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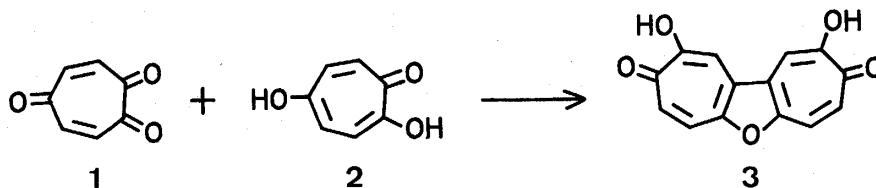


Electrochemical Oxidation of 5-Hydroxytropolone

Akira MORI*, Hiroyasu WATANABE,
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The cyclic voltammograms of 5-hydroxytropolone revealed a systematic change in shapes of redox waves by addition of HBF_4 . The mechanism of formation of 2,10-dihydroxydicyclohepta [*b, d*] furan-3,9-dione in the oxidation-reduction of *p*-tropoquinone-5-hydroxytropolone was analyzed.

Previously, we have reported the findings on the redox properties of *p*-tropoquinone (1) in respect of the half wave potentials determined by means of cyclic voltammetry (CV) in *N,N*-dimethylformamide (DMF).¹⁾ In connection to this work, an electrochemical oxidation of 5-hydroxytropolone (2),²⁾ the hydroquinone of 1, is of an interest. Herein, we wish to describe marked pH effects on the two-electron oxidation of 2 to 2,10-dihydroxy dicyclohepta [*b, d*] furan-3,9-dione (3).



Experimental

The potentials were determined in a standard three-electrode cell (working electrode, Pyrex glass-sealed Pt wire, reference electrode, standard Ag/AgCl) at 22–23°C in anhydrous DMF with 0.1 M tetrabutylammonium tetrafluoroborate under N_2 with the scan rate of 100mV/s. Electrolysis and CV measurement were performed under the same conditions.

Results and Discussions

At first, the CV of 2 in DMF is shown in Fig. 1, where three oxidation peaks (Ox_1 , Ox_2 , and Ox_3) and two reduction peaks (Red_1 and Red_2) are observed. In order to know what these peaks represent, the CV of 1 were measured in the presence of tetrafluoroboric acid (TFB). With one molar equivalent of TFB, the Ox_6 , Red_5 , and Red_6 appeared and the intensities of

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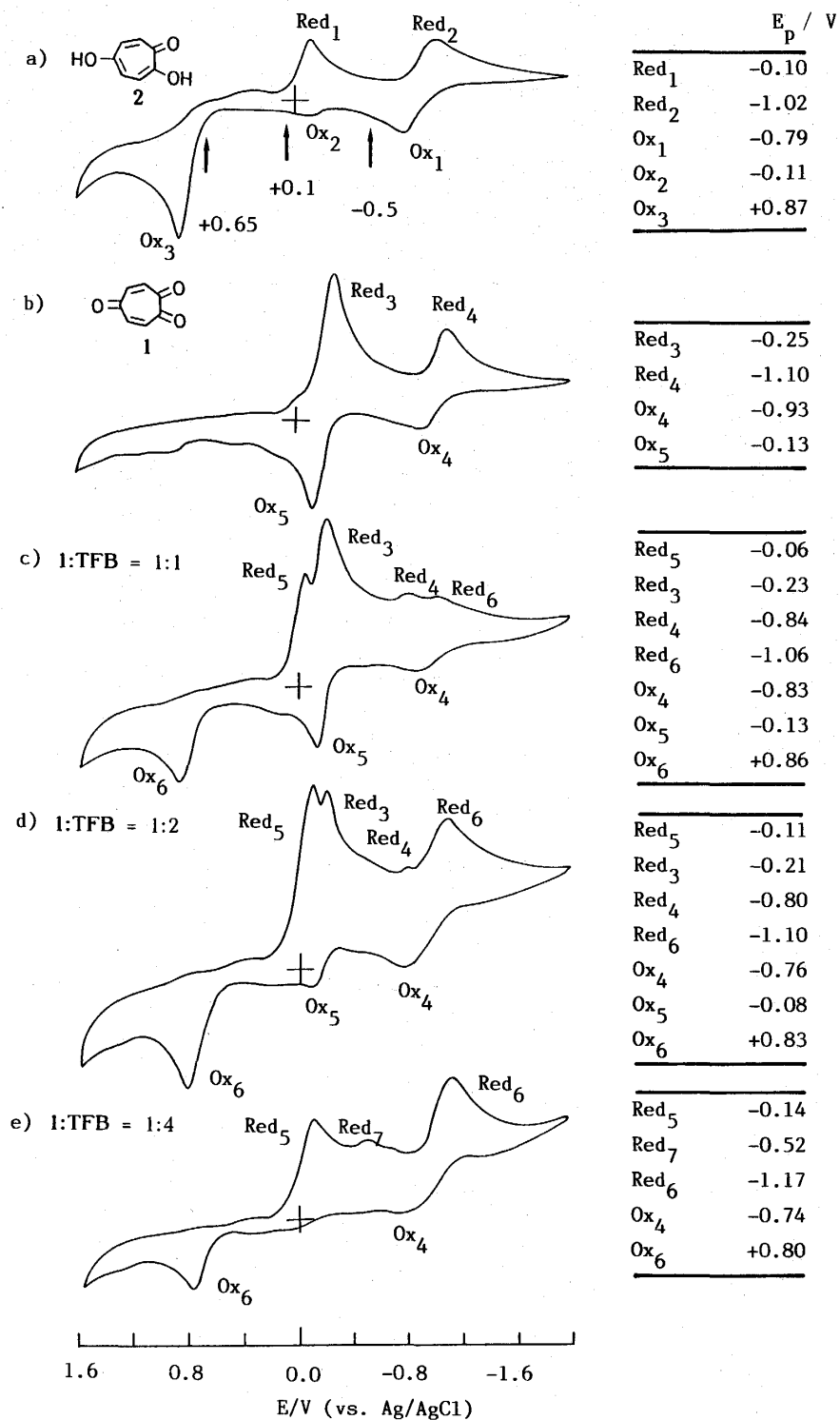
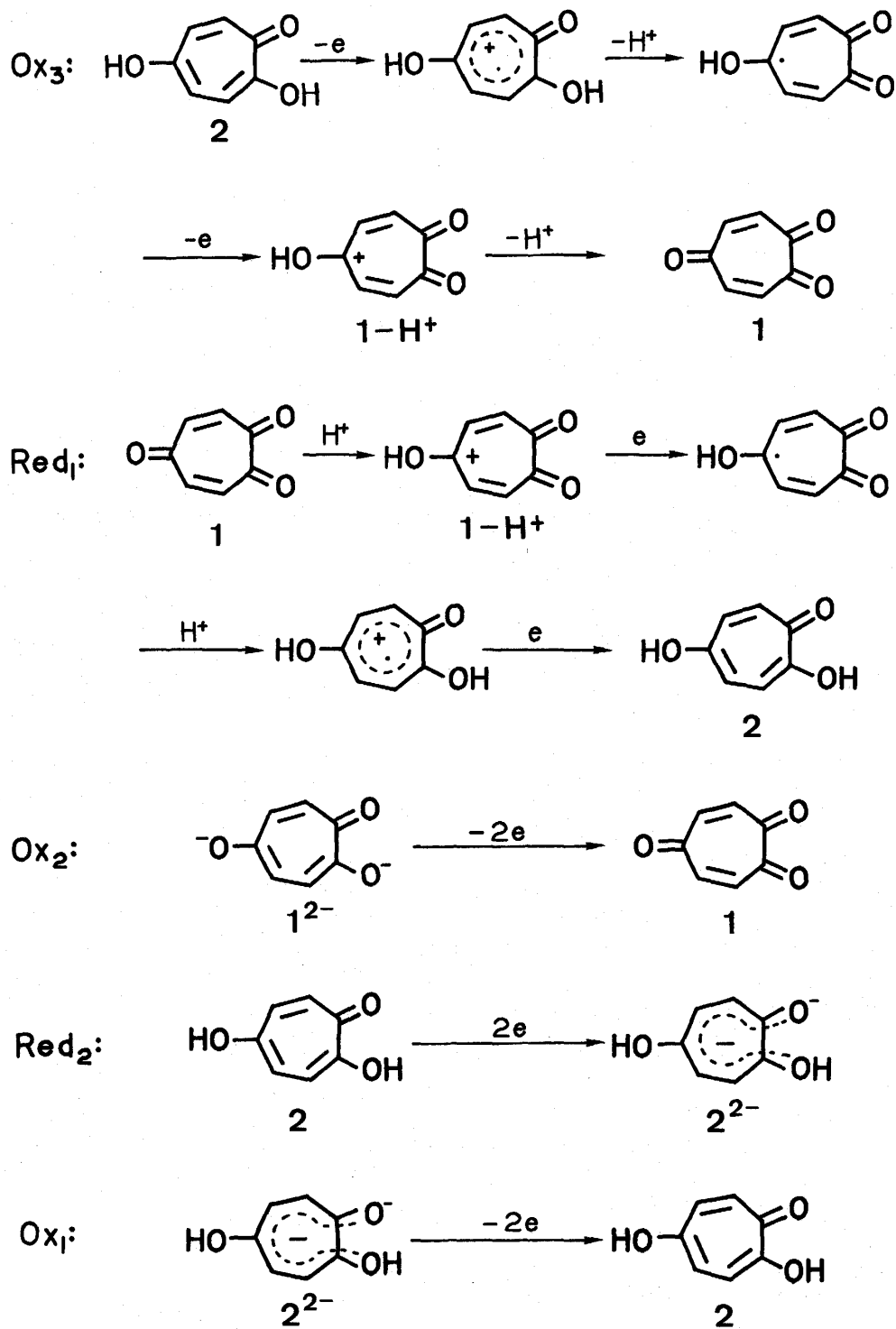


Figure 1. Cyclic voltammograms of 1, 2, and 1 in the presence of TFB: 0.1 M Bu₄ NBF₄, DMF, 100 mV/s.



Scheme 1

Ox₅, Red₃, and Red₄ decreased. When two equivalents of TFB were added, the intensities of Ox₆, Red₅, and Red₆ increased and those of Ox₅ and Red₃ decreased. In the presence of four equivalents of TFB, Ox₅ and Red₃ disappeared and the CV was almost identical with that of **2**.

In order to evaluate the oxidation potential of **2** to **1**, the DMF solution of **2** was subsequently electrolyzed³⁾ at -0.5 V, 0.1 V, and 0.65 V, respectively. Previously, we have obtained the derivatives of **3**⁴⁾⁵⁾ by a chemical oxidation of **2** with stoichiometric amount of silver acetate, a one-electron oxidizing agent. These derivatives were also prepared⁴⁾⁵⁾⁶⁾ either by the hot acetic acid-reduction of **1** or by a simple mixing of equimolar amounts of the derivatives of **1** and **2** in tetrahydrofuran (THF). The former method involves a spontaneous reduction of **1** to **2** in situ, and the latter method provided the way of getting the mixed condensates from **1** and **2**.⁶⁾ Therefore, the formation of **3** can be a verification of the oxidation process of **2** to **1**. Electrolytic oxidation of **2** at both 0.5 V and 0.1 V, however did not produce **3**. While **3** was also isolated in 44% yield for 20-h electrolysis at 0.65 V,⁷⁾ Ox₃ was characterized to be as the oxidation wave of **2** to **1**.

When a DMF solution of **2** was first electrolyzed at -0.5 V for 16 h and then at 0.1 V for 2 h, **3** was obtained in only less than 1% yield. However, the yield of **3** did not increased by further electrolysis at 0.1 V under the same conditions. This means that the species formed at -0.5 V was oxidized at Ox₂ to **1**.

By comparison of the peak area between the oxidation peak of hydroquinone (**4**)⁸⁾ at 0.44 V in DMF and that of Ox₃ of **2** under the same conditions, both showed to be nearly equal. Therefore, it is likely that a two-electron transfer occurs in the oxidation of **2** to **1** at Ox₃.

From these evidence, the CV peaks were assigned as summarized in Scheme 1. The Ox₃ is a two-electron oxidation process of **2** to **1**, and Red₁ is a two-electron reduction process of protonated **1** (**1**⁺) to **2**. Since Ox₂ is a process due to a species oxidized at lower potentials than that of **2**, it must be the oxidation process of the dianion of **1** (**1**²⁻) to **1**. Therefore, a reduction process of **1** to **1**²⁻ must be present around -0.5 V, lower than that of Red₁. And, the Red₂ is a two-electron reduction process of **2** to its dianion (**2**²⁻) and the Ox₁ is a two-electron oxidation process of **2**²⁻ to **2**. Thus, the redox behavior of **2** is rather complicated than that of **4**.⁸⁾

Further studies for related compounds are in progress.

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- 7) Since the electrolysis at 0.87 V, the potential of Ox₃ could not work due to high electric resistance, the electrolysis operated at 0.65 V, the trail of Ox₃.
- 8) The oxidation of **4** in acetonitrile has been revised to a two-electron process (V. D. Parker, *Electro. Chim. Acta*, **18**, 519 (1973)) from the previously reported one-electron process (B. R. Egdins, *J. C. S. Chem. Commun.*, **1972**, 427).