Determination of Memory Life of a Molecular Hysteresis Molecule by Thin Layer CV

Atsuko Tomita and Mitsuru Sano*
School of Informatic and Sciences, Nagoya University, and PRESTO21, J.R.D.C., Nagoya 464-01

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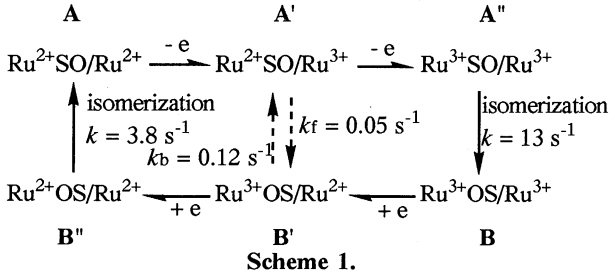
Thin layer cyclic voltammograms have been measured for (1,5-dithiacyclooctane 1-oxide) bis(pentaammineruthenium(II)) in acetone. The rates of the interconversions of the two intermediate species are determined to be 2×10^{-4} s^{-1} and 4.4×10^{-4} s^{-1} by digital simulations to the thin layer voltammograms. The half life of the memory in the molecule is 1600 s.

In earlier reports,[1-4] we described a molecule that was specifically designed to exhibit important features of a hysteresis loop. This molecule, (1,5-dithiacyclooctane 1-oxide) bis(pentaammineruthenium(II)), shows the following redox behavior:



Scheme 1.

When the molecule is fully reduced, that form is stable in which Ru^{2+} is attached to the sulfur of the sulfoxide linkage, $Ru^{2+}SO$, **A**. One electron oxidation produces **A'** in which Ru(II) is bound to sulfur of sulfoxide, a stable arrangement, but a second one electron oxidation produces **A"**, which now has Ru(III) bound to sulfur, an unstable arrangement. This isomer rearranges rapidly to **B**, where Ru^{3+} is now attached to the more negative site of the sulfoxide linkage, $Ru^{3+}OS$. Upon decrease in the applied potential, **B'** is formed, and on further decrease **B"** is formed, but this is unstable and rapidly rearranges to **A**. The mixed-valence state exists in two forms, **A'** and **B'**. In respect to geometrical structure, **A'** is similar to **A**, and **B'** to **B**, and thus, the species of **A'** and **B'** "remember" their former structures,

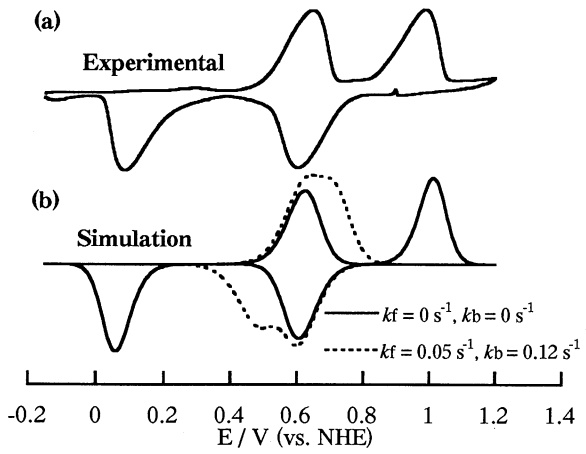


Figure 1. A thin layer cyclic voltammogram for the molecular hysteresis molecule and its digital simulations.

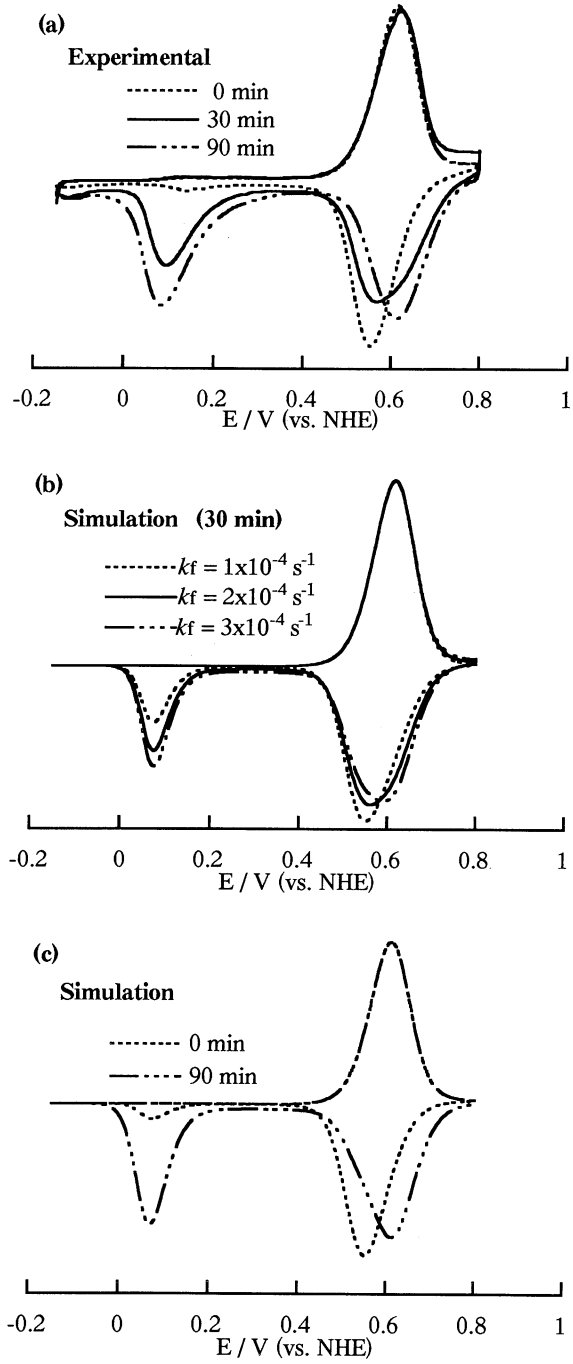


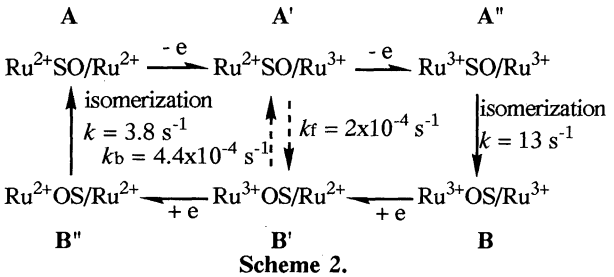
Figure 2. Thin layer cyclic voltammograms for specific intervals and the simulated voltammograms at 1 mVs^{-1}.

respectively. When **A'** is converted to **B'** or vice versa, the memory is erased.

The conversion rates k_b from **B'** to **A'** and k_f from **A'** to **B'** were estimated at 0.12 s^{-1} and 0.05 s^{-1} by simulations for cyclic voltammograms with slow scan rates.[3] However, the simulations were performed on changes in the cyclic voltammograms which were so small that we were unable to determine accurate rates of the conversions. It is very important to know the rates because of design of molecular hysteresis molecules with long-life memory. Thin layer cyclic voltammetry[5] without diffusion is one of the best methods to determine accurately the rates of the slow conversions obtaining in our system.

Thin layer cyclic voltammograms were taken on the acetone solution at 25±1 °C in an argon atmosphere.[6] One mililiter of an acetone solution 1.16 mM in the complex and 0.5 M in Bu_4NPF_6 was admitted to the compartment of the thin (0.08 mm thickness) layer electro-chemical cell equipped with a platinum 150 mesh working electrode, a platinum counter electrode, and a gold wire reference electrode with the ferrocene/ferrocenium hexafluorophosphate. The cell is connected with a BAS 100B electrochemical analyzer. Figure 1a shows an example of the thin layer cyclic voltammogram with 1 mVs^{-1} along with simulations for the fully reduced form. Figure 1b shows two simulations[7] calculated on the basis of the Scheme 1 without any conversions between **A'** and **B'** and with k_f (0.05 s^{-1}) and k_b (0.12 s^{-1}). The simulation without the conversion is in fairly good agreement with the experiments, suggesting much slower interconversions between **A'** and **B'**.

In order to determine accurately the rates of the conversion between **A'** and **B'**, another approach was made, the results of which are shown in Figure 2. When the potential is increased, $1e^-$ oxidation takes place at 0.6 V, producing **A'**. Upon further increase in the potential up to 0.8 V, the formation of **A'** is completed. Then the potential is kept at 0.8 V for specific intervals (0 min, 30 min, and 90 min). Some of **A'** is converted to **B'** with the rate k_f during the specific time. When the applied potential is now decreased, **A'** is reduced to **A** at 0.6 V. The amplitude of the reduction wave at 0.1 V is proportional to the amount of **B'** formed. Keeping the longer time increases the amount of **B'**. On changing the concentration of the complex, the results shown in Fig. 2 are reproduced well,[8] suggesting a first-order reaction. Simulations assuming first order reaction and an equilibrium constant[3] of 2.2 ($K = k_b/k_f$) have been done for the voltammogram of the specific interval of 30 min as shown in Figure 2b. The best fit simulation gives the value of $2x10^{-4}$ for k_f. Two other simulations with slightly slower and slightly faster rates give poorer agreement with the experiment. Figure 2c also shows the simulated voltammogram with the k_f values of $2x10^{-4}$ s^{-1} and with the specific intervals of 0 min and 90 min. The simulated voltammograms are in fairly agreement with the experiments. We summarize the dynamics of the "double-block" array in Scheme 2. The half-life of the memory of the molecule is calculated at 1600 s by the equation of $(ln\ 2)/(4.4x10^{-4})$.



Scheme 2.

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References and Notes

1 M. Sano and H. Taube, *J.Am.Chem.Soc.*, **113**, 2327 (1991).
2 M. Sano, *Kagaku Asahi.*, **51**(9), 34 (1991).
3 M. Sano and H. Taube, *Inorg.Chem.*, **33**, 705 (1994).
4 M. Sano, *Poly.Adv.Tech.*, **6**, 178 (1994).
5 P. Kissinger and W. R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry,* (Marcel Dekker, New York (1984), p106.
6 All manipulation was carried out under argon atmosphere in a Vacuum/Atmospheres Co. glovebox.
7 Digital simulations of proposed electrochemical mechanisms were done with a program designed to simulate thin layer cyclic voltammograms. We assumed Nernstian behavior in this simulation.
8 The same spectra were obtained in the concentrations from 0.38 mM to 7.0 mM of the complex.