

SIMULATION OF CYCLIC VOLTAMMOGRAM OF RUTHENOCENE

Inam-ul-Haque^{ab}

^aDepartment of Chemistry, University of Engineering and Technology, Lahore-54890, Pakistan

^bJ-263, D.H.A., Lahore 54792, Pakistan

(Received 7 April, 2002; accepted 25 March, 2004)

Digital simulation of cyclic voltammogram of ruthenocene in benzonitrile suggests that electrooxidation of ruthenocene at platinum electrode involves a one-electron oxidation. The ruthenium cation presumably combines with ruthenocene in a fast following chemical reaction. The proposed dimeric monocation so, formed shows a one-electron electroreduction at a much lower potential.

Key words: Simulation, Cyclic voltammetry, Ruthenocene

Introduction

Digital simulation has been found very useful in a number of complex electrochemical problems involving complicated kinetic schemes and non-uniform current distribution at the working electrode (Bard and Faulkner 1980). Electrochemical oxidation of ruthenocene employing a mercury anode has been reported (Hendrickson *et al* 1972).

$[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}]^{2+}$ undergoes a two electron reduction with a change in the coordination mode of one of the arene ligands. Digital simulation was used in a recent study to confirm that the structural change occurred during the second electron transfer reaction and to investigate the effect of the solution electron transfer reaction. These simulations are studied in this capsule using DigiSim (Digisim 2003).

The electrochemistry of 1,1-bis(diphenylphosphino)ferrocene (dppf) derivatives of $\text{Ru}_3(\text{CO})_{12}$ was investigated. Two known compounds $[\text{Ru}_3(\text{CO})_8(\text{m-dppf})_2]$ (**1**) and $[\text{Ru}_3(\text{CO})_{10}\text{dppf}]$ (**2**) and a new compound $[\text{Ru}_3(\text{CO})_{11}(\text{m-dppf})\text{Ru}_3(\text{CO})_{11}]$ (**3**) were prepared. The reductive electrochemistry of (**1**) and (**2**) showed an irreversible reduction and a follow-up oxidation, similar to $\text{Ru}_3(\text{CO})_{12}$. The electrochemistry of compound (**3**) showed two irreversible waves and a follow-up oxidation. The oxidative electrochemistry of (**1-3**) showed a dppf-based chemically reversible wave, and an irreversible wave similar to that of $\text{Ru}_3(\text{CO})_{12}$. Trends were also noted between the oxidation potential and the number of coordinated phosphorus atoms (Nataro 2003).

Splitting of a single two electron cyclic voltammetric wave for bis-arene complex $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}$ into two one-electron components involving an EE (consecutive electron transfer) mechanism has been reported (Pierce and Geiger 1989). The

electrochemical reduction of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}][\text{BF}_4]_2$ has been shown to occur into two, one-electron steps, each manifesting solvent-dependent formal potentials. The heterogeneous charge-transfer kinetics varied with electrode material. Cyclic voltammetry (CV) was found to be sensitive to homogeneous reaction, which occurred both within the electrode reaction layer, and in the bulk of solution. Whereas, the reduction waves of $(\text{C}_6\text{Me}_6)_2\text{Ru}^{2+/+0}$ were resolved in methylene chloride and separated by -0.14 V ($E_2^\circ - E_1^\circ, E_{2-}^\circ - 1.45$ V vs. Fc/Fc^+), only a single two-electron wave was observed in acetonitrile because of a negative shift of E_1° with respect to E_2° ($E_2^\circ - E_1^\circ = +0.03$ V, $E_{2-}^\circ = -1.40$ V). Both reductions displayed Nerstian behavior at mercury electrodes. However, the Ru(I/0) couple showed quasi-reversible charge-transfer kinetics at platinum disk electrodes. At platinum, the single two electron wave was found to split into two, one-electron components over a range of sweep rates, which varied with analyte concentration. The Ru(I) complex was also subject to a follow-up reaction having a rate constant of 1.0 s^{-1} . Detailed explicit finite difference simulations of the CV curves allowed solution of the electron-transfer parameters for the two, one-electron couples in acetonitrile at platinum, a scan rate range $0.4 - 100 \text{ Vs}^{-1}$, and a concentration range of $0.50 - 1.3 \text{ mM}$. The equilibrium constants and rate constants for the disproportionation reaction were 2.0 and $6.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The diffusion coefficient of the Ru(II) complex was about 0.45 times that of the Ru(0) complex. This redox system obeyed an $E_{\text{rev}} E_{\text{qrev}}$ model down to experimental times of $10 \mu\text{s}$. This was believed to be the first recognized example of kinetic discrimination between one-electron processes of two-electron EE wave (Pierce and Geiger 1992).

Homogeneous cross-section rates for electron transfer between Ru(II) and Ru(0) were estimated. Synthesis and

voltammetric behavior of decamethylruthenocene were discussed in detail (Koelle and Salzar 1983). ESR spectra were utilized to characterize the compound. Cyclic voltammetric behaviors of homo- and hetero-binuclear [1.1] metallocenophanes have been studied (Diaz *et al* 1982). Cyclic voltammetric behavior of ruthenocene was interpreted as an electrochemical irreversible two electron oxidation at comparatively high potential (Diaz *et al* 1982). However, [1.1] ruthenocenophane showed electrochemical quasi - reversible two - electron oxidation.

Materials and Methods

The cyclic voltammogram of ruthenocene was recorded at room temperature using benzonitrile as solvent, a sodium chloride calomel (NaSCE) reference electrode and tetrabutylammonium tetrafluoroborate as electrolyte (Diaz *et al* 1982). At 50 mV /s scan rate, Fig 2, ruthenocene showed irreversible oxidation with peak potential at 920 mV vs NaSCE. The corresponding reduction peak appears at approximately + 400 mV, depending on solvent and scan rate. The peak heights scaled linearly with the square root of the scan rate, as is expected for a diffusion controlled process. The coulometrically determined number of electrons (n) involved in the oxidation step was 2.

Results and Discussion

Digital simulation program for the Cottrell experiment. System performance was checked by running a computer coded simulation of Cottrell experiment in FORTRAN (Bard and Faulkner 1980). The FORTRAN version was rewritten into Turbo-Pascal, given in Table 1. The symbols are as per glossary before the references. A plot of concentration profiles as a function of f_A and f_B vs. X for $t/t_k = 0.5$, from the simulation listing, is shown in Fig 1.

Table 1
Program simulation (output)

```

LABEL 100;
CONST
L=300;
DMA=0.45;
DMB=0.45;
{SET UP ARRAYS}
TYPE
ALLARRAY=ARRAY[1.300]OF REAL;
VAR
J,K:INTEGER;
T,X,JMAX,ZCOTT,R:REAL;
FAOLD,FANEW,FBOLD,FBNEW,Z:ALLARRAY;

```

```

BEGIN
{MAIN PROGRAM}
{INITIAL CONDITIONS}
FOR J:=1 TO L DO
BEGIN
FAOLD[J]:=1;
FANEW[J]:=1;
FBOLD[J]:=0;
FBNEW[J]:=0;
END;
FOR K:=1 TO L DO
BEGIN
{DIFFUSION BEYOND THE FIRST BOX}
JMAX:=4.2*SQRT(K);
FOR J:=2 TO ROUND(JMAX) DO
BEGIN
FANEW[J]:=FAOLD[J]+DMA*(FAOLD[J-1]-
2*FAOLD[J]+FAOLD[J+1]);
FBNEW[J]:=FBOLD[J]+DMB*(FBOLD[J-1]-
2*FBOLD[J]+FBOLD[J+1])
END;
{DIFFUSION INTO THE FIRST BOX}
FANEW[1]:=FAOLD[1]+DMA*(FAOLD[2]-FAOLD[1]);
FBNEW[1]:=FBOLD[1]+DMB*(FBOLD[2]-FBOLD[1]);
{FARADAIC CONVERSION AND CURRENT FLOW}
Z[K]:=SQRT(L/DMA)*FANEW[1];
FBNEW[1]:=FBNEW[1]+FANEW[1];
FANEW[1]:=0;
{TYPE OUT CONCENTRATION ARRAYS FOR K=50}
IF(K<>50) THEN
GOTO 100;
WRITELN;
WRITELN;
FOR J:=1 TO ROUND(JMAX) DO
BEGIN
X:=(J-1)/SQRT(DMA*L);
WRITELN(X,FANEW[J],FBNEW[J])
END;
WRITELN;
WRITELN;
{SET UP OLD ARRAY FOR NEXT ITERATION}
100: FOR J:=1 TO ROUND(JMAX) DO
BEGIN
FAOLD[J]:=FANEW[J];
FBOLD[J]:=FBNEW[J];
END;
END;
{RETURN FOR THE NEXT ITERATION IF K<L}
{TYPE OUT CURRENT--TIME CURVE}
WRITELN;
WRITELN;
FOR K:= 1 TO L DO
BEGIN
T:=(K-0.5)/L;

```

```
ZCOTT:=/SQRT(3.141592*T);
R:=Z[K] ZCOTT;
WRITELN(T:12:5,Z[K]:12:5,ZCOTT:12:5,R:12:5)
END;
END.
```

Simulated cyclic voltammetry of ruthenocene. Oxidation of ruthenocene in benzonitrile at platinum electrode is reported to proceed by an irreversible, two-electron process (Diaz *et al* 1982). It was (Hill *et al* 1991) established that the three metallocenes namely ferrocene, ruthenocene and osmocene exhibit a single, quasi-reversible one-electron oxidation. Using a microcomputer based simulation program for cyclic voltammetry (Gosser Jr. and Zhang 1991). The cyclic voltammogram for the electrochemical oxidation of ruthenocene in benzonitrile at platinum electrode was simulated. The parameters used in the simulation are given in Table 2.

Table 2
Simulation parameters

- * I_{cap} Calc = n * IR corr = n
- * Initial Potential = -0.1000
- * Switching Potential = 1.3000
- * Final Potential = -0.1000
- * Scan Rate = 0.0500
- * Concentrations – normalized units
1: 1.000 2: 0.000 3: 0.000 4: 0.000
- * Diffusion Coefficients * 1.0000000000000000E-0005
1: 1.000 2: 1.000 3: 1.000 4: 1.000
- * Electrode Reactions
2 + e⁻ ⇌ 1 E = 0.980 khet = 0.0100 A1 = 0.4000
3 + e⁻ ⇌ 4 E = 0.500 khet = 1.0000 A1 = 0.4000
- * Chemical Reactions
2 + 1 = 3 + 0
- * K – forward = 1000.000 * K-Reverse = 0.000
- * Area, Normal Conc., Cap and IR
1.0E-0002 1.0E0006
- * Temperature = 298.150
- * Number of time increments = 280000
- * Number of space increments = 46

A typical simulation is shown in Fig 3. This voltammogram shows good agreement with the experimentally observed cyclic voltammogram featured as in Fig 2 (Diaz *et al* 1982).

The simulation is based on the presumption that the oxidation of ruthenocene proceeds through an EC mechanism reactions (1) and (2) in scheme 1 below:

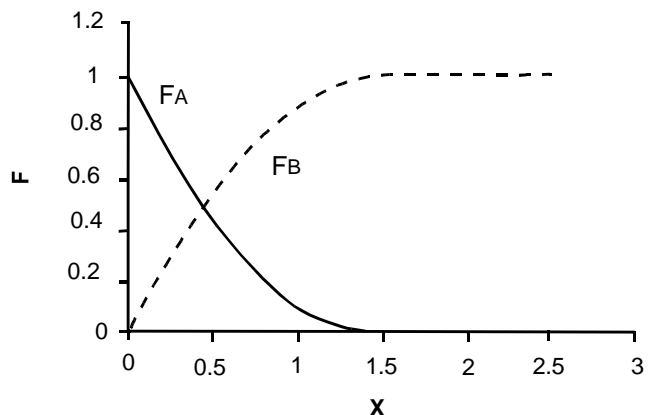
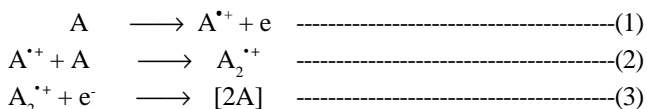


Fig 1. Simulated concentration profile from the simulation program in Table 1, for L= 300, D_M= 0.45, t/t_k= 0.5.

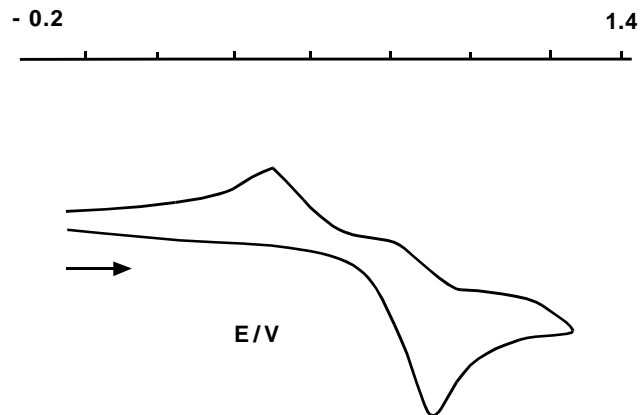


Fig 2. Cyclic voltammogram of ruthenocene in benzonitrile solution containing Bu₄NBF₄ as the electrolyte. The scan rate was 50 m V/s. Potentials are given relative to SCE reference electrode (Diaz *et al* 1982).

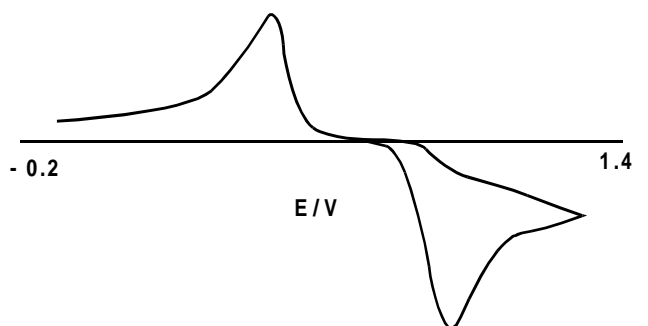


Fig 3. Simulation of cyclic voltammogram of ruthenocene (simulation of Fig 2).

Where A represents ruthenocene. According to this scheme ruthenocene is proposed to undergo a 1-electron oxidation at E_{p,a} = 0.943 V to a monocation, A^{*+} as shown in eq. 1 in scheme 1. The irreversibility of this initial oxidation is caused by the disappearance of the monocation, A^{*+}, due to its inter-

action with a neutral ruthenocene **A** as shown in eq. 2 in scheme 1. The dimeric monocation, A_2^{*+} then reduces at a much lower potential, as shown in eq. 3.

Glossary

Symbol	Meaning	Usual Dimensions
A1	Transfer co-efficient	None
DMA	Model diffusion co-efficient for species A in simulation	None
DMB	Model diffusion co-efficient for species B in simulation	None
FA	Fractional concentration of species A in simulation	None
FB	Fractional concentration of species B in simulation	None
J	Box index in a simulation	None
K	Iteration number in a simulation	None
R	Z/ZCOTT	None
T	Time	Second
t_k	Known characteristic time in a simulation	Second
X	Distance of the centre of the box from the electrode	cm
Z	Dimensionless current parameter in simulation	None
ZCOTT	Dimensionless current calculated from the Cottrell equation	None

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