CAPSULES
notes and applications from Bioanalytical Systems, Inc.
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Digital Simulation of Cyclic Voltammetry
Two-Electron Reduction of $[(\eta^6\text{-}C_6Me_6)_2\,Ru]^{2+}$

Purpose

Both the chemical (1) and the electrochemical (2,3) two-electron reductions of $[(\eta^6\text{-}C_6Me_6)_2\,Ru]^{2+}$ (1^{2+}) have been reported, and it has been shown that this reduction is accompanied by a change in the coordination mode of one of the arene ligands from η^6 to η^4 (F1) (presumably to restore a formal 18 electron count at the metal center). Digital simulation was used in a recent study to confirm that the structural change occurred during the second electron transfer, and to investigate the effect of the homogeneous Solution Electron Transfer (SET) reaction.

Reference

Electrochemical Kinetic Discrimination of the Single-Electron-Transfer Events of a Two-Electron-Transfer Reaction: Cyclic Voltammetry of the Reduction of the Bis(hexamethylbenzene)ruthenium Dication, D.T. Pierce and W.E. Geiger, J. Am. Chem. Soc. 114 (1992) 6063-6073.

Method

Cyclic voltammetry is a powerful technique for the qualitative investigation of the redox mechanisms of electroactive molecules. However, it is often difficult to extract quantitative data directly from the cyclic voltammograms, since the effects of electron transfer kinetics and homogeneous chemical reactions often cannot be separated. Quantitative mechanistic analysis using cyclic voltammetry data typically requires the use of digital simulation software. BAS has recently released DigiSim®, a simulation program developed in collaboration with Manfred Rudolph (Jena University, Germany) and Stephen W. Feldberg (Brookhaven National Laboratory). In this Capsule, DigiSim is used to reproduce some of the simulation results reported in the literature.

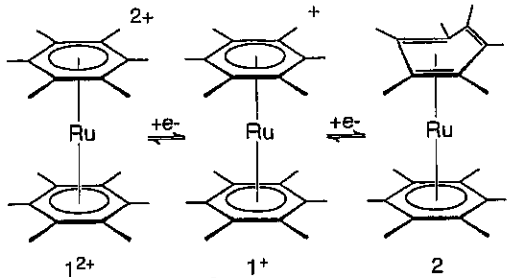


Figure 1. Structures of $[(\eta^6\text{-}C_6Me_6)_2\,Ru]^{n+}$ (1^{n+}) (n = 0, 1, 2).

Results

The cyclic voltammogram of 1^{2+} in methylene chloride shows two one-electron reductions at low scan rates (F2A) (the separation of the redox potentials is 0.1 V). In contrast, a two-electron reduction is observed at a scan rate of 0.1 V s^{-1} when acetonitrile is

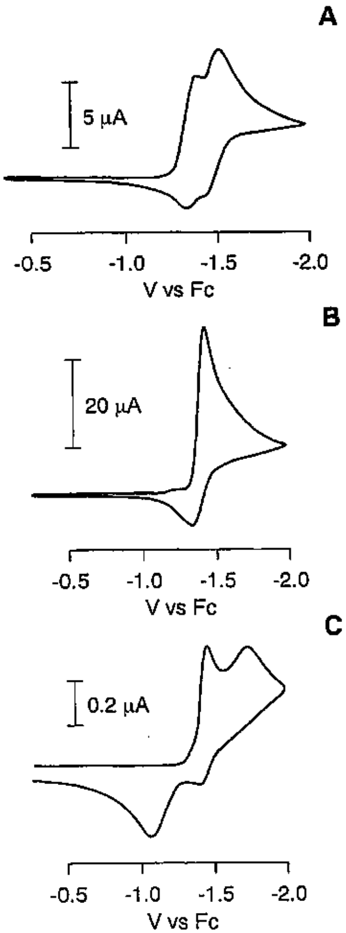


Figure 2. Cyclic voltammograms of 1^{2+} at a platinum electrode in a) methylene chloride, scan rate = 0.1 V s^{-1} b) acetonitrile, scan rate = 0.1 V s^{-1} c) acetonitrile, scan rate = 50 V s^{-1}. Adapted from the primary reference.

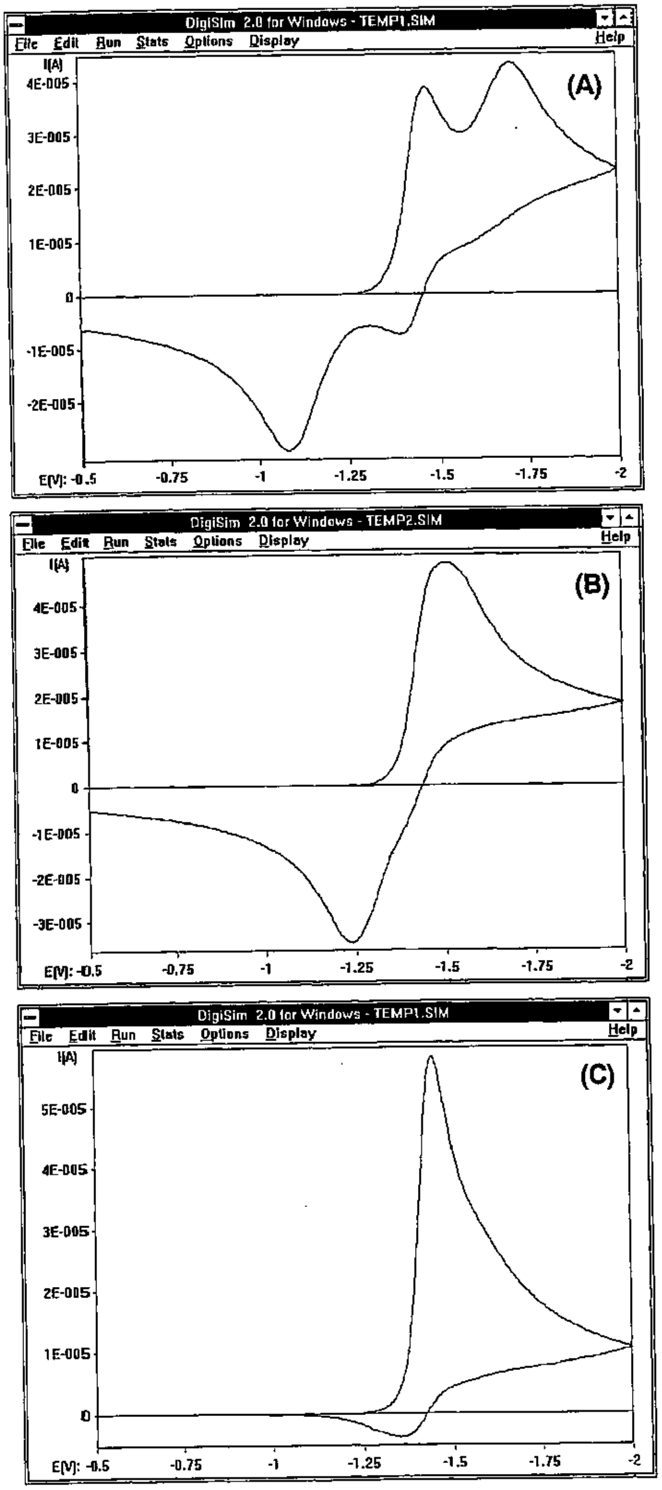
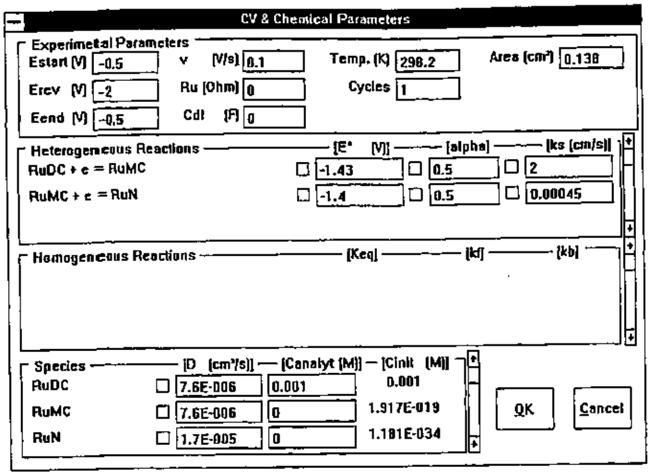


Figure 3. Simulated voltammograms for I^{2+}. a) EE mechanism, scan rate = 50 V s^{-1}, b) EE mechanism, scan rate = 0.1 V s^{-1}, c) EE-Disp mechanism, scan rate = 0.1 V s^{-1}.

used as the solvent (F2B). This change from two, one-electron processes to one, two-electron process, requires a negative shift of the first redox potential relative to the second redox potential, which was attributed to stronger solvation of the more positively charged species by acetonitrile; that is; the dication is preferentially stabilized by solvation.

As the scan rate is increased, the two-electron process becomes resolved into two one-electron processes (the cyclic voltammogram at 50 V s^{-1} is shown in F2C). This behavior was attributed to the difference in the electron transfer kinetics of the two reductions ($k_{s1} > 2$ cm s^{-1}, $k_{s2} = 4.5 \times 10^{-4}$ cm s^{-1}). Hence, the separation of the cathodic and anodic peaks (ΔE_p) increases with scan rate at a faster rate for the second redox process than for the first redox process (it should be noted that this splitting of the two redox processes also requires that the one-electron redox potentials are similar).

The cyclic voltammogram at 50 V s^{-1} can be approximately simulated by DigiSim using a EE mechanism (i.e., a mechanism consisting of two heterogeneous sequential one-electron transfer reactions) (F3A), but this mechanism is not adequate for the simulation at 0.1 V s^{-1} (F3B) (the simulation parameters for the EE mechanism are shown in F4). In particular, the peaks are smaller and broader than those in the experimental voltammogram, and the peak current on the reverse scan is too large. The latter discrepancy was attributed to a slow homogeneous chemical reaction of the monocation to form an uncharacterized species, and the difference in the peak widths could be corrected by the inclusion of the *homogeneous* SET reaction $2I^{+} \Leftrightarrow I^{2+} + I$ (F3C) (the simulation parameters for this EE-Disp (disproportionation) mechanism are shown in F5). This reaction provides an alternate route for the interconversion of I^{+} and I; therefore, the effect of this reaction on the current response depends on the rate of the second heterogeneous electron transfer reaction. This is illustrated in F6, which shows the simulated voltammograms (for the EE mechanism (a) and the EE-Disp mechanism (b)) when k_{s2} is one order of magnitude larger than it is for the simulation shown in F3C. It can be seen that there is little difference in the current response of the two mechanisms at this faster rate of electron transfer. As the scan rate is increased, the effects of the two homogeneous reactions are diminished, and



CV & Chemical Parameters

Experimetal Parameters

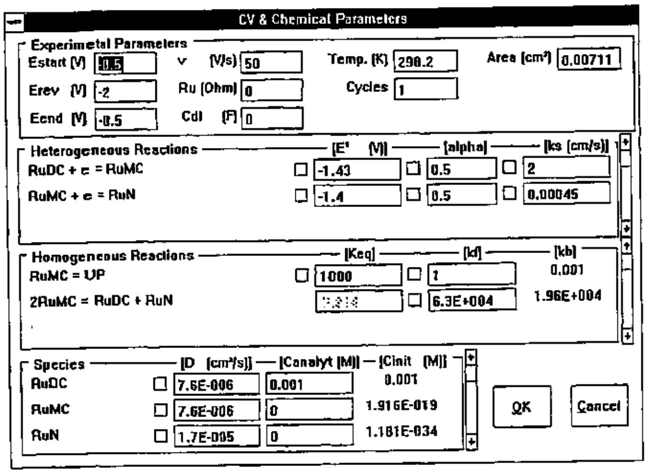
Estart (V)	-0.5	v (V/s)	0.1	Temp. (K)	298.2	Area (cm²)	0.138
Erev (V)	-2	Ru (Ohm)	0	Cycles	1		
Eend (V)	-0.5	Cdl (F)	0				

Heterogeneous Reactions	[E° (V)]	[alpha]	[ks (cm/s)]
RuDC + e = RuMC	☐ -1.43	☐ 0.5	☐ 2
RuMC + e = RuN	☐ -1.4	☐ 0.5	☐ 0.00045

Homogeneous Reactions	[Keq]	[kf]	[kb]

Species	[D (cm²/s)]	[Canalyt (M)]	[Cinit (M)]
RuDC	☐ 7.6E-006	0.001	0.001
RuMC	☐ 7.6E-006	0	1.917E-019
RuN	☐ 1.7E-005	0	1.181E-034

Figure 4. Simulation parameters for the EE mechanism.



CV & Chemical Parameters

Experimetal Parameters

Estart (V)	0.5	v (V/s)	50	Temp. (K)	298.2	Area (cm²)	0.00711
Erev (V)	-2	Ru (Ohm)	0	Cycles	1		
Eend (V)	-0.5	Cdl (F)	0				

Heterogeneous Reactions	[E° (V)]	[alpha]	[ks (cm/s)]
RuDC + e = RuMC	☐ -1.43	☐ 0.5	☐ 2
RuMC + e = RuN	☐ -1.4	☐ 0.5	☐ 0.00045

Homogeneous Reactions	[Keq]	[kf]	[kb]
RuMC = UP	☐ 1000	☐ 1	0.001
2RuMC = RuDC + RuN	[illegible]	☐ 6.3E+004	1.96E+004

Species	[D (cm²/s)]	[Canalyt (M)]	[Cinit (M)]
RuDC	☐ 7.6E-006	0.001	0.001
RuMC	☐ 7.6E-006	0	1.916E-019
RuN	☐ 1.7E-005	0	1.181E-034

Figure 5. Simulation parameters for the EE-Disp mechanism.

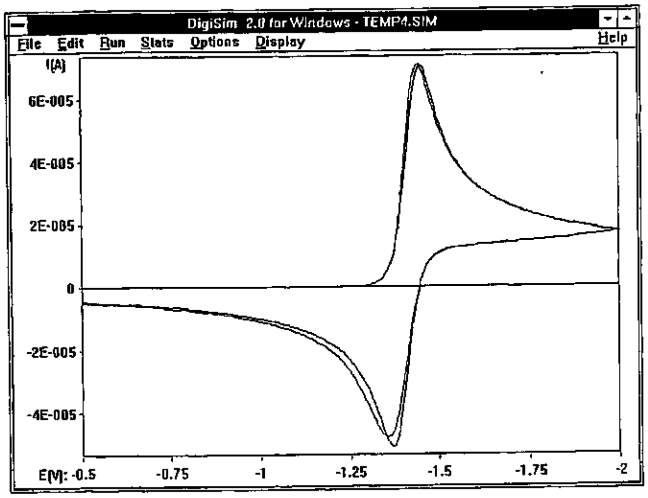


Figure 6. Simulated voltammograms for I^{2+}. a) EE mechanism, scan rate = 0.1 V s^{-1}, k_{s2} = 4.5 x 10^{-3} cm s^{-1} b) EE-Disp mechanism, scan rate = 0.1 V s^{-1}, k_{s2} = 4.5 x 10^{-3} cm s^{-1}.

these reactions have only a small effect at a scan rate of 50 V s^{-1}.

Two other parameters were found to have a significant influence on the current response in the original study:

1. The best fit between the experimental and simulated voltammograms was obtained when the ratio of the diffusion coefficients of the neutral species:dication was set to 0.38. Although such a large difference in the diffusion coefficients was initially thought to be unusual, it was confirmed using rotating disk voltammetry.
2. It was found that the kinetics for the second heterogeneous electron transfer did not conform to Butler-Volmer kinetics, and that a potential-dependent α was required to obtain a good match (this is consistent with Marcus kinetics).

DigiSim is a registered trademark of Bioanalytical Systems, Inc.

Additional References

1. *E.O. Fischer and C. Elsenbroich, Chem. Ber. 103 (1970) 162-168.*
2. *E.D. Laganis, R.H. Voegeli, R.T. Swann, R.G. Finke, H. Hopf and V. Boekelheide, Organometallics 1 (1982) 1415-1422.*
3. *R.G. Finke, R.H. Voegeli, E.D. Laganis and V. Boekelheide, Organometallics 2 (1983) 347-355.*