Hydrazines are useful building blocks for many important drugs, agrochemicals and dyestuffs. Recently, we have described a new methodology for the step-wise synthesis of hydrazine derivatives where a protecting group approach has been used.

We have noticed that the introduction of different substituents is often accompanied by side reactions because it has to be carried out in the presence of oxidants. The best example is the N-arylation of hydrazine derivatives with organobismuth reagents. On the other hand, the purposeful oxidation of 1,2-disubstituted hydrazines yields azo-compounds, which are known as versatile reagents for electrophilic amidation. Therefore, knowledge of the oxidation potentials for these compounds could help to choose the appropriate reagent for the oxidation and also to avoid unwanted side reactions.

The anodic oxidation of substituted hydrazines in aprotic solutions has not been thoroughly studied, but it is known that in acetonitrile hydrazines are oxidised through a two-electron process (via radical cation):\(^\text{3}\)

\[
R^1\cdot\text{NH}\cdot\text{NH}\cdot R^2 \Rightarrow R^1\cdot \text{N}\cdot\text{N}\cdot R^2 + 2\text{H}^+ + 2\text{e}^- \quad (1)
\]

Figure 1 represents the cyclic voltammetric behaviour of several 1,2-disubstituted hydrazines in acetonitrile.

Cyclic voltammograms of all the hydrazine derivatives showed an irreversible response with two anodic peaks. Note that the values of the peak current densities are rather similar. The dependence of the value of peak potentials on the concentration and scan rate was noticed and is quite typical for irreversible electrode processes.

The first oxidation potential (vs SCE) of various substituted hydrazines is listed in Table 1, where the abbreviations used are given.

**Table 1 Oxidation potentials and yields of chemical oxidation for studied hydrazines**

<table>
<thead>
<tr>
<th>Compound</th>
<th>E / V (vs SCE)</th>
<th>Yield/% (chemical oxidant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhNHNHPh</td>
<td>0.68</td>
<td>100 (Br_2)</td>
</tr>
<tr>
<td>PhNHNHAc</td>
<td>0.93</td>
<td>98 (Br_2, mixture with MnO_2)</td>
</tr>
<tr>
<td>BocNHNHBoc</td>
<td>0.97</td>
<td>97 (Br_2)</td>
</tr>
<tr>
<td>PhNHNHBoc</td>
<td>1.02</td>
<td>92 (MnO_2)</td>
</tr>
<tr>
<td>BocNHNHBoc</td>
<td>1.26</td>
<td>100 (Br_2)</td>
</tr>
<tr>
<td>ZHNHNTos</td>
<td>1.69</td>
<td>mixture (MnO_2, Br_2)</td>
</tr>
<tr>
<td>ZHNHNTroc</td>
<td>1.79</td>
<td>mixture (MnO_2, Br_2)</td>
</tr>
<tr>
<td>ZHNHH_2</td>
<td>0.95</td>
<td>-</td>
</tr>
<tr>
<td>BocNHNNH_2</td>
<td>0.95</td>
<td>-</td>
</tr>
<tr>
<td>TrocNHNHH_2</td>
<td>1.10</td>
<td>-</td>
</tr>
</tbody>
</table>

(Troc=trichloroethoxycarbonyl; Boc=tert-butoxycarbonyl; Z=benzyloxycarbonyl; Ph=phenyl; Tos=4-methylphenylsulfonyl; Tol=tolyl; Ac=acetyl).

Controlled potential electrolysis (CPE) is a valuable tool in an attempt to ascertain the products formed at various voltammetric peaks. As an example, we were able to identify the consumption of BocNHNHBoc by holding the electrode at 2 V. The starting compound was converted into the product in a reasonable time-scale.

It was determined by CPE and following structure analysis of products that the first maximum of the cyclic voltammograms corresponds to the formation of aza-compounds. At higher positive potential values all compounds exhibit also the second peak of oxidation (see Fig. 1), except for ZHNHNTroc. The potential cycling over this maximum distinctly decreases the peak current during the next run, which can be explained either by decomposition of hydrazine or by blocking of the electrode surface. The dependence of the value of peak potentials on the concentration and scan rate was noticed and is quite typical for irreversible electrode processes.

Monosubstituted hydrazines, known to be easily chemically oxidised and decomposed, showed relatively low values of the first oxidation potential. However, during the CV studies in the current work, nothing resembling destruction was noticed even while cycling over the second maximum.

It is evident from Table 1 that the donor–acceptor properties of substituents have a strong effect on the value of the oxidation potential of substituted hydrazines. The compounds with at least one phenyl group are easily oxidised at relatively low potential values. Increasing the electron withdrawing effect of the substituent the oxidation potential was substantially increased up to nearly 1.8 V (ZHNHNTroc). Two examples with the highest potential value (ZHNHNTos; ZHNHNTroc) did not yield any aza-compounds by CPE probably due to decomposition. Analogously, their chemical oxidation afforded complex mixtures. The rest of the disubstituted hydrazines purified pure aza-compounds with excellent yields by oxidation with activated MnO_2 or bromine. Despite the relatively high oxidation potential value (1.62 V) for BocNHNHBoc, both electrochemical and chemical oxidation of this compound proceeded smoothly.

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**Keywords:** hydrazines, aza-compounds, controlled potential electrolysis, cyclic voltammetry

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In conclusion we have demonstrated the behaviour of 1,2-di- and monosubstituted hydrazines in the electrochemical cell and under chemical oxidation conditions. The values of oxidation potentials determined are valuable characteristics for the prediction of the properties of new hydrazine compounds.

### Experimental

All solvents were analytical grade. The starting compounds were purchased (ZNHNHTos, PhHNHPh, BocNHNHTroc, activated MnO₂) or synthesised according to published procedures (BocNHNHBoc, p-TolNHNHBoc and o-TolNHNHBoc, TosNHNHZ, ZNHNHTroc, PhHNHPh). A GC plate with large surface area (12 cm²) was used as a working electrode. The reference electrode was a saturated calomel electrode (SCE). The CV curves were recorded at scan rates of 50, 100, 200 and 500 mV/s.

**Controlled potential electrolysis (CPE)**

CPE experiments were performed with five hydrazines: BocNHNHBoc; PhHNHPh; ZNHNHTos; ZNHNHTroc; PhHNHPh. A GC plate of large surface area (12 cm²) was used as a working electrode. The counter electrode (Pt coil) was separated from the working electrode compartment with a sintered glass frit. CPE was conducted by holding the working electrode potential at ca 200 mV more positive than that of the first anodic oxidation maximum. After 1 h of electrode-oxidation the analyte was evaporated and the residue purified by column chromatography on silica. The products were identified by ¹H and ¹³C NMR spectroscopy (see Table 2).

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### References

9 The Aldrich ¹H and ¹³C FT-NMR spectra 1H, 1993.