Investigations on Redox Behaviour of Some 3-Benzothiazolyldydra-
zonopentane-2,4-diones at DME

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Received 9 October 1980; revised and accepted 17 January 1981

Polarographic studies of some 3-benzothiazolyldydrazonopentane-2, 4-diones have been carried out in B. R. buffers in the pH range 2.0-12.0 and in 0.1M NaOH. All the compounds give a single, well-defined, irreversible, diffusion-controlled reduction wave whose \( E_{1/2} \) value is pH-dependent but \( I_d \) remains constant throughout the entire pH range. The \( E_{1/2} \) shifts towards negative potentials with increase in pH thereby showing that protonation precedes reduction. A linear correlation is observed between the \( E_{1/2} \) values and the Hammett substituent constants, indicating that substituents appreciably affect the reduction of \(-\text{NH}-\text{N}=\text{C}\) group by polar and mesomeric effects. Moreover, the effect of the double layer structure on the \( E_{1/2} \) has been also studied.

Although the polarographic behaviour of a number of sulphur containing compounds like those containing \(-\text{SH}, -\text{S-S}, \text{R}_2\text{N-C=S}, \text{NH-CS-N}=\text{C}\)

-NH-CS-NH-, -NH-CS-S- and RS\(_2\)H groups\(^1\)\(^-\)\(^4\) has been studied, not much has been done on the polarography of thiiazoles and benzothiazoles\(^5\)\(^-\)\(^7\) which are of great medicinal and biological importance. A knowledge of their redox behaviour at the solution-mercury interface may prove quite useful from physiological point of view. Polarographic studies on the reduction of these compounds at DME were therefore, undertaken. The present paper describes the results of such studies on some recently synthesised hydrazono derivatives of 2-aminobenzothiazoles (I)\(^8\).

Materials and Methods

The hydrazono derivatives of 2-aminobenzothiazoles with substituents in the benzene ring were synthesised by the method reported from this laboratory\(^8\).

Stock solutions of \((1.0 \times 10^{-3} M)\) of the above mentioned compounds were prepared in distilled DMF (AR). Britton-Robinson buffers in the pH range 2.0-12.0 were prepared by adding requisite amounts of 0.2M sodium hydroxide solution in stock B.R. buffer of pH 1.8, composed of boric acid, phosphoric acid and acetic acid. The chemicals used were of A.R. grade.

A cambridge pen recording polarograph was used. The capillary characteristics were: 2.040 mg\(^{2/3}\) sec\(^{-1/2}\) SCE was used as the reference electrode.

For recording polarograms, 2.0 ml of stock solution \((1.0 \times 10^{-3} M)\) of the compound, 1.0 ml of 1M KCl and 7.0 ml of buffer were mixed and a stream of pure hydrogen gas was passed for about 5 min so as to ensure complete de-aeration. The cell was kept in a thermostated water-bath (temp. 25 ± 0.1°C). The number of electrons involved in the reduction process were calculated by the milli-coulometric method\(^8\) using CdSO\(_4\) as a reference solution. The controlled potential electrolysis was carried out at potential corresponding to the plateau (1.6 V) of the wave. The electrolysis cell was H-shaped, the cathodic and anodic compartments being separated by a diaphragm of sintered glass. Mercury was used as the electrode material. After complete electrolysis (≈ 6 hr) the catholyte was analysed for the identification of the end product.

Results and Discussion

The compounds listed in Table 1 gave a single \( 4e \) reduction wave in B.R. buffer of pH range 2.0-12.0 and in 0.1M NaOH. The nature of the wave was found to be diffusion-controlled as shown by the linear dependence of limiting current on \( \sqrt{I} \) and concentration of depolarizer. The constancy of wave height in the pH range studied together with the fact that \( di/dt \) had a very low value of temperature coefficient further confirmed that the reduction waves were fully diffusion-controlled. The wave characteristics are shown in Table 1.

The half-wave potentials of these compounds were found to be dependent on pH and shifted towards more negative potentials with increase in pH. The plots of \( E_{1/2} \) vs pH were linear with slopes in the range 0.084-0.090, V/pH upto pH 8.5 and after that there was only a small change in \( E_{1/2} \), the value of the slope was significantly small. The irreversible nature of the waves was confirmed by log plots. The fact that \( E_{1/2} \) shifted towards more negative potentials with increasing concentration of depolariser further point-
Table 1 — Polarographic Characteristics of 3-Benzothiazolylhydrazono-Pentane-l, 4-Diones at pH 10.4 and Conc. 2.0 x 10⁻⁴ M.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>R in (I)</th>
<th>(-E_{1/2}, ) V</th>
<th>(i_0, ) µA</th>
<th>(dE_1/2/dpH, ) V/µH</th>
<th>(\Delta E_{1/2}, ) V</th>
<th>(\alpha_n)</th>
<th>(p)</th>
<th>(K_r \times 10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1.05</td>
<td>1.42</td>
<td>0.076</td>
<td>0.00</td>
<td>0.61</td>
<td>0.61</td>
<td>1.32</td>
</tr>
<tr>
<td>2</td>
<td>4-CH₃</td>
<td>1.11</td>
<td>1.82</td>
<td>0.071</td>
<td>0.06</td>
<td>0.61</td>
<td>0.59</td>
<td>1.24</td>
</tr>
<tr>
<td>3</td>
<td>5-CH₃</td>
<td>1.04</td>
<td>1.37</td>
<td>0.076</td>
<td>0.01</td>
<td>0.61</td>
<td>0.59</td>
<td>1.32</td>
</tr>
<tr>
<td>4</td>
<td>6-CH₃</td>
<td>1.05</td>
<td>1.20</td>
<td>0.076</td>
<td>0.00</td>
<td>0.61</td>
<td>0.57</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>4-Cl</td>
<td>1.04</td>
<td>1.42</td>
<td>0.071</td>
<td>0.01</td>
<td>0.58</td>
<td>0.59</td>
<td>1.03</td>
</tr>
<tr>
<td>6</td>
<td>5-Cl</td>
<td>1.06</td>
<td>1.10</td>
<td>0.071</td>
<td>0.01</td>
<td>0.60</td>
<td>0.61</td>
<td>1.03</td>
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<tr>
<td>7</td>
<td>6-Cl</td>
<td>1.00</td>
<td>1.20</td>
<td>0.071</td>
<td>0.05</td>
<td>0.61</td>
<td>0.61</td>
<td>1.24</td>
</tr>
<tr>
<td>8</td>
<td>4-OCH₃</td>
<td>1.12</td>
<td>1.37</td>
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<td>0.14</td>
<td>0.59</td>
<td>0.60</td>
<td>1.11</td>
</tr>
<tr>
<td>9</td>
<td>6-OCH₃</td>
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<td>1.15</td>
<td>0.076</td>
<td>0.05</td>
<td>0.69</td>
<td>0.64</td>
<td>1.10</td>
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<td>10</td>
<td>4,6-Cl</td>
<td>1.19</td>
<td>1.82</td>
<td>0.066</td>
<td>0.14</td>
<td>0.59</td>
<td>0.60</td>
<td>1.11</td>
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<tr>
<td>11</td>
<td>4,7-diCl</td>
<td>1.24</td>
<td>1.82</td>
<td>0.071</td>
<td>0.19</td>
<td>0.59</td>
<td>0.59</td>
<td>1.10</td>
</tr>
</tbody>
</table>

†Log plots method¹⁰
‡Oldham and Perry method¹¹.

The values of \(\alpha_n\) (product of transfer coefficient and number of electrons transferred in the rate determining step) and \(p\) (number of protons involved during the rate determining step of the reaction) were determined using the expressions:

\[
E_{1/2} - E_{N/2} = \frac{0.0517}{\alpha_n} \\
\frac{dE_{1/2}}{dpH} = \frac{0.05915}{\alpha_n} \cdot p
\]

The values of \(\alpha_n\) and ratio constant \(K_r\) were also determined by the method of Oldham and Perry¹¹ using the expression,

\[
E_{1/2} = E_r + \frac{0.592}{\alpha_n} \log \left[ 1.35 \frac{K_r}{t} \right]
\]

where \(t\) is the drop time at the potential \(E_r\). The values of half-wave potentials together with \(dE_{1/2}/dpH, \alpha_n, p\) and \(K_r\) are given in Table 1.

Since the half-wave potentials of these thiazoles were pH-dependent and the limiting current pH-independent up to pH 10.4, it was concluded that both acidic and basic forms of the compounds reached the electrode surface and were electroactive. Thus the proton transfer reaction precedes the electrode process in such cases. Out of the two general sequences for the proton and electron addition viz. \(H^+, e, H^+\) and \(H^+, e, e, H^+\). The former sequence is more probable for these compounds in the light of their structural genesis. After the uptake of a proton and one electron the radical (III) would accept a proton to form a protonated radical (IV) which after taking one electron gets cleaved at nitrogen bond with the formation of aniline. The imine (V) formed gets further protonated and reduced.

Alternatively, the radical (III) could also combine with an electron instead of proton but this possibility is ruled out by the fact that such a reduction would involve only 2 electrons whereas polarographic data clearly indicate 4-electron transfer reaction at the dme.

These mechanistic steps find support from the increase in \(E_{1/2}\) with pH as protons are consumed in the reduction. As the rate of protonation becomes slow the \(E_{1/2}\) tends to become constant. Fig. 1 shows that above pH 8.5 (in alkaline region), the shifting of half-wave potential with pH towards negative potentials is not so marked as in the acidic range. Moreover, above pH 8.5, the \(E_{1/2}\) is practically constant. In the pH range studied where both the electroactive form (acidic as well as basic) are reduced half-wave potentials of the two forms are so close that the waves merge and no separation of the two waves can be observed.

Similar steps for the reduction of hydrazono group involving cleavage of the N–N bond have also been proposed by other workers¹²⁻¹⁵. Due to acid base equilibrium that exist between two structural forms of the compounds, height of the wave remains pH-independent as long as the formation of the acidic form from the basic form is fast enough. When pH increases, rate of protonation decreases and the wave height decrease as well.
When depolariser solution was tested after controlled potential electrolysis, it gave dye test thereby showing that at least one of the reduction products is an aromatic amine. UV spectra of the solutions during electrolysis were recorded at different intervals on a UV-VIS spectrophotometer. \( \lambda_{\text{max}} \) (CH\(_3\)OH) at 415 nm due to\(-\text{NH-}N=\text{C}\)-grouping showed a decrease in the peak height after each interval of time and finally it disappeared, confirming the above reduction mechanism.

**Effect of substituents** — The effect of substitution on the ease of reduction was determined quantitatively by applying Hammett equation. Since the values of \( \alpha \)(transfer coefficient) and \( \frac{\Delta E_{1/2}}{\Delta \rho H} \) were the same for all the thiazoles, Hammett equation was applied successfully\(^{16,17}\). When half-wave potentials of these compounds were plotted against Hammett substituent constant \( (\sigma) \), a linear relationship was obtained (Fig. 2). It will be observed that the values for meta and para derivatives fit in the straight line while ortho derivatives, viz. 4-CH\(_3\) and 4-Cl deviate significantly from the linear plot.

From the plot of \( E_{1/2} \) vs \( \sigma \), (Fig. 2), the specific reaction constant \( (\rho) \) was found to be 0.23V. Its positive sign indicated the nucleophilic nature of the electrode process. The observed linear relationship of \( E_{1/2} \) vs \( \sigma \) indicated that the substituents appreciably affected the reduction of hydrazono group by polar and mesomeric effects through the benzene ring.

It has been reported\(^{16}\) that the magnitude of the ortho effect can be obtained by comparing the \( E_{1/2} \) of ortho and para substituted compounds. In the above series of compounds the values of polargraphic ortho shift \( (\Delta \rho) \) are: methyl \((-0.06V)\), chloro \((-0.04V)\) and methyl \((-0.16V)\) The negative ortho shift can be explained on the basis of the bulky nature and possible mesomeric interaction with the aromatic ring. The disubstituted derivatives e.g. 4, 7-DiCl as well as 4,5-(CH\(_3\))\(_2\) did not show additivity of structural effects\(^{16,19}\). This difference of 0.14V and 0.19V in their \( E_{1/2} \) may be due to the bulkiness of these groups.

**Effect of supporting [electrolyte]** — The effect of the double layer structure on the \( E_{1/2} \) of a process preceded by the protonation is given by the equation\(^{20}\)

\[
\Delta E_{1/2} \approx \Delta \Psi_1 \left( \frac{a_{\text{H}^+} - Z}{a_{\text{H}^+}} - \frac{\partial E_{1/2}}{\partial \rho H} \frac{F}{2.30 R T} \right) \quad (1)
\]

where \( \Psi_1 \) is the variation in the double layer potential, \( \alpha \) is the transfer coefficient, \( n_\text{e} \) is the number of electrons transferred in the rate determining step, \( Z \) is the charge of the particle being discharged. Undoubtedly a marked effect of change in ionic strength on \( E_{1/2} \) should be observed in cases where the depolarizer is in the ionic form, no such effect should be observed when it is in the non-ionic form, i.e. when \( Z = 0 \). Since the second term in the bracket of Eq. (1) is nearly \(-1\) and \( Z = 0 \), \( E_{1/2} \) will be almost

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**Fig. 1** — Plots of \( E_{1/2} \) versus \( \rho H \) for some 3-benzothiazolylhydrazonopentane-2,4-diones.

**Fig. 2** — Dependence of \( E_{1/2} \) of 3-benzothiazolylhydrazonopentane-2,4-diones on Hammett substituent constant \( (\sigma) \) in B.R. buffer at \( \rho H \) 10.4.
independent of $\Psi$ or of ionic strength. This was verified by carrying out experiments with varying concentration of KCl (0.01 M to 0.25 M). The values of $dE_{1/2}/dpH$, thus obtained fell in the range 60–70 mV/pH and $E_{1/2}$ and $i_k$ remained unaffected by the change in concentration of the supporting electrolyte.

Effect of solvent composition — The polarograms of the above mentioned thiazoles were recorded in the minimum amount of DMF (20%) necessary for the dissolution of the compound. The DMF percentage was then progressively increased from 20% to 70% to see the effect of solvent composition on the electrode process. $E_{1/2}$ of the compound was found to shift towards more negative potentials with increase in [DMF] in the solvent mixture.

It has been observed\textsuperscript{11} that in cases in which a proton transfer precedes the electrode process, the shift in $E_{1/2}$ towards more negative side caused by the increasing concentration of organic solvents is much more as compared to that caused by the change in the pH of the solution.

In the presently studied thiazoles the $E_{1/2}$ shifts towards more negative potentials almost linearly and this effect is much marked in the compounds having comparatively more positive potentials. This shift may be attributed\textsuperscript{12} to a decrease in the surface concentration of the electroactive species in addition to a change in pH and $pK_a$ of the protonated depolarizer.

References