Facile Analysis of EC Cyclic Voltammograms

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It has been found empirically that, for an $E_{rev}C_{irrev}$ process, the forward/backward ratio of the peak height magnitudes in cyclic voltammetry equals $1 + k\tau$, where k is the rate constant of the chemical reaction and τ is the time required for the scan to travel between the half-wave and reversal potentials. The relationship is largely independent of the scan rate and the reversal potential, except insofar as these influence τ. Though not exact, the relationship is obeyed closely enough to provide accurate rate constants under favorable conditions. The utility of this simple formula in extracting homogeneous kinetic information is demonstrated using experimental data for the electron-transfer-induced isomerization of an octahedral manganese complex. An explanation of the relationship is presented, as is a more exact formula that reduces to $1 + k\tau$ when k is small. A semiquantitative explanation of the relationship is provided.

Not infrequently, the product P of an electron-transfer reaction undergoes a subsequent first-order homogeneous reaction. If the lifetime of P is long enough, the process can be described successfully within the framework of the EC model. This constitutes an important class of mechanisms, with implications in many areas of interest in chemistry. For example, the chemical step may involve intermediates of consequence in electrosynthetic reactions.[1,2] Moreover, conformational changes or other molecular motions may be involved which are of significance in the field of nanotechnology,[3] or the reactions may be important in the area of organometallic catalysis.[4]

Our interest here is in the frequently encountered case in which the electrode reaction is reversible, whereas the homogeneous chemical reaction is irreversible

$$S(\text{soln}) - n e^- \underset{E_{1/2}}{\overset{\text{reversible}}{\rightleftarrows}} P(\text{soln}) \overset{\text{irreversible}}{\underset{k}{\longrightarrow}} X(\text{soln}) \quad (1)$$

One of the most popular tools for investigating such reaction mechanisms is cyclic voltammetry. There are many published instances of homogeneous rate constants being measured by such a procedure.[5,6] Typically, the scan rate is varied, and the dependence on the experimental timescale of the peak potential,[7] the peak current,[8] or the ratio of forward to back peak currents[9,10] is probed to gain an estimate of the homogeneous rate constant. These methods usually require comparison of the data with a working curve, as described, for example, by Nicholson and Shain[10] for the relationship between peak current ratio and experimental time scale. Another common approach for obtaining the desired kinetic information from voltammetric data has been the comparison of experimental results with simulations of the diffusion/electrochemical/chemical problem,[11,12] but although these methods are of great value in terms of the accuracy of the results they yield, they are often laborious and sometimes mathematically demanding.

We have found an intriguingly simple relationship which reveals that for an $E_{rev}C_{irrev}$ process, the forward/backward ratio of the peak height magnitudes in cyclic voltammetry equals $1 + k\tau$, where k is the rate constant of the chemical reaction and τ is the time required for the scan to travel between the half-wave and reversal potentials. Ideally, and if available, the use of an exact mathematical equation would most likely be recommended in preference to all the approaches presently employed. In this context, the empirical, approximate equation presented in this paper may be advocated as an interim measure that may be considered until such time as an exact analytical solution to the EC mechanism becomes available under conditions of cyclic voltammetry.

A recent interest in this laboratory has been the investigation of the electrochemical properties of the 18-electron octahedral-type complex *cis*-[bis(diphenylphosphino)methane]cyanodicarbonyl(triphenyl phosphite)manganese(II).[13] The oxidation of this species, at a potential of 1.17 V vs Ag/AgCl in acetonitrile, is followed by a chemical step corresponding to the isomerization of the thermodynamically unstable 17-electron cis+ complex, as shown in Scheme 1.

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Scheme 1. Electron Transfer-Induced Cis−Trans Isomerization of [Mn(CN)(CO)₂{P(OPh)₃}(Ph₂PCH₂PPh₂)][a]
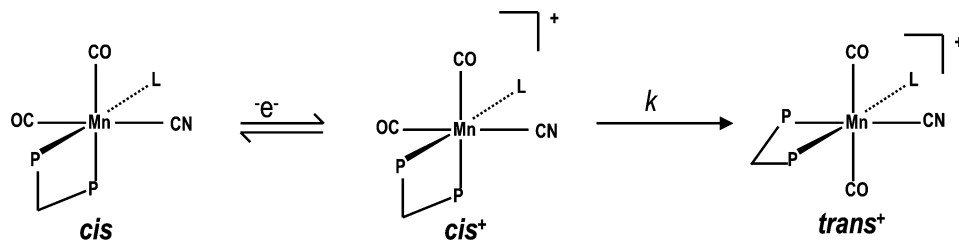
[a] L = P(OPh)$_3$ where Ph = C$_6$H$_5$.

Previously,[13] the kinetics of the cis−trans isomerization of this complex was quantitatively probed using rapid-scan cyclic voltammetry, and comparison with digitally simulated responses gave a value of 38 s^{-1} for k. In the present contribution, we report a new simple method for the calculation of homogeneous rate constants, following an electron-transfer step, which was discovered while modeling the process depicted in Scheme 1.

The relationship is tested by comparison with simulated data as well as with experimental data, both from the above-mentioned study and from recently performed additional experiments.

EXPERIMENTAL SECTION

The oxidation of [Mn(CN)(CO)$_2${P(OPh)$_3$}(Ph$_2$PCH$_2$PPh$_2$)] dissolved in acetonitrile with 0.1 M [Bu$_4$N][PF$_6$] as supporting electrolyte was investigated using an Autolab PGSTAT100 potentiostat (ECO-Chemie, Utrecht, Netherlands). The working electrode was a 25-μm-diameter Pt disk electrode inlaid in glass, and a 1-cm^2 Pt gauze served as the auxiliary electrode. The reference electrode was Ag/AgCl (3 M KCl), which was separated from the test solution by a double frit. Cyclic voltammetry was carried out at scan rates such that semi-infinite linear diffusion prevailed. The experimental data used in this study includes data previously presented in ref 13 and is augmented with new data obtained under identical experimental conditions.

RESULTS AND DISCUSSION

A Novel Relationship. Figure 1 shows a simulation of a typical cyclic voltammogram predicted for mechanism 1 in both its classical current-versus-potential presentation and the corresponding "unfolded" current-versus-time version. This figure serves to define the notation we use for certain key quantities associated with the voltammogram. Because time is a more pertinent variable than potential in this study, the unfolded voltammogram is a better vehicle for understanding the principles involved. Note that our discussion applies equally to oxidations and reductions; n is positive for an oxidation, negative for a reduction; the scan rate v shares the sign of n, as does the current I for most of the time.

The EC voltammogram is similar in shape to the stereotypical cyclic voltammogram arising from the reversible conversion of the substrate to a stable product, except that the backward peak is smaller. This height diminution is to be expected, because the backward peak arises from the conversion of the product P back to the original substrate S, and the occurrence of the chemical P → X reaction diminishes the amount of P present. It is therefore not surprising that the backward peak is found to be smaller the larger the rate constant k and the longer the time $t_{bp} - t_{fp}$ that
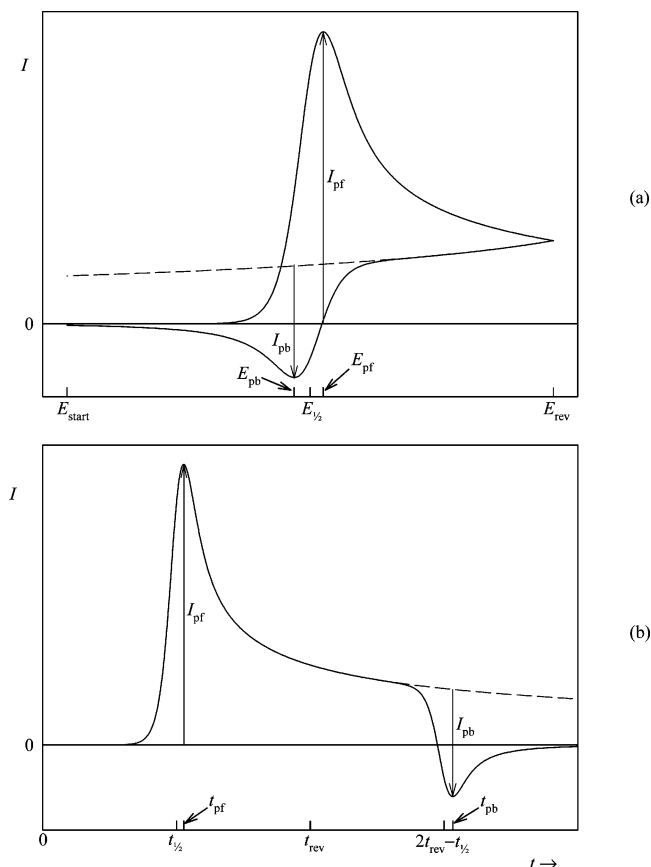

Figure 1. Simulation of a typical EC cyclic voltammogram (a) in the standard current-versus-potential presentation and (b) in the current-versus-time format.

elapses between the forward peak and the backward peak. What *is* surprising is the simplicity of the relationship

$$\frac{I_{pf}}{-I_{pb}} = 1 + \frac{k[t_{pb} - t_{pf}]}{2} \qquad (2a)$$

that we find to be obeyed, at least approximately, between the peak heights and the two factors that determine the decrease in the concentration of the product. As is standard in cyclic voltammetry, the backward peak height, I_{pb}, is measured from an extrapolated baseline, as indicated in Figure 1.

Because for reversible electron transfers, the difference between the half-wave and peak potentials is a constant (in fact, 1.109 RT/nF), it follows that $t_{pb} - [2t_{rev} - t_{1/2}] = t_{pf} - t_{1/2}$, and
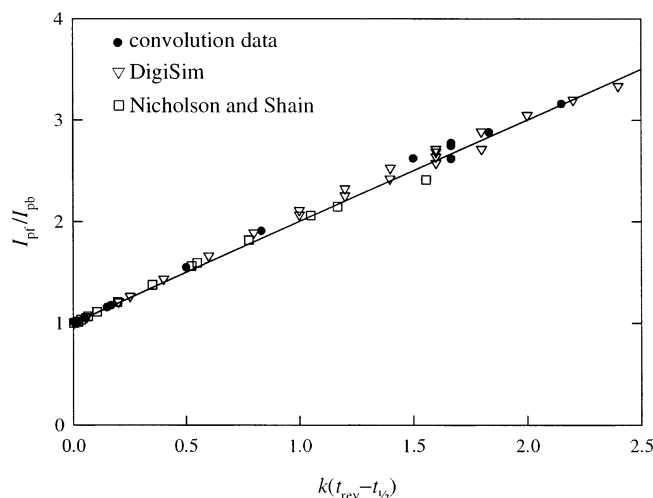
Figure 2. Test of relationship 2b (solid line) employing simulated data from three sources.

therefore, relationship (2a) may be recast into the equivalent form

$$\frac{I_{pf}}{-I_{pb}} = 1 + k[t_{rev} - t_{1/2}] \qquad (2b)$$

or, in terms of potentials, as

$$\frac{I_{pf}}{-I_{pb}} = 1 + \frac{k[E_{rev} - E_{1/2}]}{v} \qquad (2c)$$

The scan rate v, the reversal potential E_{rev}, and the rate constant k are mutually independent parameters, and an important consequence of the postulated relationship is that the peak height ratio does not depend separately on these three parameters, but only on the composite dimensionless grouping in eq 2c.

As far as we are aware, none of formulas 2a, 2b, or 2c has been published previously. Relationship 2 was stumbled upon in the course of modeling reaction 1 by digital simulation using Digisim software[14] and was subsequently confirmed by the semianalytical technique of convolutive modeling.[15] Figure 2 is a test of the relationship, comparing data from three sources: digital simulation, convolutive modeling, and the integral equation method. The simulation employed the commercial Digisim software.[14] The convolutive modeling used the semianalytic procedures described by Mahon and Oldham.[16] Nicholson and Shain's findings[10] comprise the third data set. One might conclude from Figure 2 that digital simulation and convolutive modeling give slightly discrepant results. This is not the case: the cyclic voltammograms produced by the two procedures superimpose *exactly*. The minor discrepancies (typically <1%) evident in the figure between the Digisim and convolutive data arise because of

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(15) Mahon, P. J.; Oldham, K. B. *Electrochim. Acta* **2001**, *46*, 953–965, and citations therein.
(16) Strictly, this is true only if reversal is indefinitely delayed; however, it is close to correct under most experimental conditions, and there is reason to expect that any discrepancy will affect the numerator and denominator in eq 2d similarly.
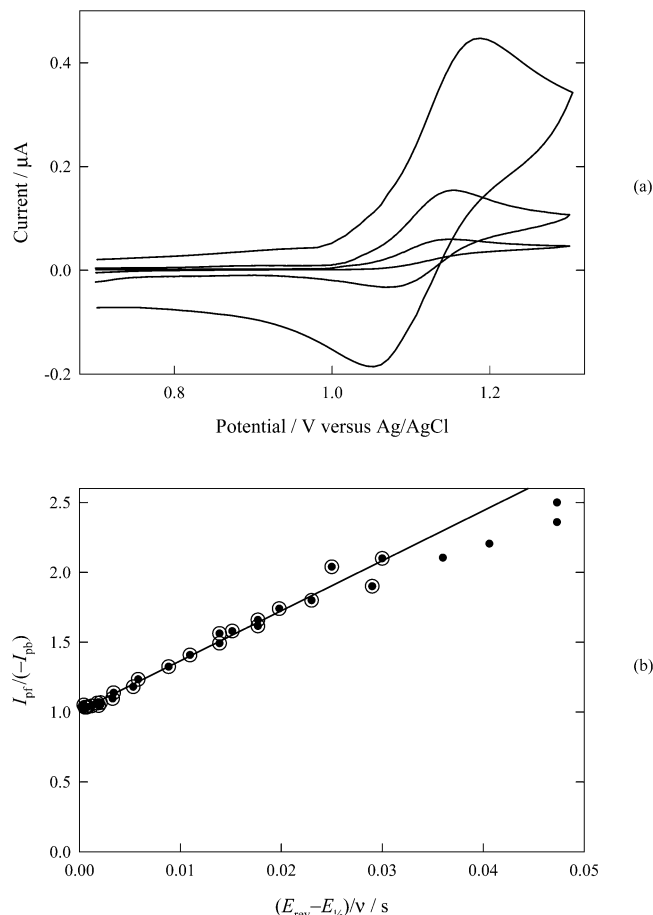
Table 1. Demonstration That the Peak Height Ratio Is Determined Mainly by the Composite Constant $k[E_{rev} - E_{1/2}]/v$ but also, to Some Small Extent, by $E_{rev} - E_{1/2}$ and k/v Individually

k, s^{-1}	E_{rev}-$E_{1/2}$, V	v, V s^{-1}	$k[E_{rev}$-$E_{1/2}]/v$	$I_{pf}/-I_{pb}$
1000	0.20	120	1.67	1.62
500	0.30	90	1.67	1.70
1000	0.40	240	1.67	1.74
1000	0.50	300	1.67	1.77
100	0.50	30	1.67	1.77
2000	0.70	840	1.67	1.81

the subjectivity inherent in extrapolating the baseline in the Digisim method, limiting to a small extent the precision of the ordinate data in Figure 2. It also leads to the data's being more suspect at the right-hand side of that diagram, where the magnitude of I_{pb} is smallest. For the convolution data, the baseline subtraction is performed automatically. Not surprisingly, considering the numerical technology available in the early 1960s, the data of Nicholson and Shain[10] is sparse and somewhat discordant with the newer data. The solid line in Figure 2 represents relationship 2b, that is, both the slope and y intercept have a value of 1. Linear least squares lines plotted through each of the data sets, with the intercept set to 1 in each case, returned slopes of 1.04, 1.03, and 0.97 for the convolution data, the Digisim data, and Nicholson and Shains's data respectively, though these numbers have no great significance, since they partly reflect the parameters arbitrarily selected in generating the data.

Table 1 lists peak height ratios measured from six simulated EC cyclic voltammograms that are predicted by eq 2c to have identical values of I_{pf}/I_{pb}. Apart from data for experiments that employ premature reversal, the tabulation confirms that the composite variable $k[E_{rev} - E_{1/2}]/v$ is the most important factor, rather than the individual values of k, $E_{rev} - E_{1/2}$ and v. There is, however, a distinct trend for the magnitude of the peak height ratio to increase with increasing $E_{rev} - E_{1/2}$. This trend is accompanied by an undermining of the accuracy of relationship 2c, and it is therefore advocated that $n[E_{rev} - E_{1/2}]$ be kept below 500 mV. This restriction also lowers the risk that secondary processes, such as solvent decomposition, interfere with the chemistry.

Figure 3a shows the cyclic voltammetric responses at differing scan rates for the oxidatively induced isomerization of *cis*-[Mn-(CN)(CO)$_2$\{P(OPh)$_3$\}(Ph$_2$PCH$_2$PPh$_2$)] dissolved in acetonitrile. At the slow scan rate of 1 V s^{-1}, the chemical step goes virtually to completion, as evidenced by the absence of a return peak. At the faster scan rate of 10 V s^{-1}, however, a return peak is present due to the reduction of the cis$^+$ species back to cis^0. At sufficiently short cyclic voltammetric experimental timescales, as in the cyclic voltammogram of Figure 3 run at 98 V s^{-1}, the isomerization step is outrun, and the I_{pf}/I_{pb} ratio approaches unity in magnitude.

Figure 3b shows a plot of the experimental data in the form of eq 2c. The value of k, as given by the slope of a graph such as this when all the data are used to estimate the least squares line, is 32 s^{-1}, which is in reasonable agreement with the value of 38 s^{-1} previously obtained by comparing entire experimental voltammograms with simulated versions.[13] We have found that the experimental data agree best with the model and the simulated
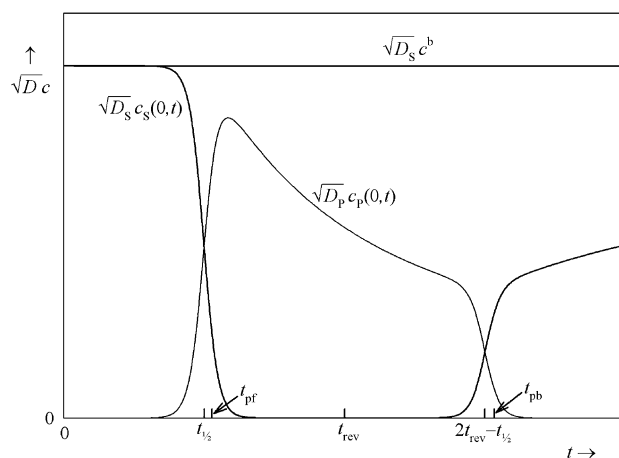
Figure 4. Convolutively derived graphs versus time of the surface and bulk concentrations of the substrate and product during EC cyclic voltammetry, each concentration being multiplied by the square-root of the corresponding diffusivity. The parameters assumed were $k = 300 \text{ s}^{-1}$, $v = 100 \text{ V s}^{-1}$, and $E_{rev} - E_h = 0.500$ V. There are 1000 data points with a time interval of 0.00002 s between them.

by recalling that for reversible cyclic voltammetry with a *stable* product (i.e., when $k = 0$), the peak heights are equal,[16] apart from sign. Therefore, conjecture 2b may be rewritten as

$$\frac{-I_{pb,k=0}}{-I_{pb}} = 1 + k[t_{rev} - t_{1/2}] \tag{2d}$$

Of course, the negative signs cancel, but they are included in eq 2d to remind the reader that backward peak currents have a sign opposite to that of the forward peak current.

Before proceeding further, it is instructive first to inspect Figure 4, which was constructed by standard convolutive modeling procedures.[15] On this diagram, we are using D to denote a diffusivity (or diffusion coefficient) and $c(0,t)$ to represent a time-dependent concentration at the electrode surface; in each case, the subscript indicates the species in question. The figure shows plots of $\sqrt{D}c(0,t)$ as functions of time for both the substrate S and the product P, for the particular voltammetric conditions identified in the caption. Notice that, as expected, the two curves cross twice: on each occasion when the half-wave potential is encountered, that is, at $t = t_{1/2}$ and $t = 2t_{rev} - t_{1/2}$. The backward peak is seen to occur immediately after the second crossing, and therefore, it is not unreasonable to postulate the proportionality

$$I_{pb} \propto \sqrt{D_P}c_P(0,2t_{rev} - t_{1/2})$$

involving P's concentration at the instant of the second crossing. The proportionality of faradaic currents to the surface concentration of the electroreactant and to the square-root of its diffusivity is common throughout voltammetry.

Let us now make some semiquantitative arguments concerning the concentration of the electroproduct P. Starting at around $t = t_{1/2}$, P is being injected into the solution by the electron-transfer reaction proportionally to the current, which itself falls off at a rate very close to $FAc^b\sqrt{D_S/\pi(t-t_{1/2})}$. Simultaneously, P is being removed by a chemical reaction to form its isomer X. The

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Figure 3. (a) Experimental cyclic voltammograms showing the oxidation at a platinum electrode and subsequent isomerization of the manganese complex dissolved in acetonitrile containing 0.1 M [Bu$_4$N][PF$_6$] as supporting electrolyte. The scan rates for the three voltammograms are, from top to bottom; 97.8, 9.9, and 1.0 V s^{-1}. (b) All of the experimental voltammetric data are plotted in the form of eq 2c. The least squares line is fitted to the circled data points only and has been forced through 0,1.

data (within 4%) in the region where the forward peak is no more than twice the magnitude of the back peak. Both the deviation from the predicted values (up to 13%) and the scatter in the data are most significant for higher values of I_{pf}/I_{pb}. This is not surprising, considering the aforementioned difficulties in estimating the position of the baseline when I_{pb} is small, and that these difficulties will be exacerbated, in this instance, by the proximity of the oxidation process to the solvent decomposition limit. If the data where the peak height ratio is greater than 2 are omitted, then the slope of the line in Figure 3 returns a value of 36 s^{-1} for the rate constant, which is in excellent agreement with the previously determined value.

The conclusion to be drawn from Figures 2 and 3 is that, although relationship 2 is not exact, it is nevertheless an excellent approximation under a wide range of conditions. It may be used to provide a reliable estimate of chemical rate constants over a wide range of magnitudes, faster reactions demanding faster scan rates. Bearing in mind the difficulty in measuring $[I_{pf}/(-I_{pb})] - 1$ precisely when the ratio of peak heights has a large magnitude, it is optimal to select a scan rate such that $k[E_{rev} - E_{1/2}]/v$ is <2.

Explaining the Relationship. It is far from obvious why relationship 2 should be obeyed, even approximately. We start

net effect of these two processes is to produce a concentration profile of complicated and changing shape. A standard Laplace-transform argument, however, easily shows that P's concentration at the electrode surface is given by

$$c_P(0,t) = c^b \sqrt{\frac{D_S}{D_P}} \exp\left\{\frac{-k(t - t_{1/2})}{2}\right\} I_0\left\{\frac{-k(t - t_{1/2})}{2}\right\} \quad (4)$$

during the relatively lengthy period when the potential travels out to E_{rev} and back again. Here $I_0\{\}$ denotes the hyperbolic Bessel function of zero order. At the instant $t = 2t_{rev} - t_{1/2}$, therefore, when the potential has reached $E_{1/2}$ for the second time, one finds

$$c_P(0,2t_{rev} - t_{1/2})\sqrt{D_P} = c^b\sqrt{D_S}$$
$$\exp\{-k(t_{rev} - t_{1/2})\}I_0\{k(t_{rev} - t_{1/2})\} \quad (5)$$

Now, the hyperbolic Bessel function of zero order resembles the exponential function in adopting the value unity at zero argument and in having a simple power-series expansion. In fact,

$$\exp\{-k(t_{rev} - t_{1/2})\}I_0\{k(t_{rev} - t_{1/2})\} = 1 + k(t_{rev} - t_{1/2}) +$$
$$\text{higher terms} \quad (6)$$

Combining eqs 3, 5, and (6), we arrive at

$$I_{pb} \propto \sqrt{D_P}c^b[1 + k(t_{rev} - t_{1/2}) + \cdots] \quad (7)$$

from which 2d immediately follows. This is far from being a rigorous proof, but it does provide some theoretical underpinning for our empirical finding.

CONCLUSIONS

Relationship 2c predicts that the expression $-v[I_{pf} + I_{pb}]/I_{pb}[E_{rev} - E_{1/2}]$ will provide a reliable estimate of the rate constant

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(17) The half-wave potential is well approximated by the mean peak potential, $[E_{pf} + E_{pb}]/2$.

of the homogeneous chemical reaction that is directly accessible from clear features[17] of an EC cyclic voltammogram. This prediction has been shown to be substantially correct. The method can be "tailored" to give an optimal value (<2.0) of $k[E_{rev} - E_{1/2}]/v$ by adjusting v suitably. $E_{rev} - E_{1/2}$ should be kept below $500/n$ millivolt for the best precision.

Simulated and modeled data from three sources plotted in the form of relationship 2b all returned a value of k within 4% of the nominal value. The usefulness of the relationship for the estimation of first-order homogeneous rate constants was demonstrated by applying it to experimental data for the oxidation and subsequent isomerization of the octahedral-type manganese complex cis-[Mn(CN)(CO)$_2${P(OPh)$_3$}(Ph$_2$PCH$_2$PPh$_2$)]. The rate constant estimated from a plot of eq 2c agrees with the value previously determined by digital simulation of the voltammetric response within 15%. If data which are problematic as a result of baseline uncertainty, that is, where $|I_{pf}/I_{pb}|$ is greater than ~2, are discarded, the divergence is <5%.

However, we do not advocate the use of the peak heights as a means of generating definitive data. It is better to match the *entire* experimental voltammogram with a simulated version, rather than to rely on two small regions of the curve. Nevertheless, the method disclosed in this article is useful for providing a rough and ready estimate of k that can then be refined iteratively in the search for the best simulative match.