Supporting Information for

“Non-aqueous electrochemistry of rhodamine B acylhydrazone”

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1 Calibration of the reference electrode

The following procedure was employed for the calibration of the Ag/Ag⁺ reference electrode. A cyclic voltammogram for 0.25 mM solution of ferrocene in the supporting electrolyte (MeCN with 0.1 M LiClO₄) was acquired (Fig. S1). The formal potential of the Fc⁺/Fc couple was taken as the average of the peak potentials of the anodic and cathodic waves¹. Thus, the formal potential of the Fc⁺/Fc couple vs. the reference electrode under study was found to be 86 mV. Using this value, all potential in this work were recalculated from the Ag/Ag⁺ scale to the Fc⁺/Fc scale.

Fig. S1. Cyclic voltammogram for 0.25 mM ferrocene in MeCN with 0.1 M LiClO₄.

2 Cyclic voltammetry

Peak currents in cyclic voltammograms for RBA were assessed as described in the textbook by Bard et al.\textsuperscript{2} The baselines were obtained by extrapolating the first and second anodic waves with $E^{-1/2}$ functions and folding these functions back along the potential axis. The peak currents were calculated against the baselines as shown in Fig. S2. Note that the peak current ratio for the second wave ($|i_{pa2}/i_{pc2}|$) is larger than unity at $v = 1000$ mV/s due to the influence of the other cathodic wave. Thus, the presented peak current values are approximate.

Fig. S2. Cyclic voltammograms for 1 mM RBA in MeCN with 0.1 M LiClO$_4$. The reversal potential was 0.6 V (a, b) or 0.8 V (c, d) and the scan rate was 100 mV s$^{-1}$ (a, c) or 1000 mV s$^{-1}$ (b, d). The dashed curves show the extrapolation with $E^{-1/2}$ functions.

\textsuperscript{2} A.J. Bard, L.R. Faulkner, and H.S. White. \textit{Electrochemical methods: fundamentals and applications}. John Wiley & Sons, 2022
Fig. S3. Cyclic voltammograms for 1 mM RBA in MeCN with 0.1 M LiClO$_4$ acquired in different potential ranges at a 200 mV s$^{-1}$ scan rate.

Fig. S4. Cyclic voltammograms for 1 mM RBA in MeCN with 0.1 M LiClO$_4$ containing 0 to 5 vol% deionized water (the water concentrations are shown in the figure). The scan rate was 200 mV s$^{-1}$. 

S4
3 Bulk electrolysis and spectrophotometry

Fig. S5. (a) Changes in the absorption spectrum for 0.2 mM RBA in MeCN with 0.1 M LiClO₄ during electrolysis at 0.6 V. (b) Absorbance at 558 nm vs. time during electrolysis at 0.5 and 0.6 V.
4 LC/MS and MS/MS data

Table S1. Possible chemical structures of compounds 1–7 present in the electrolyzed RBA solutions (the corresponding analytical data are shown in Table 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Chemical structure for compound 1" /></td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Chemical structure for compound 2" /></td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Chemical structure for compound 3" /></td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Chemical structure for compound 4" /></td>
</tr>
</tbody>
</table>
| 5        | ![Chemical structure for compound 5](image5)  
          | (a dinitrogen adduct of compound 7) |
| 6        | ![Chemical structure for compound 6](image6) |
| 7        | ![Chemical structure for compound 7](image7) |
Fig. S6. Chromatograms for RBA solutions electrolyzed at 0.5 V (a), 0.6 V (b), and 0.8 V (c). The chromatograms were acquired at 510 nm by a photodiode detector. Mobile phase A was 0.1 vol.% trifluoroacetic acid, and mobile phase B was MeCN. The dotted vertical lines show the chromatographic peaks 1–7 corresponding to compounds 1–7 (see Table 1). Chromatographic separation was incomplete for peaks 3 and 5 (see Fig. S7). Note that peak 6 in panel (c) is quite weak. However, the main absorption band of the corresponding compound 6 is peaked at 703 nm (see Fig. S8), and its absorbance at 510 nm is weak. Thus, the actual concentration of compound 6 is significantly higher.
Fig. S7. Mass spectra for chromatographic peaks 1–7 shown in Fig. S6.

Fig. S8. Absorption spectra for chromatographic peaks 1, 2, 4, 6, and 7 shown in Fig. S6. Spectra for peaks 3 and 5 are not shown because chromatographic separation was incomplete (see Figs. S6 and S7).
Fig. S9. MS/MS spectrum for compound 2 with \( m/z = 443 \) (see Table 1). Ion kinetic energy during collisionally induced dissociation was 60 eV.

Fig. S10. MS/MS spectra for compounds 3, 4, and 7 with \( m/z = 485 \) (see Table 1). Ion kinetic energy during collisionally induced dissociation was 60 eV.
**Fig. S11.** Chromatogram for RBA solution electrolyzed at 0.5 V and mass spectra corresponding to chromatographic peaks a, b, and c. Note that only peaks corresponding to compounds with $m/z = 485$ are highlighted. The chromatogram was acquired at 510 nm by a photodiode detector. Mobile phase A was 0.1 vol.% trifluoroacetic acid, and mobile phase B was MeOH.
Fig. S12. MS/MS spectra for compounds 5 and 7 (see Table 1). Ion kinetic energy during collisionally induced dissociation was 40 eV.