of (E1/2) on pH suggests that the slow reduction step of process (Eqn (1)) characterised by ana = 0.44, is preceded by protonation of diazoacetone. As mentioned above, wave (I) splits into two waves at pH > 5 and in unbuffered solutions. The voltammetric and polarographic data clearly show that these two waves correspond to two successive reduction stages of diazoacetone, and not to the reduction of protonated and non-protonated molecules as was previously proposed. The most probable explanation to account for this is that the first reduction stage corresponds to formation of hydrazone:

\[
\text{CH}_2\text{COCH}_2\text{N}_2 + 4e + 4\text{H}^+ \rightarrow \text{CH}_2\text{COCH}_2\text{NH}_2 + \text{NH}_3
\]