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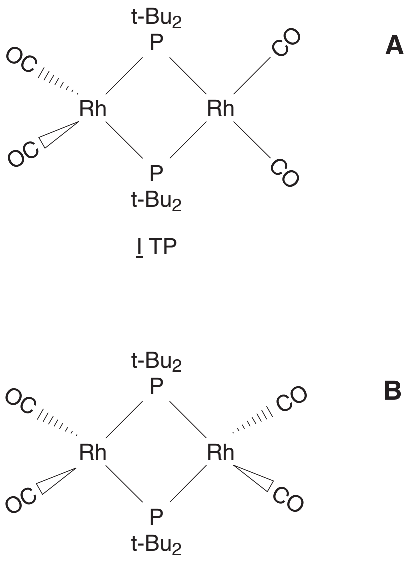
Digital Simulation of Cyclic Voltammetry. Isomerization of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$

Purpose

There are two possible structures for $[Rh(\mu\text{–}t\text{-}Bu_2P)(CO)_2]_2$ (I), which differ in the geometries of the terminal carbonyl ligands. In one isomer (labeled TP), the carbonyls coordinated to one Rh center are perpendicular to those coordinated to the other Rh center, whereas in the other isomer (labeled TT), they are coplanar (F1). The relative stability of the isomers varies with oxidation state, so isomerization is induced by electron transfer. In this study, digital simulation was used to investigate the electrochemical behavior of this system, particularly the relationships between the electron transfer reactions and the isomerization steps, and the effect of the homogeneous Solution Electron Transfer (SET) reaction.

Reference

Electrochemical Reduction and Reoxidation Accompanied by Reversible Geometric Isomerization. Electrochemistry of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$. Isolation and X-ray Crystal Structure of $[N(n\text{-}Bu)_4]_2^+[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2^{2-}$ J.G. Gaudiello, T.C. Wright, R.A. Jones and A.J. Bard. J. Am. Chem. Soc. 107 (1985) 888-897.



I TP

I TT

Figure 1. Isomers of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (I) - TP (a) and TT (b).

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 information directly from the cyclic voltammograms, since the effects of electron transfer kinetics and homogeneous chemical reactions cannot be easily separated. Quantitative mechanistic analysis using cyclic voltammetry generally 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 above reference.

Results

The redox mechanisms of molecules that exist in two isomeric forms, and undergo a single one-electron transfer reaction can be represented using a “square scheme.” This idea can be extended to isomeric species that undergo two or more electron transfers, and such representations are often referred to as “fence schemes” (1). The fence scheme for I is shown in F2. It is important to note that many of the thermodynamic parameters of such schemes are interdependent; for example, the equilibrium constant for the reaction TPN + TTA = TPA + TTN is related to the redox potentials for the reductions of TPN and TTN

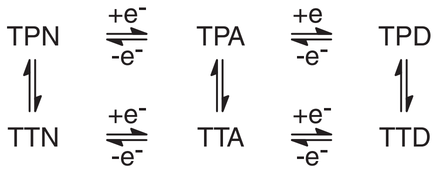


Figure 2. “Fence scheme” for the redox reactions of I.

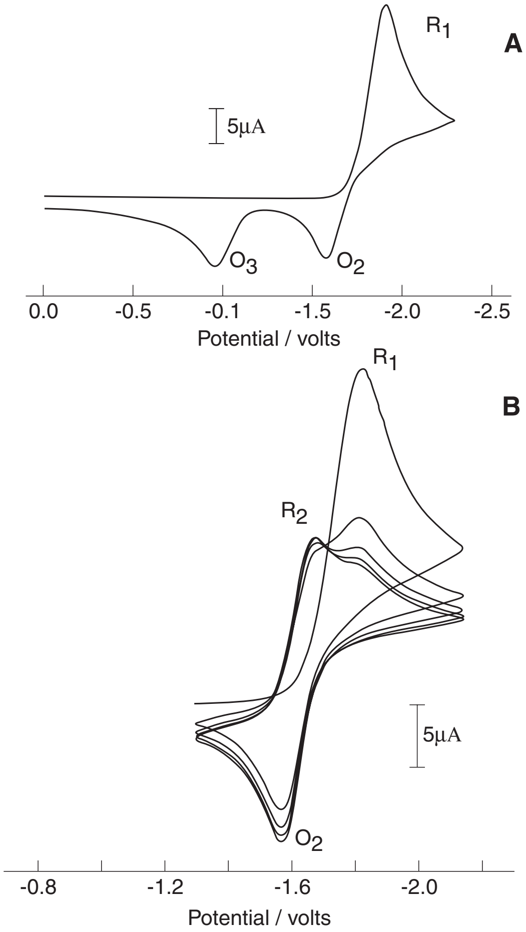
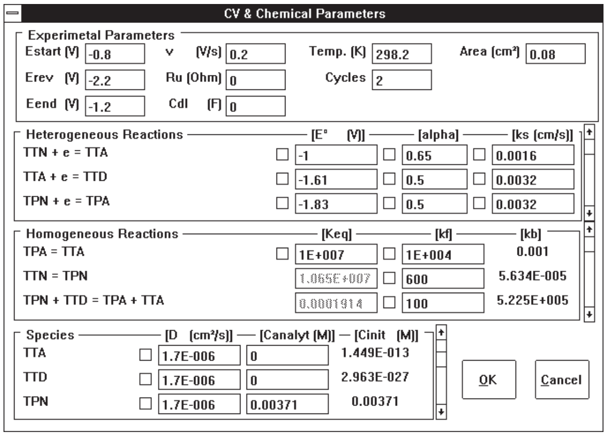


Figure 3. Cyclic voltammogram of I (3.71 mM) in THF/0.5 M TBAB, scan rate = 0.2 V s^{-1}. a) 1 cycle between 0 V and -2.25 V, b) 5 cycles between -1.2 V and -2.25 V. Adapted from the primary reference.

(the idea of Thermodynamically Superfluous Reactions has been discussed in detail elsewhere (2)).

The cyclic voltammogram of the neutral TP complex (TPN) between 0 and -2.25 V is shown in F3a. There is one two-electron reduction on the forward scan (R_1) and two one-electron oxidations on the reverse scan (O_2 and O_3). If the potential is cycled between -1.2 V and -2.25 V, a second reduction appears (R_2) that is associated with O_2 (F3b). The peak current of R_2 increases and the peak current of R_1 decreases with each additional scan until a steady state is attained after about 10 scans. This behavior is characteristic of an ECE process. TPN is reduced at R_1 to the TP monoanion (TPA), which then isomerizes to TTA at the electrode surface. The reduction potential of TTA (R_2) is more positive than that of TPN, so TTA is instantaneously reduced to the TT dianion (TTD).



Experimetal Parameters

Estart (V) -0.8
v (V/s) 0.2
Temp. (K) 298.2
Area (cm²) 0.08
Erev (V) -2.2
Ru (Ohm) 0
Cycles 2
Eend (V) -1.2
Cdl (F) 0

Heterogeneous Reactions		[E° (V)]		[alpha]		[ks (cm/s)]
TTN + e = TTA	☐	-1	☐	0.65	☐	0.0016
TTA + e = TTD	☐	-1.61	☐	0.5	☐	0.0032
TPN + e = TPA	☐	-1.83	☐	0.5	☐	0.0032

Homogeneous Reactions		[Keq]		[kf]	[kb]
TPA = TTA	☐	1E+007	☐	1E+004	0.001
TTN = TPN		1.065E+007	☐	600	5.634E-005
TPN + TTD = TPA + TTA		0.0001914	☐	100	5.225E+005

Species		[D (cm²/s)]	[Canalyt (M)]	[Cinit (M)]
TTA	☐	1.7E-006	0	1.449E-013
TTD	☐	1.7E-006	0	2.963E-027
TPN	☐	1.7E-006	0.00371	0.00371

Figure 4. Parameter set of an ECE mechanism including a SET.

However, it is not possible to reproduce the experimental voltammograms using digital simulation based only on this three-step mechanism. In particular, the peak current for R_1 decreases faster and the peak current for R_2 increases faster in the experimental voltammograms than in the simulated voltammograms (and the steady state is therefore attained more quickly). Hence, there must be an additional reaction that consumes TPN and generates TTA, the most probable reaction being the SET (solution electron transfer) reaction TPN + TTD = TPA + TTA. As discussed above, the equilibrium constant for this reaction is determined by the TPN/TPA and TTA/TTD redox potentials, and has a value of 1.98×10^{-4}; that is, the equilibrium lies well to the left. However, it is important to note that this equilibrium cannot be attained, due to the rapid isomerization of TPA to TTA. This reaction drives the SET reaction, leading to an increase in the rate of the net conversion of TPN to TTA. The inclusion of this SET reaction in the simulation mechanism leads to a good match between the simulated and experimental data (the parameter set is shown in F4). The relative peak currents are sensitive not only to the rate of the SET reaction and the rate of the forward isomerization reaction (F5) (3-5) but also to the reversibility (i.e., the rate of the reverse reaction) of the isomerization reaction (F6) (4).

The effect of the combination of the isomerization and SET reactions can also be shown using CV - the Movie™, and "frames" at various points are shown in F7 for the ECE mechanism with (b) and without (a) the SET reaction. For the ECE mechanism without the SET reaction, TTA is generated only

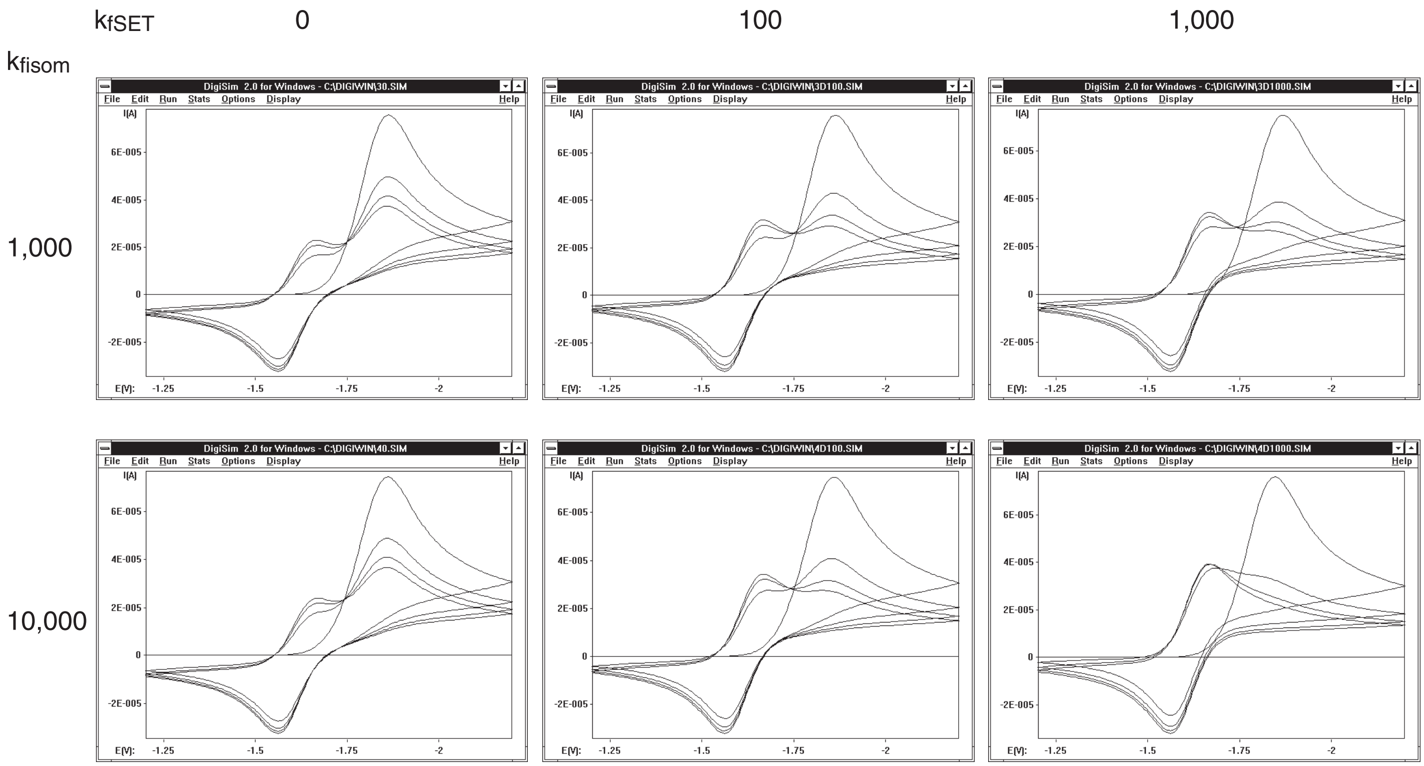


Figure 5. Simulated voltammograms of I showing effect of the variation of k_{fisom} (isomerization reaction) and k_{fSET} (SET reaction) (K_{isom} adjusted such that $k_{bisom} = 1 \times 10^{-4}$ s^{-1}).

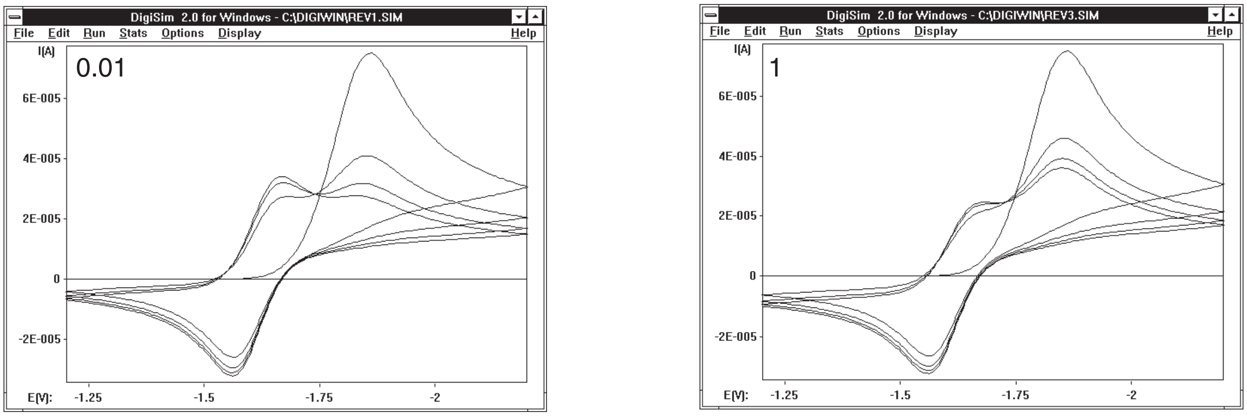


Figure 6. Simulated voltammograms of I showing effect of the variation of k_{bisom}. $k_{fisom} = 1 \times 10^4$ s^{-1}, $k_{fSET} = 100$ M^{-1} s^{-1}.

at the electrode surface, whereas the SET reaction leads to the formation of additional TTA *in the reaction layer* (the solution layer next to the electrode surface). This can lead to *curve-crossing* (3,5) (provided the rates of the homogeneous reactions are fast enough). This shows that there is a net cathodic current at these potentials, which is due to the reduction of TTA generated in the reaction layer (curve-crossing cannot occur for an ECE mechanism, since, at this potential, no TTA is available for reduction).

One further difference between the current responses for the ECE mechanism with and without the SET reactions should be noted. In the simulated response for the ECE mechanism, all cycles pass through an isopotential point; this is similar to the isosbestic point observed in spectroscopy, and shows quantitative conversion between the products and the reactants (i.e., there are no side reactions) (3-5). In contrast, if the SET reaction is included, the first cycle does not necessarily pass through the isopotential point (F8).

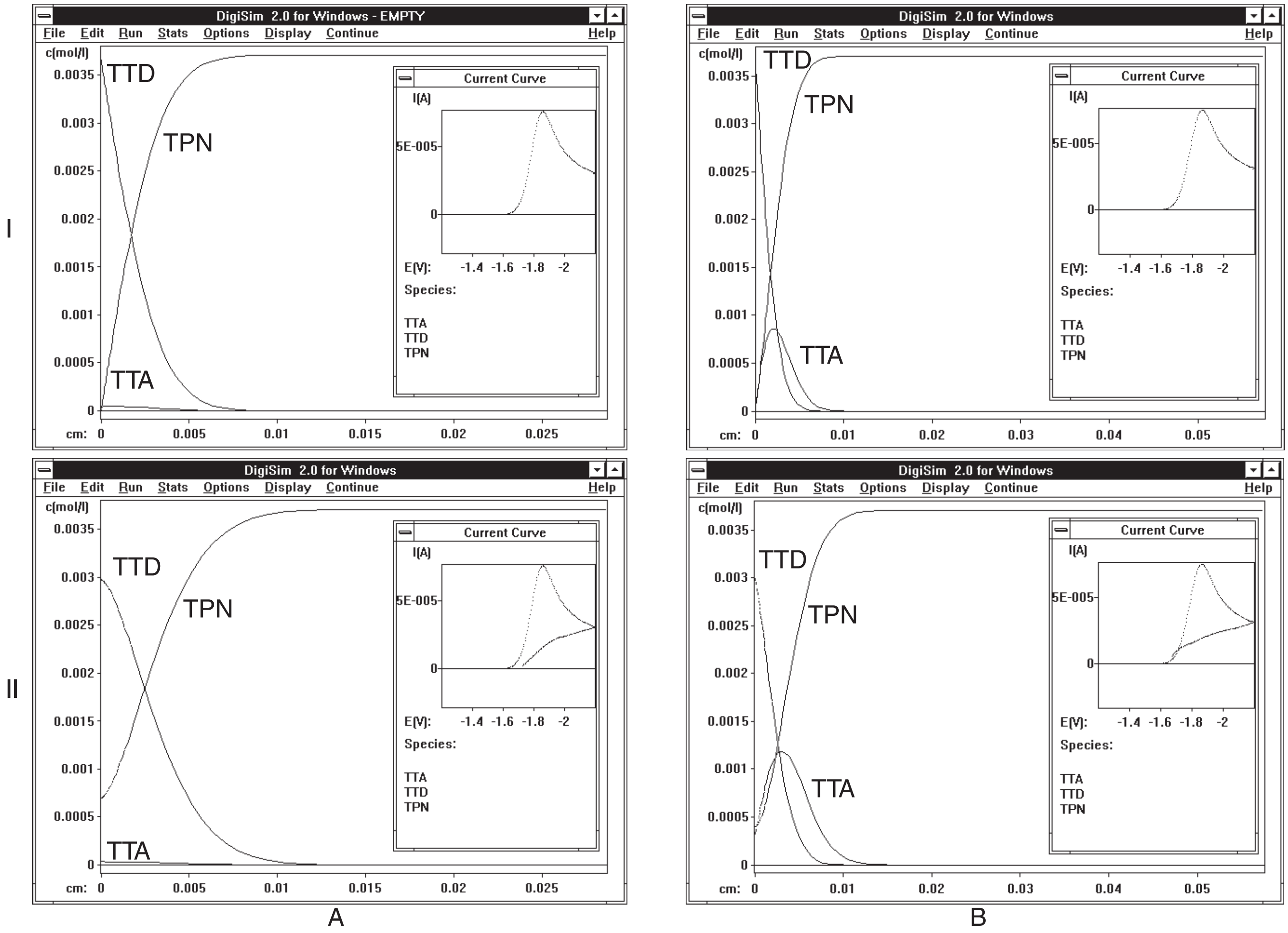


Figure 7. CV - the Movie frames for a) ECE mechanism with no SET reaction b) ECE mechanism including SET reaction. $K_{isom} = 1 \times 10^7$, $k_{fisom} = 100\ s^{-1}$, $k_{fSET} = 1 \times 10^3\ M^{-1}\ s^{-1}$.

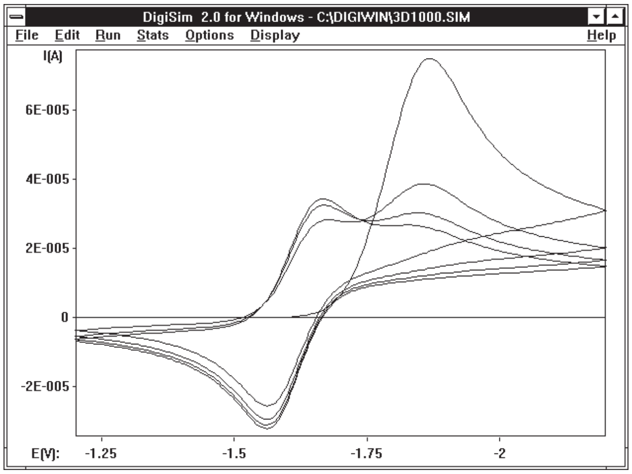


Figure 8. Simulated voltammogram of I showing isosbestic point for second and subsequent cycles. $Kisom = 1 \times 10^7$, $kfisom = 1 \times 10^3\ s^{-1}$, $k_{fSET} = 1 \times 10^3\ M^{-1}\ s^{-1}$.

O_3 can be attributed to the oxidation of TTA (F3A). Therefore, the mechanism for the reverse reaction is TTD → TTA → TTN → TPN (i.e., the reverse isomerization reaction occurs in the neutral oxidation state, due to the slow rate of the reverse isomerization reaction for the monoanion species). The potential required for the oxidation of TTA (O_3) is sufficiently positive of that required for the oxidation of TTD (O_2) that the isomerization reaction that follows the oxidation of TTA cannot cause the two oxidations to occur at the same potential.

References

1. *D.H. Evans, Chem. Rev. 90 (1990) 739-751.*
2. *W. Luo, S.W. Feldberg and M. Rudolph, J. Electroanal. Chem. 368 (1994) 109-113.*
3. *D.J. Kuchynka and J.K. Kochi, Inorg. Chem. 27 (1988) 25742581.*
4. *D.J. Kuchynka and J.K. Kochi, Inorg. Chem. 28 (1989) 855-863.*
5. *K. Hinkelman, J. Heinze, H-T. Schacht, J.S. Field and H. Vahrenkamp, J. Am. Chem. Soc. 111 (1989) 5078-5091.*