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Mechanistic Studies on *trans*-Dicarbonyl Phosphine Complexes of Molybdenum(I)

Refat ABDEL-HAMID,* Ahmed A. EL-SAMAHY, Mostafa K. M. RABIA,
Norman TAYLOR,† and Bernard L. SHAW†
Department of Chemistry, Faculty of Science, Sohag University, Sohag, Egypt
†School of Chemistry, University of Leeds, Leeds Ls2 9JT, U. K.

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The electrode mechanism of *trans*-dicarbonyl phosphine complexes of molybdenum(I), *trans*-[Mo(CO)$_2$(P-P)$_2$]PF$_6$ [where P-P=ph$_2$PCH$_2$CH$_2$Pph$_2$(dppe), or ph$_2$PCH=CHPph$_2$ (dppen)] was investigated by cyclic voltammetry and convolution and deconvolution potential sweep voltammetry in 0.1 mol dm^{-3} TBAP/CH$_2$Cl$_2$ solution at a platinum electrode. The complexes are both oxidized and reduced in one-electron processes. The oxidation and reduction processes are follows a well-defined EC$_{\mathrm{irrev}}$ mechanism. Digital simulation and comparison with the experimental cyclic voltammetric results was used for determination of homogeneous and heterogeneous rate constants values.

The chemical and electrochemical oxidation of 18-electron metal carbonyl complexes has been investigated extensively in the past few years.[1—10] After loss of one or more electrons, the resulltant formally 17- or 16-electron species tend to be labile and undergo a wide range of chemical reactions. The stereochemistry of these electrochemical reactions has also been investigated.

The present work describe the electrochemical redox behavior of two of 17-electron metal carbonyl complexes viz. *trans*-[Mo(CO)$_2$(dppe)$_2$]PF$_6$ and *trans*-[Mo(CO)$_2$(dppen)$_2$]PF$_6$. The objective is to deduce the electrode machanism of the redox reactions. The sequence of the individual electron transfer and chemical steps comprising the overall redox process is described for each complex. These studies were carried out in dichloromethane using cyclic voltammetry and convolution and deconvolution potential sweep voltammetry. The proposed mechanism was confirmed using digital simulation. Moreover, homogeneous and heterogeneous rate constants of the redox reactions were determined on the comparison of experimental and simulated cyclic voltammetric data.

Experimental

Materials: The dichloromethane (HPLC grade), solvent was dried and stored under nitrogen over 4A molecular sieves. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was recrystallized twice from pure ethanol, vacuum dried at[1] room temperature, and stored in a vacuum desicator. *trans*-[Mo(CO)$_2$(dppe)$_2$]PF$_6$ and *trans*-[Mo(CO)$_2$(dppen)$_2$]PF$_6$ were prepared according to literature procedures.[11]

Electrochemical Measurements: Measurements were made in the three-electrode configuration with a platinum disk working electrode having a geometrical surface area of around 0.2 cm^2. The reference electrode was Ag in saturated LiCl/CH$_2$Cl$_2$. A 1 cm^2 platinum sheet auxiliary electrode was used. All experiments were performed at 20 °C in CH$_2$Cl$_2$ containing 0.1 mol dm^{-3} TBAP as supporting electrolyte. Solutions were purged with nitrogen before each experiment and an atmosphere of nitrogen was maintained above the working solution. Internal resistance ohmic drop distortions were minimized by applying the positive feedback compensation available at the potentiostate.

Cyclic voltammetry was performed using an EG & G PAR model 363 potentiostat/galvanostat and model 175 universal programmer. The current response and applied potentials were stored on magnetic disk via a fast capture system, based upon twin channel 12-bit analogue-to-digital converter (50 μs conversion time) and a GEMINI GALAXY 1 microcomputer. The data capture routine was written in Macro 80 Assembler Language which allowed a minimum acquisition time of 100 μs per point. In all experiments 500 data points were routinely captured, equally spaced in time and with a time interval appropiate to the time scale of the particular experiment. Background data were also stored and were substracted from the experimental data set, minimizing effects such as double layer charging currents.

Treatment of Electrochemical Data: The general relationship between the curren and convolutions of the currents for E and EC$_{\mathrm{irrev.}}$ mechanisms for any voltammetric response is given by[12)]

$$\frac{iD_{\mathrm{A}}^{1/2}\mathrm{e}^{-\alpha f}}{k_{\mathrm{f}}^{\circ}} = I_{\mathrm{lim}} - I_1 - I_2(D_{\mathrm{A}}/D_{\mathrm{B}})^{1/2}\mathrm{e}^{-f} \qquad (1)$$

where D_{A} and D_{B} are respective diffusion coefficients of reactant and product, α and k_{f}° are the symmetry factor and standard heterogeneous rate constant of the electron transfer process, and f is the dimensionless voltage deprature from E° i. e. $f=(E-E^{\circ})nF/RT$. Here n is the number of electron transferred. The convolution I_1 and I_2 are as follows: for E processes

$$I_1(=I_2) = 1/\pi^{1/2}\int_0^t [i(u)/(t-u)^{1/2}]\mathrm{d}u \qquad (2)$$

where as for EC$_{\mathrm{irrev}}$ I_2 takes the form

$$I_2 = I_2(k_{\mathrm{c}}, t) = 1/\pi^{1/2}\int_0^t [i(u)\exp[-k_{\mathrm{c}}(t-u)]/(t-u)^{1/2}]\mathrm{d}u \qquad (3)$$

Digital Simulation: A digital simulation program using based on the explicit-finite-difference method[13)] was used to generate the theoretical cyclic voltammograms and hence to calulate K_h° and K_c (heterogeneous and homogeneous rate constants, respectively).

Results and Discussion

The electrochemical properties of *trans*-dicarbonyl bis(diphenylphosphino)ehane- and *trans*-dicarbonyl bis(diphenylphosphino)ethene molybdenum(1+) complexes were investigated at platinum electrode in dichloromethane solutions containing 0.1 mol dm^{-3} TBAP as supporting electrolyte. Figure 1A shows (as an example) a cyclic voltammogram of *trans*-[Mo(CO)$_2$(dppe)$_2$]PF$_6$ over a potential range of +1.2 to −0.4 V relative to Ag (in saturated LiCl/0.1 mol dm^{-3} TBAP/CH$_2$Cl$_2$). The sweep here commenced at 0.0 V and went initiallty to more positive potentials. The distinctive feature of the whole voltammogram is that, *trans*-[Mo(CO)$_2$(dppe)$_2$PF$_6$ exhibits two voltammetric waves, an irreversible oxidation wave (Ia) with peak located at +1.04 V and a more reversible reduction (IIc) with peak at −0.216 V. On multicycling of the voltammograms, another oxidation wave (IIIa) appears at +0.149 V. This wave (IIIa) is related to the oxidation of products formed by reduction wave (IIc).

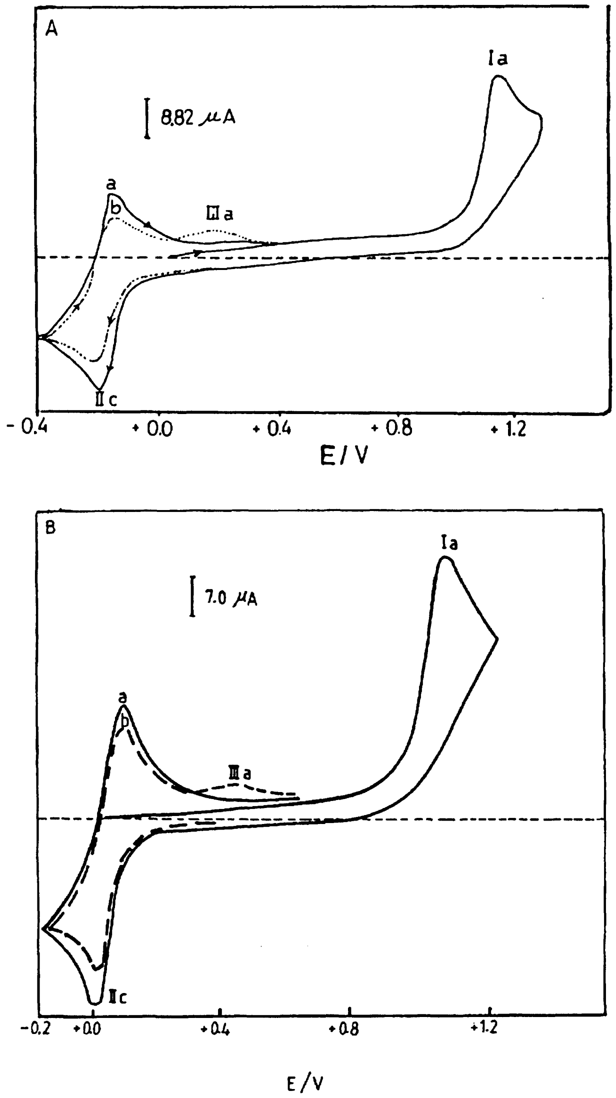

Fig. 1. Cyclic voltammograms in 0.1 M TBAP/CH$_2$Cl$_2$ of 8.5×10^{-4} mol dm^{-3} of both A) *trans*-[Mo(CO)$_2$(dppe)$_2$]PF$_6$ and B) *trans*-[Mo(CO)$_2$(dppen)$_2$]PF$_6$, ν=500 mV s^{-1} (a) 1st cycle (b) 10th cycle (1 M=1 mol dm^{-3}).

The dependence of the peak current, i_p, of the oxidation CV wave (Ia) on the square root of the scan rate, $\nu^{1/2}$, is linear with correlation coefficient, r, of 0.9996. Likewise the reduction wave (IIc) correlates with $\nu^{1/2}$ with r=1.0. This indicates that, these waves are virtually diffusion-controlled[14] in nature but more rigorous electrochemical criteria to establish the nature of these two waves will be made.

Only the anodic peak of the oxidation wave is observed with peak width, $E_p - E_{p/2}$, (see Table 1A) deviating only slightly from the expected value for a 'reversible' i. e. fast one-electron transfer process ($E_p - E_{p/2} = 55.5/n$ mV at 293 K).[15] This indicates that, probably a chemical irreversibility is mainly responsible for the lack of a return wave. Moreover, the peak current potential, E_p, shifts towards more negative potentials to the extent of 26.7 mV per decade according to the following linear least-square equation:

$$E_p/\mathrm{V} = 1.052 + 0.0267 \log (\nu/\mathrm{V\,s^{-1}}) \quad r = 0.952 \qquad (4)$$

From the general relationship Eq. 1, it is seen that the plateau $I_{\lim}$ should not depend on sweep rate for an EC$_{\mathrm{irrev}}$ mechanism and this is born out by the results of Table 2A. Results are thus consistent with an EC$_{\mathrm{irrev}}$ mechanism i. e.

$$\begin{aligned} &trans-[\mathrm{Mo(CO)_2(dppe)_2}]^{+} \rightleftharpoons \\ &\quad trans-[\mathrm{Mo(CO)_2(dppe)_2}]^{2+} + \mathrm{e}^{-} \\ &\qquad \downarrow \text{rapid} \\ &\text{Rearrangment and/or decomposition products} \end{aligned} \qquad (5)$$

It is also observed that convoluted data I_1 neither returns to its initial (zero) value nor superimposes during the reverse half of the sweep with I_1 on the forward one regardless of the scan rate.

Deconvolution ($\mathrm{d}I_1/\mathrm{d}t$) of the cyclic voltammetric results of Ia reveal here the limited response (ca. 20%) on the return sweep. The small return deconvoluted current peak is however found at a similar potential to the forward peak ($\Delta E_p \approx 13.4$ mV at ν=1000 mV s^{-1}, cf. Table 2A) demonstrating that slow electron transfer is not evident and therefore not responsible for the shape of the wave.

To estimate the k_c ($\mathrm{B} \xrightarrow{k_c} \mathrm{P}$) value, the relative heights of the deconvoluted peaks were used in a comparison of the experimental with simulated data. This is still expedient even with the almost total lack of current "after the wave" and also yields k_h°.

Table 1. Cyclic Voltammetric Data for 8.5×10^{-4} mol dm^{-3} *trans*-$Mo(CO)_2(P\text{-}P)_2]PF_6$ at 293 K

A: Oxidation Wave (Ia)

P-P	dppe			dppen		
ν	i_p	E_p	$E_p-E_{p/2}$	i_p	E_p	$E_p-E_{p/2}$
mV s^{-1}	µA	V	mV	µA	V	mV
100	14.08	1.028	61.00	13.11	1.073	61.00
200	18.94	1.030	60.50	18.06	1.078	59.00
500	29.94	1.040	55.00	27.49	1.095	62.00
1000	40.77	1.055	58.10	37.05	1.103	58.00

B: Reduction Wave (IIc)

P-P	dppe						dppen					
ν	$-i_p$	$-E_{pc}$	ΔE_p	$E_{p/2}-E_p$	i_{pa}/i_{pc}	$i_p/\nu^{1/2}$	$-i_p$	E_{pc}	ΔE_p	$E_{p/2}-E_p$	i_{pa}/i_{pc}	$i_p/\nu^{-1/2}$
mV s^{-1}	µA	V	mV	mV		µA V$^{-1/2}$	µA	V	mV	mV		µA V$^{-1/2}$
100	15.1	0.214	65	57.4	0.93	47.9	11.2	0.029	64	61	0.90	35.4
200	21.1	0.215	64	61.4	0.96	47.2	16.1	0.029	64	59	0.95	36.0
500	32.6	0.216	65	59.8	0.97	46.1	25.8	0.028	63	56	0.98	36.5
1000	45.4	0.211	60	56.8	0.97	45.4	36.0	0.028	63	57	0.96	36.0

Table 2. Convolution and Deconvolution Voltammetric Data for 8.5×10^{-4} mol dm^{-3} *trans*-$[Mo(CO)_2(P\text{-}P)_2]PF_6$ at 293 K

A: Oxidation Wave (Ia)

P-P	dppe					dppen				
ν	I_{lim}	E_{pa}	ΔE_p	dI_{pc}/dI_{pa}	$W_{1/2}$	I_{lim}	E_{pa}	ΔE_p	dI_{pc}/dI_{pa}	$W_{1/2}$
mV s^{-1}	µA	V	mV		mV	µA	V	mV		mV
100	1.7	0.989	18	0.21	97.0	1.6	1.043	20	0.26	98.5
200	1.6	1.004	20	0.19	94.5	1.6	1.049	19	0.26	96.7
500	1.55	1.020	17	0.19	94.0	1.5	1.062	16	0.28	92.9
1000	1.55	1.030	13	0.20	92.5	1.4	1.070	12	0.30	91.8

B: Reduction Wave (IIc)

P-P	dppe					dppen				
ν	I_{lim}	E_{pc}	ΔE_p	dI_{pa}/dI_{pc}	$W_{1/2}$	I_{lim}	E_{pc}	ΔE_p	dI_{pa}/dI_{pc}	$W_{1/2}$
mV s^{-1}	µA	V	mV		mV	µA	V	mV		mV
100	1.8	0.185	3.0	0.92	98.5	1.4	0.057	0.0	0.91	91.5
200	1.8	0.184	1.0	0.96	99.1	1.4	0.061	1.0	0.94	91.3
500	1.7	0.185	3.0	0.98	94.5	1.3	0.062	1.0	0.97	92.9
1000	1.7	0.182	1.0	0.98	98.2	1.3	0.056	4.0	0.95	92.2

Also the general relationship shows that I_2 reaches zero at the end of the sweep when the correct k_c value is used. This method loses sensitivity as the return currents are progressively reduced but did yield values broadly in line with those obtained with simulation.

The CV reduction wave IIc is nearly reversible since ΔE_p and $(E_{p/2}-E_p)$ are 60—65 mV and 56.8—61.4 mV, respectively dependent on scan rate (cf. Table 1B). The theoretical values for the reversible system are 58/n mV[16)] and 55.5/n mV,[15)] respectively at 293 K. Moreover, the deviation of the anodic to cathodic peak currents ratio, i_{pa}/i_{pc}, is within 4% of unity. The peak current, i_p, correlates with the square root of scan rate, $\nu^{1/2}$, (r=1.0) and also the ratio $i_p/\nu^{1/2}$ is almost invariant on increasing the scan rate demonstrating that these tests are not particularly sensitive to some deviation from reversible behavior. All the above evidences suggest that, the reduction wave IIc is a quasi-reversible, one-electron transfer diffusion-controlled process.[14,17)]

On multicycling, at slow scan rate another oxidation wave (IIIa) appears at +0.149 V (cf. Fig. 1A). On examination of the electrochemical redox behavior of the cis-isomer of the subject complexes at the same conditions, it reveals that their cyclic voltammograms exhibits two CV waves in the voltage range of +0.3 to −0.4 V. The first is an irreversible oxidation wave at +0.146 V and the second is a revesible reduction one at −0.219 V. Thus, this peak is attributed to a slow-isomerization of the *trans*-metal(0) complexes generated on reduction to cis-configuration giving a total behaviour of EC_{irrev} with a small k_c i. e.

$$\begin{aligned} &\mathit{trans}-[Mo(CO)_2(dppe)_2]^+ + e^- \rightleftharpoons \\ &\qquad \mathit{trans}-[Mo(CO)_2(dppe)_2]^\circ \\ &\qquad\qquad \downarrow k_c \text{ small} \\ &\qquad \mathit{cis}-[Mo(CO)_2(dppe)_2]^\circ \end{aligned} \tag{6}$$

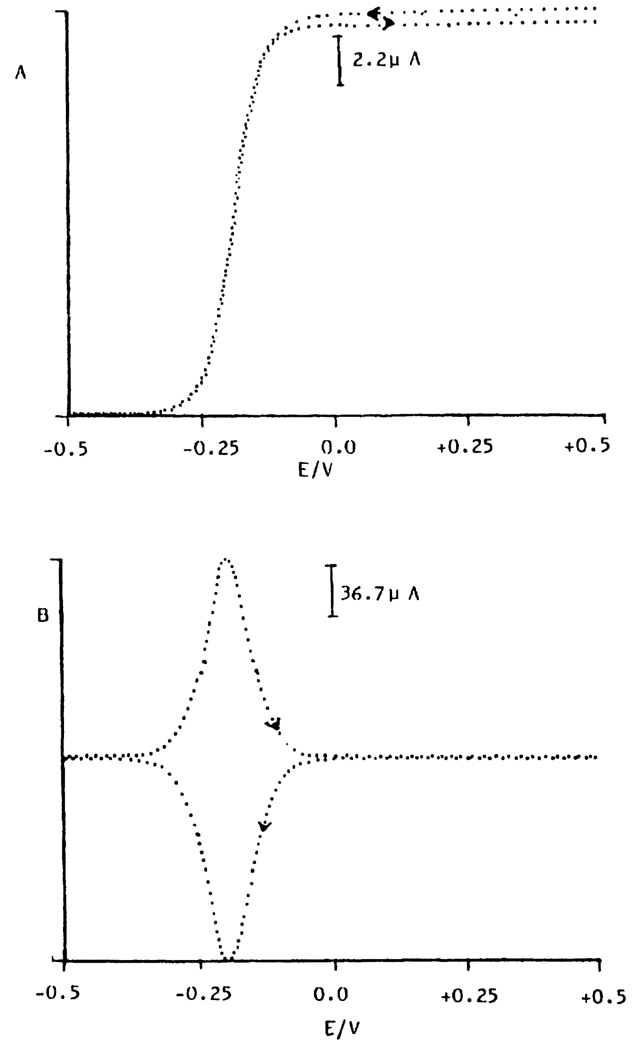

Fig. 2. A) Convolution and B) deconvolution voltammograms, for the reduction of 8.5×10^{-4} mol dm^{-3} *trans*-[Mo(CO)$_2$(dppe)$_2$]PF$_6$, ν=500 mV s^{-1}.

Thus I_l returns during the reverse halfe, to its initial (zero) value (cf. Fig. 2A) at the faster scan rates but on the other hand, at slow scan rate (ca. 50 mV s^{-1}) I_l does not 'return'. This is reflected even more clearly in deconvolution Fig. 2B. This again is completely consistent with the slow isomerisation proposed. The value of k_c (0.045 s^{-1}) for the isomerisation follow-up chemical reaction was obtained from the comparison of the experimental with the simulated data using the 'shrinking' of the reverse deconvoluted peak and the appearance of the cis species. This was accomplished necessarily at several scan rates to confirm proposals. Figure 3A illustrates some of the data obtained at 50 mV s^{-1}.

The number of electrons, n, transferred in the reduction process are determined from the half-peak width, $W_{1/2}$, of the deconvoluted peak. For a 'reversible' system $W_{1/2}$=89.1/n mV at 20 °C. The $W_{1/2}$ values obtained (cited in Table 2B) indicate that, the reduction process is an almost 'reversible' one-electron transfer. A sharpes peak would be observed for higher values of n.

A logarithmic analysis of the convoluted data can likewise be used to establish n from the slope of the polarographic relationship

$$(E - E_{1/2}) = RT/nF \ln\left[(I_{\mathrm{lim}} - I_l)/I_l\right] \quad (7)$$

(where $E_{1/2} = E^\circ + RT/nF\ \ln(D_A/D_B)$ is the "half-wave" potential and E° is the standard electrode potential, $I_{\mathrm{lim}} = (nFAC^{\mathrm{BULK}}D_A^{1/2})$ is the limit of I_l as E approaches infinity, and D_A is the diffusion coefficient of the oxidized or reduced bulk species). These tests to determine n from a slope etc. do not require complete adherence to reversibility. The 'polarographic' relationship yields

$$E = (-0.183+0.00) + (39.08\pm0.27)\ln\left[(I_{\mathrm{lim}} - I_l)/I_l\right] \quad r = 1.0 \quad (8)$$

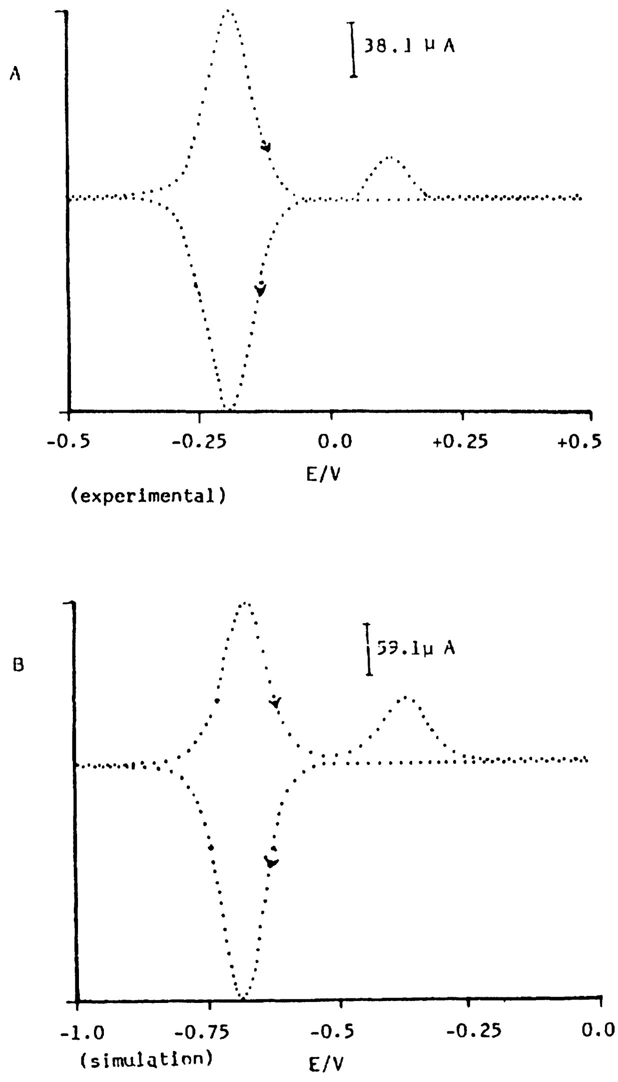

Fig. 3. Cyclic deconvolution voltammograms for the reduction of 8.5×10^{-4} mol dm^{-3} *trans*-[Mo(CO)$_2$(dppe)$_2$]PF$_6$, ν=50 mV s^{-1}.

i. e. slope close to 39.6 V^{-1} (at 293 K) which is expected for the 'reversible' one-electron transfer process.

Digital simulation of the voltammograms was also used to determine the heterogeneous rate constant of the electron-transfer, k°_{h}. In a simulation the E° values, the standard heterogeneous rate constants (k°_{h1} and k°_{h2}), the chemical rate constant (k_{c}), the transfer coefficient (α), and the diffusion coefficients ($D_{\text{A}}=D_{\text{B}}$) must all be introduced by trial and error. The peak to peak separation, ΔE_{p}, of the deconvoluted data from experimental is used as a sensitive test for the determination of the heterogeneous rate constant of the electron transfer by comparison with simulated data, α was assumed to be 0.5. The effectiveness of the digital simulation procedure is illustrated in Fig. 3B for the reduction process IIc as an example. The values of heterogeneous rate constant obtained for the oxidation and reduction waves are 9.5×10^{-3} and 8.7×10^{-4} s^{-1} (dppe) and 0.15×10^{-1} and 1.05×10^{-3} s^{-1} (dppen). The values indicate that, the oxidation wave Ia and the reduction wave IIc are both consistent with a quasi-reversible one-electron transfer process with a coupled irreversible chemical reaction.

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