

## ELECTROCHEMICAL STUDIES OF THE COMPLEX (OC-6-22)-W(CO)<sub>3</sub>(dppm)<sub>2</sub> AT A GLASSY CARBON ELECTRODE IN CH<sub>2</sub>Cl<sub>2</sub>

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Received July 9, 1998

Accepted March 12, 1999

Electrochemical behaviour of tricarbonylbis[methylenebis(diphenylphosphine)] tungsten has been studied by convolution-deconvolution voltammetry and chronopotentiometry with glassy carbon electrode in dichloromethane solution. Electrochemical parameters of the investigated system have been determined and confirmed by theoretical treatment and by the proposed electrode mechanism.

**Key words:** Convolution-deconvolution voltammetry; Chronopotentiometry; Tungsten complexes; Phosphines; Electrochemistry.

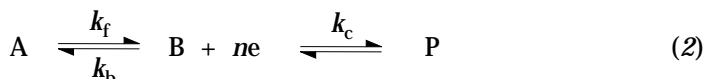
Electrochemical behaviour of some group VI metal dicarbonyl complexes containing two didentate ligands has been thoroughly investigated<sup>1-3</sup>. The general formula for these complexes is M(CO)<sub>2</sub>(L-L)<sub>2</sub>, where M = Cr, Mo, W, and L-L is methylenebis(diphenylphosphine) (dppm) or ethylenebis(diphenylphosphine) (dppe). These complexes form *cis* and *trans* isomers. Upon oxidation of the *cis* isomer, isomerization to the *trans* cation occurs.

It was shown<sup>4-7</sup> that the chemical and electrochemical oxidation of (OC-6-22)-Mn(CO)<sub>3</sub>dppmX (X = Cl, Br) at room temperature gave meridial cation which could be readily reduced to otherwise inaccessible facial form. If the oxidation state of the metal can vary, the situation can be described<sup>8-11</sup> by using the square scheme first proposed by Jacq<sup>12</sup>.

For a simple electron transfer, convolution of the current is obtained from Eq. (1), where *t* is the total elapsed time. However, this does not simplify the treatment of data for an electron transfer followed by a chemical reaction<sup>13-18</sup> (EC mechanism).

$$I_1 = i^* \frac{1}{(\pi t)^{1/2}} = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \quad (1)$$

Hence, in this study we will use a more general convolution for the EC mechanism (irreversible) case<sup>14</sup>. The reaction scheme



(A is reduced species, B oxidized species, and P is the product of the chemical step) yields relationships (3) and (4) for the concentrations of A and B at the electrode<sup>14</sup>

$$C_A(0, t) = C_A^{(\text{init})} - \frac{1}{nFSD^{1/2}} i_{(t)} \cdot \frac{1}{(\pi t)^{1/2}} = C_A^{(\text{init})} - \frac{1}{nFSD^{1/2}} I_1 \quad (3)$$

and

$$C_B(0, t) = \frac{1}{nFSD^{1/2}} i_{(t)} \cdot \frac{e^{-kct}}{(\pi t)^{1/2}} = \frac{1}{nFSD^{1/2}} I_2, \quad (4)$$

where  $n$  is the number of electrons and  $S$  is the electrode area. The diffusion coefficients  $D$  of species A and B are assumed to be equal for the sake of simplification of the equations. Introducing potential from the Butler-Volmer relation gives Eq. (5), where  $I_1$  and  $I_2$  are the convolutions from Eqs (3) and (4), respectively,  $I_{\text{lim}}$  is the limit of  $I_1$  as  $E$  approaches infinity,  $\zeta = (E - E^0)nF/RT$ ,  $i_0$  is the exchange current density for the electron transfer process at  $E = E^0$ ,  $i = nFSk_f^0 C_A^{(\text{init})}$  and  $k_f^0$  is the standard forward heterogeneous rate constant.

$$\frac{I_{\text{lim}}}{i_0} e^{-\alpha\zeta} i = I_{\text{lim}} - I_1 - I_2 e^{-\zeta} \quad (5)$$

Ferrocene is used as an internal standard<sup>19</sup> for electrochemical measurements, in organic solvents at temperatures up to 275 °C. The values of  $k_s = 2.2 \cdot 10^{-3}$  m/s (25 °C) and  $D = 2.6 \cdot 10^{-10}$  m/s for Fc were estimated by Crooks and Bard<sup>20</sup>. Up to scan rates of 0.3 V/s the  $\Delta E_p$  values for ferrocene in DMF are about 60 mV, suggesting reversible one-electron charge transfer<sup>21</sup>. For higher scan rates, the process becomes a quasireversible. In ethanolic solutions<sup>21</sup> Diggle and Parker<sup>22</sup> suggested quasireversible charge transfer ( $k_s = 1.6 \cdot 10^{-4}$  m/s).

Cabon *et al.*<sup>23</sup> observed an 88 mV difference between the anodic and cathodic peak potentials for the FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup> couple in ethylene carbonate at 40 °C, while Courtot-Coupez and L'Her<sup>24</sup> reported  $\Delta E_p = 100$  mV. The observed behaviour was attributed to an uncompensated ohmic drop or, alternatively, to a deviation from reversibility.

An interest has been focused on electrochemistry of group VI metal carbonyl complexes<sup>25,26</sup>.

This work represents the electrochemical study of *fac*-W(CO)<sub>3</sub>(dppm)<sub>2</sub> complex providing further development in organometallic electrochemistry. The electrochemical parameters  $k_s$ ,  $E^0$ ,  $D$ ,  $\alpha$ , and  $k_c$  were determined and the proposed electrode mechanism was discussed.

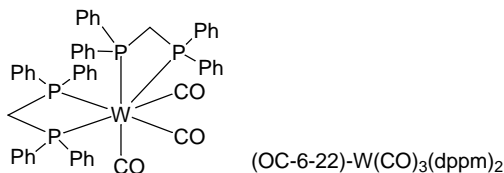
## EXPERIMENTAL

### Instrumentation

Voltammograms and chronopotentiograms were measured in 0.1 M Bu<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup> in dichloromethane using a potentiostat/galvanostat (PAR model 362, EG&G Princeton Applied Research) and a conventional three-electrode cell. Scan rates up to 100 V/s were used in cyclic voltammetry. Background data were subtracted from the experimental data set to minimize double-layer charging currents. Electrochemical measurements were performed with glassy carbon electrode as a working electrode, Ag/AgCl reference electrode in saturated LiCl-CH<sub>2</sub>Cl<sub>2</sub> and 1 cm<sup>2</sup> platinum-sheet counter-electrode. All solutions were degassed with nitrogen and maintained under nitrogen atmosphere throughout the measurements. Data processing and simulations were performed using the Condecon and Condesim software packages (EG&G). The temperature during measurements was kept at 22 ± 2 °C.

### Materials

The investigated complex (OC-6-22)-W(CO)<sub>3</sub>(dppm)<sub>2</sub> provided by Prof. B. Shaw at School of Chemistry, Leeds University, U.K., has the following structure<sup>27</sup>.



Tetrabutylammonium perchlorate (analytical grade) was used as supplied (Fluka, AG). A fresh solution of the investigated complex ( $1 \cdot 10^{-3}$  mol l<sup>-1</sup>) was prepared in 0.1 M TBAP-CH<sub>2</sub>Cl<sub>2</sub>.

## RESULTS AND DISCUSSION

Cyclic voltammogram of  $2.5 \cdot 10^{-4}$  M (OC-6-22)- $W(CO)_3(dppm)_2$  (Fig. 1) exhibits two anodic peaks (1 and 2) at +0.235 and +0.488 V, associated with a cathodic peak (3) at -0.34 V. When the potential is extended in the negative direction, a reduction peak (4) appears at -0.975 V with a coupled oxidative peak (5) at -0.745 V on the reverse scan (Fig. 1). Further extension of potential range to +1.8 and -1.43 V does not bring any additional changes.

TABLE I

Electrochemical parameters for the electrode processes of the complex  $fac-W(CO)_3(dppm)_2$  at glassy carbon electrode, in  $CH_2Cl_2$ , at 294 K using cyclic voltammetry (CV), convolution (conv), deconvolution (deconv) voltammetry and chronopotentiometry (CP) techniques

Parameter	Techniques			
	CV	conv	deconv	CP
$k_s \cdot 10^4, m s^{-1}$	3.00 3.10 <sup>a</sup>	-	-	-
$E^0, V$	-	-	0.285 <sup>b</sup> 0.432 <sup>c</sup> 0.164 <sup>d</sup>	-
$D \cdot 10^{10}, m^2 s^{-1}$	6.50	5.9	-	6.2
$\alpha$	0.61	-	-	-
$k_c, s^{-1}$	10 <sup>e</sup>	-	-	-

<sup>a</sup> Determined theoretically work; <sup>b</sup>  $fac/fac^+$ ; <sup>c</sup>  $fac^+/fac^{2+}$ ; <sup>d</sup>  $mer^+/mer$ ; <sup>e</sup> estimated theoretically for  $fac^+/mer^+$  conversion.

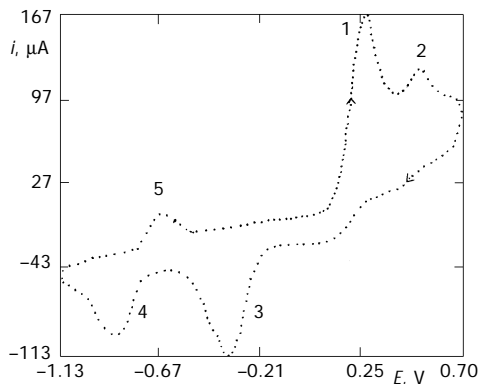


FIG. 1

Cyclic voltammogram for  $fac-W(CO)_3(dppm)_2$  at the glassy carbon electrode (sweep rate 0.2 V/s). 1, 2 Anodic peaks (at +0.235 and +0.488 V), 3 cathodic peak (at -0.34 V), 4 reduction peak (at -0.975 V) and 5 oxidative peak (at -0.745 V)

### Oxidation Process

The current–voltage curve for peaks 1 and 2 (Fig. 1) indicates a fast chemical reaction following a quasireversible electron transfer. At sweep rates higher than 0.2 V/s, the reduction peaks coupled with oxidation peaks 1 and 2 do not appear. According to Nicholson and Shain<sup>28</sup> the values of  $E_p - E_{p/2}$  and  $E_p - E^0$  were used for calculation of the standard heterogeneous rate constant,  $k_s$ , given in Table I as well as for the determination of the transfer coefficient  $\alpha = 0.61 \pm 0.02$  (Eq. (6)).

$$E_p - E_{p/2} = 48/(\alpha n_a) \quad (6)$$

$$i_p = (2.99 \cdot 10^5) n(\alpha n_a)^{1/2} S C^{\text{bulk}} D v^{1/2} \quad (7)$$

After background subtraction and correction for the uncompensated resistance, the diffusion coefficient  $D = (6.5 \pm 0.1) \cdot 10^{-10} \text{ m}^2/\text{s}$  was determined from Eq. (7) and from the  $I_1$  convolution, using relation<sup>14</sup>

$$I_{\text{lim}} = n F S D^{1/2} C^{\text{bulk}}, \quad (8)$$

where  $I_{\text{lim}}$  is the limiting convoluted current for  $I_1$  and the potential driven past the wave. Other terms have their usual meaning. The value of the diffusion coefficient was found to be  $(5.9 \pm 0.1) \cdot 10^{-10} \text{ m}^2/\text{s}$ .

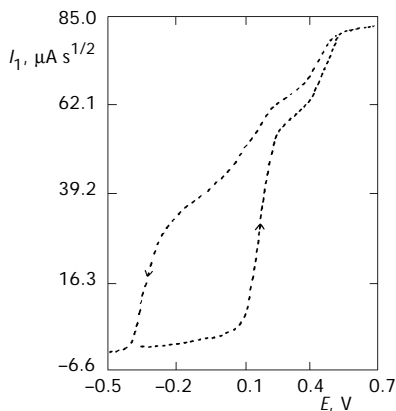


FIG. 2

The  $I_1$  convolution in the oxidation process for the *fac*-W(CO)<sub>3</sub>(dppm)<sub>2</sub> (sweep rate 0.2 V/s)

Figure 2 gives an example of the  $I_1$  convolution of peaks 1 and 2 associated with reduction peak 3 illustrating quasireversibility of the electron transfer.

As shown in Fig. 3 different peak heights in forward and backward sweeps of "deconvoluted" current ( $dI_1/dt$ ) give a strong evidence for a chemical reaction following the quasireversible electron transfer. The mean values of the anodic and cathodic peak potentials were taken as the redox potentials ( $E^0$ ) of the system under consideration. The estimated values of  $E^0$  are given in Table I. The anodic half-peak width ( $W^p$ ) was taken as assertion for the nature of electron transfer<sup>29</sup>. The values found in the range 94–102 mV at  $v = 0.2$  V/s (Table II), confirm the quasireversibility of the system.

Figure 4 shows a chronopotentiogram used for determination of diffusion coefficient of the investigated complex as a support for the value estimated from cyclic and convolution voltammetry. The diffusion coefficient calculated from a chronopotentiometric experiment<sup>29</sup> (Eq. (9)).  $D = (6.2 \pm 0.1) \cdot 10^{-10}$  m<sup>2</sup>/s resembled well the values obtained from CV and convoluted  $I_{lim}$  (Table I).

TABLE II

Wave characteristics of the *fac*-W(CO)<sub>3</sub>(dppm)<sub>2</sub> complex extracted from cyclic and convolution–deconvolution voltammetry by digital simulation techniques at 0.2 V/s

Parameter	<i>fac</i> / <i>fac</i> <sup>+</sup>	<i>fac</i> <sup>+</sup> / <i>fac</i> <sup>++</sup>	<i>mer</i> <sup>+</sup> / <i>mer</i>
$E_p - E_{p/2}$ , mV	50.0	75.8	70.7
$E_p - E^0$ , mV	30.4	25.3	50.5
$W^p$ , mV	100.0	94.0	102.0
$\Delta E_{pdeconv}$ , mV	10.0	10.2	30.4
$\frac{(dI_1/dt)_f}{(dI_1/dt)_b}$	4.99	2.52	5.36

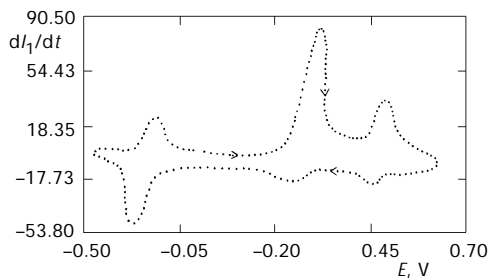


FIG. 3  
Differentiated current of the oxidation process of *fac*-W(CO)<sub>3</sub>(dppm)<sub>2</sub> (sweep rate 0.2 V/s)

$$I_{\text{lim}} = 2 i_c (t_s/\pi)^{1/2} \quad (9)$$

Here  $i_c$  is the current and  $t_s$  is the transition time.

Simulated cyclic voltammograms of the first anodic and associated peaks were used for testing the experimentally evaluated kinetic parameters. Figure 5 shows a good agreement between experimental and simulated data for the (OC-6-22)-W(CO)<sub>3</sub>(dppm)<sub>2</sub>, confirming the accuracy of experimental electrochemical parameters.

The course of the  $I_1$  convolution shown in Fig. 2 suggests that the electrode process involves the isomerization mechanism. In the forward sweep only EC<sub>irr</sub> reaction (10) takes place assuming that meridial species is absent initially. The time spent in potential regions of the non zero  $I_1$  implies the formation of the facial cationic species ( $fac^+$ ), and, consequently, of the isomeric meridial ( $mer^+$ ) form.



In the reverse sweep, an important diagnostic point is given by the  $I_1$  convolution return to zero which indicates complete conservation of material

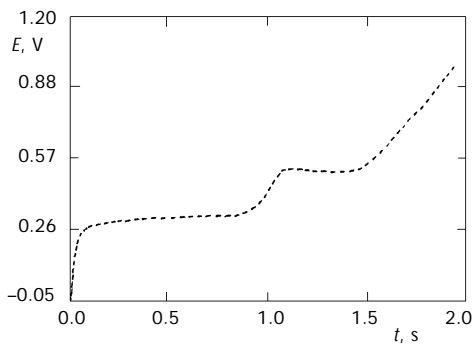


FIG. 4

Chronopotentiogram for the oxidation of  $fac$ -W(CO)<sub>3</sub>(dppm)<sub>2</sub> at the glassy carbon electrode

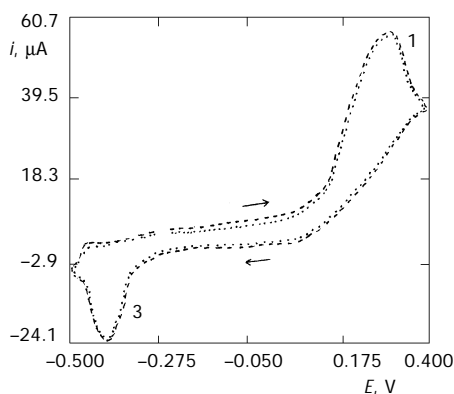


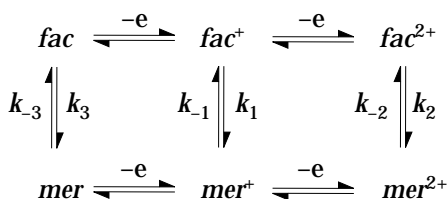
FIG. 5

Cyclic voltammograms showing the first anodic peak (1) with the associated peak (3) for  $fac$ -W(CO)<sub>3</sub>(dppm)<sub>2</sub> at the glassy carbon electrode: - - - experimental, . . . theoretical (sweep rate 0.1 V/s)

within the proposed scheme. Side reactions to nonelectroactive species are evidenced by means of failure to return  $I_1$  to zero at the end of the experiment.

Due to the absence of reduction peaks coupled to peaks 1 and 2 in the reverse sweep up to the rate of 5 V/s, the homogeneous rate constant ( $k_c$ ) of the isomerization reaction is not determined by kinetic convolution ( $I_2$ ). The value of  $k_c$ , yielding a good agreement between the experimental and formulated voltammograms, was taken instead.

On the basis of the above discussion we have to invoke the following scheme.



### Reduction Process

A typical cyclic voltammogram for the reduction of (OC-6-22)- $W(CO)_3(dppm)_2$  in  $CH_2Cl_2$  in 0.1 M TBAP at a GC-electrode and sweep rate 0.2 V/s is shown in Fig. 6. The reduction wave observed in this process involves quasireversible one electron reduction followed by a chemical step (EC mechanism). The reverse scan shows a wave corresponding to one-electron oxidation. The cathodic peak potential ( $E_{pc}$ ) of the reduction wave

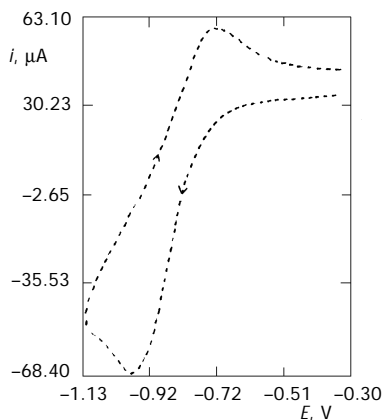


FIG. 6  
Voltammogram for the reduction process of the investigated complex at the glassy carbon electrode (sweep rate 0.2 V/s)



is located at  $-0.975$  V, while the anodic peak potential ( $E_{pa}$ ) of oxidation wave is located at  $-0.745$  V. In the selected range of scan rates, the difference in the peak potentials ( $\Delta E_p = E_{pa} - E_{pc}$ ) is  $230.0 \pm 5$  mV, larger than expected 58 mV for one-electron Nernstian process<sup>28</sup>. This can be attributed to the slow rate of electron transfer in addition to some uncompensated solution resistance in the CH<sub>2</sub>Cl<sub>2</sub> solution<sup>30</sup>.

The values of  $k_s$ ,  $D$ ,  $\alpha$ , and  $E^0$ , determined experimentally from cyclic voltammetric data are shown in Table III.

TABLE III

Values of kinetic parameters obtained from the reduction process of the investigated complex at glassy carbon electrode using cyclic (CV), convolution (conv), deconvolution (deconv) voltammetry and chronopotentiometry (CP) techniques

Parameter	Techniques			
	CV	conv	deconv	CP
$k_s \cdot 10^5, \text{m s}^{-1}$	1.72	-	-	-
$E^0, \text{V}$	-0.850	-0.852 <sup>a</sup>	-0.851	-
$D \cdot 10^{10}, \text{m}^2 \text{s}^{-1}$	7.20	7.30	-	7.15
$\alpha$	0.35	-	-	-
$k_c, \text{s}^{-1}$	-	1.5	-	-

<sup>a</sup> Determined from combination of the  $I_{lim} - I_1$  with  $I_2$  convolution.

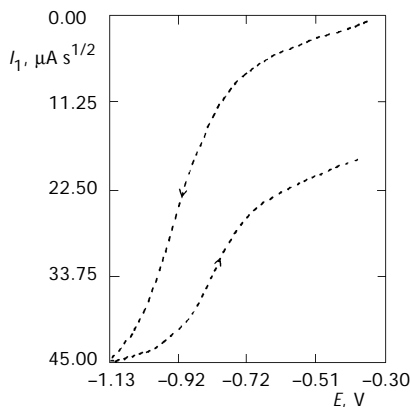


FIG. 7

The  $I_1$  convolution of the reduction process for *fac*-W(CO)<sub>3</sub>(dppm)<sub>2</sub> (sweep rate 0.2 V/s)

The EC mechanism for reduction process was evidenced from the  $I_1$  convolution where  $I_1$  does not return to its initial value at the end of scan (Fig. 7). Also, the missing coincidence of backward and forward sweeps indicates deviation from the Nernstian behaviour. The diffusion coefficient ( $(7.3 \pm 0.1) \cdot 10^{-10} \text{ m}^2/\text{s}$ ) (Eq. (8)) was in accord with the value calculated from CV.

Figure 8 shows the "kinetic" convolution ( $I_2$ ) of the investigated complex at  $v = 0.2 \text{ V/s}$ , representing the evaluation of the homogeneous rate constant of chemical reaction ( $k_c$ ) in nonaqueous medium at GC-electrode. The true value of  $k_c$  was calculated by iteration performed until  $I_2$  returned to zero<sup>14</sup> yielding  $k_c = 1.5 \text{ s}^{-1}$ .

The  $E^0$  of the complex  $\text{W}(\text{CO})_3(\text{dppm})_2$  at GC-electrode in  $\text{CH}_2\text{Cl}_2$ -0.1 M  $\text{Bu}_4\text{NClO}_4$  was determined from  $I_{\text{lim}} - I_1$  and  $I_2$  vs  $E$  (applied potential) plot at  $v = 0.2 \text{ V/s}$  (Fig. 9). Crossing points in this diagram give the true value of  $E^0$ . The slight displacement of the crossing points from the true  $E^0$  value

TABLE IV

Wave characteristics of the (OC-6-22)- $\text{W}(\text{CO})_3(\text{dppm})_2$  complex extracted from cyclic and convolution-deconvolution voltammetry

$v, \text{ V s}^{-1}$	$\Delta E_p, \text{ mV}$	$I_{1(\text{end})}, \mu\text{A s}^{1/2}$	$\Delta E_{\text{pdeconv}}, \text{ mV}$	$W^p, \text{ mV}$	$\frac{(dI_1/dt)_f}{(dI_1/dt)_b}$
0.1	172.3	-5.197E-5	58.6	132.0	1.85
0.2	230.3	-4.560E-5	91.3	149.0	1.80
0.5	253.3	-3.951E-5	115.8	153.0	1.78
1.0	294.2	-3.415E-5	148.9	181.2	1.75
2.0	326.9	-3.033E-5	177.1	198.7	1.67

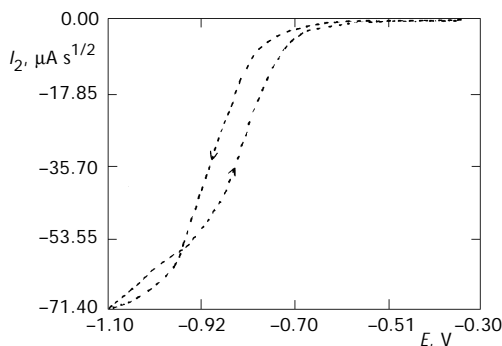
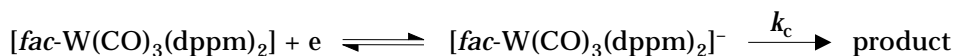


FIG. 8  
Kinetic convolution ( $I_2$ ) of the cathodic peak for *fac*- $\text{W}(\text{CO})_3(\text{dppm})_2$  (sweep rate  $0.2 \text{ V/s}$ )

can be explained by the uncompensated resistance. This method provides a new way of evaluation of  $E^0$  in agreement with that obtained from cyclic voltammetry and differentiation voltammetry.

Digital simulations of the voltammograms were used to test the validity of the EC model. The  $E^0$  values, the standard heterogeneous rate constant ( $k_s$ ), chemical rate constant ( $k_c$ ), diffusion coefficients ( $D$ ), and the transfer coefficient ( $\alpha$ ) were taken for generation of simulated cyclic voltammograms. Figure 10 shows an agreement between simulation and experiment at  $\nu = 0.2$  V/s. It confirms the suggested electrode mechanism as well as the accuracy of determined electrochemical parameters listed in Table IV.

Accordingly, the reduction process corresponds to the following scheme.



## CONCLUSION

It can be concluded that, the electrochemical oxidation of complex  $fac-W(CO)_3(dppm)_2$  in  $CH_2Cl_2$ -0.1 M TBAP at GC-electrode takes place in two anodic peaks associated with a cathodic process. Scanning in the negative direction reveals a reduction peak coupled with oxidation peak. The

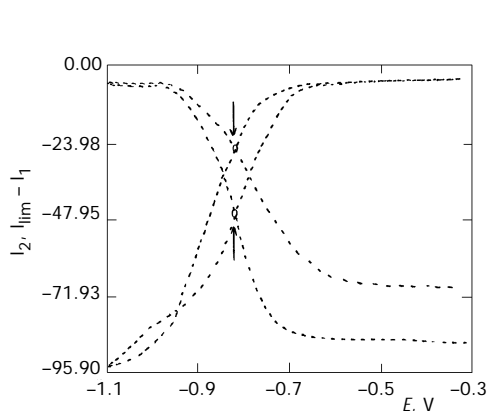


FIG. 9  
Combination of  $I_{2,lim} - I_1$  with  $I_2$  for the cathodic peak of  $fac-W(CO)_3(dppm)_2$  vs applied potential  $E$  (sweep rate 0.2 V/s)

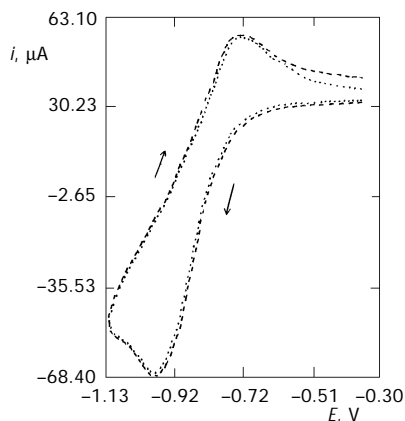


FIG. 10  
Voltammograms of the reduction wave for  $fac-W(CO)_3(dppm)_2$  at the glassy carbon electrode: - - - experimental, · · · theoretical (sweep rate 0.2 V/s)

electrochemical parameters and the electrode mechanism of above processes were determined and discussed.

The  $I_1$  convolution of oxidation process indicated that the isomerization process is involved while the reduction consists of quasireversible charge transfer followed by fast chemical step indicating EC reaction scheme. The redox potential  $E^0$  for the reduction process was obtained using new method from  $I_1$  and  $I_2$  convolution versus the applied potential, while for the oxidation process  $E^0$  was determined from deconvolution voltammetry. From the variation of  $\Delta E_p$  with  $v$ , the mean value of  $k_s = (1.72 \pm 0.2) \cdot 10^{-5}$  m/s for the reduction process was determined. The diffusion coefficient  $D = (6.6 \pm 0.2) \cdot 10^{-10}$  m<sup>2</sup>/s of the complex evaluated from the limiting convoluted current is in a good agreement with values obtained from other methods.

*The authors are grateful to Prof. B. Shaw, School of Chemistry, University of Leeds, U.K., for preparing and providing the investigated complex.*

## REFERENCES

1. Wimmer F. L., Snow M. R., Bond A. B.: *Inorg. Chem.* **1974**, *13*, 1617.
2. Bond A. M., Colton R., Jackowski J. J.: *Inorg. Chem.* **1975**, *14*, 274.
3. Bond A. M., Grabaric B. S., Jackowski J. J.: *Inorg. Chem.* **1978**, *17*, 2153.
4. Bond A. M., Colton R., McCormick M. J.: *Inorg. Chem.* **1977**, *16*, 155.
5. Bond A. M., Grabaric B. S., Grabaric Z.: *Inorg. Chem.* **1978**, *17*, 1013.
6. Bond A. M., Colton R., McDonald M. E.: *Inorg. Chem.* **1978**, *17*, 2842.
7. Bond A. M., Darensboarg D. J., Mocellin E., Stewart B. J.: *J. Am. Chem. Soc.* **1981**, *103*, 6827.
8. Rieke R. D., Kojima H., Ofele D. J.: *J. Am. Chem. Soc.* **1976**, *58*, 6735.
9. Bond A. M.: *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *50*, 285.
10. Mugnier Y., Moise C., Lauiron E.: *J. Organomet. Chem.* **1981**, *204*, 61.
11. Faure D., Lexa D., Saveant J. M.: *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *140*, 269.
12. Jacq J.: *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *29*, 149.
13. Grenness M., Oldham K. B.: *Anal. Chem.* **1972**, *44*, 1121.
14. Blagg A., Carr S. W., Cooper G. R., Dobson I. D., Jill J. B., Goodal D. C., Shaw B. L., Taylor N., Boddington T.: *J. Chem. Soc., Dalton Trans* **1985**, 1213.
15. Imbeaux J. C., Saveant J. M.: *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *44*, 169.
16. Nadjo L., Saveant J. M., Tessier D.: *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *52*, 403.
17. Saveant J. M., Tessier D.: *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *61*, 251.
18. Saveant J. M., Tessier D.: *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *65*, 57.
19. Gangne R. R., Koval C. A., Lisensky G. C.: *Inorg. Chem.* **1980**, *19*, 28543.
20. Crooks R. M., Bard A. J.: *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *243*, 117.

21. Zara A. J., Machado S. S., Bulhoes L. S., Benedetti A. V., Rabockai T.: *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, 221, 165.
22. Diggle J. W., Parker A. J.: *Electrochim. Acta* **1973**, 18, 975.
23. Cabon J. Y., L'Her M. L., LeDemezet M.: *Bull. Soc. Chim. Fr.* **1975**, 1020.
24. Courtot-Coupez J., L'Her M.: *Bull. Soc. Chim. Fr.* **1970**, 1631.
25. Bond A. M., Carr S. W., Colton R.: *Inorg. Chem.* **1984**, 23, 2343.
26. Bond A. M., Carr S. W., Colton R.: *Organometallic* **1984**, 3, 541.
27. a) Carr S. W., Shaw B. L.: *J. Chem. Soc., Dalton Trans.* **1986**, 1815; b) Shaw B. L.: Personal communication.
28. Nicholson R. S., Shain I.: *Anal. Chem.* **1964**, 36, 706.
29. El-Hallag I. S., Ghoneim M. M.: *Monatsh. Chem.* **1996**, 127, 487.
30. Gaudiello J. G., Wright T. C., Jones R. A., Bard A. J.: *J. Am. Chem. Soc.* **1985**, 107, 888.