

Precise Electrode Potential Measurements by Cyclic Voltammetry and the Application to the Measurement of Heterogeneous Charge Transfer Rates

ELISABET AHLBERG,^a BO SVENSMARK^b and VERNON D. PARKER^{a,*}

^a Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, 7034 Trondheim-NTH, Norway and ^b Department of General and Organic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Cyclic voltammetric peak potential differences were measured to a precision of 0.5 mV at a voltage sweep rate of 100 V s⁻¹ using a selective amplifier to differentiate the analog signal coupled to a digital data retrieval system with a time resolution of 0.5 μs per data point. Heterogeneous charge transfer rate constants for a number of aromatic compounds were determined in dimethylformamide. The method was found to give high precision even in the case of very fast electron transfers that take place upon reduction of anthracene and perylene. The measurements are compared with previously reported AC results. The method has the advantage over more elaborate steady state methods in that the time of measurement is minimal which greatly reduces troublesome problems such as product adsorption.

Cyclic voltammetry is generally regarded as a qualitative technique, useful in the general characterization of electrode processes, but inferior to other electroanalytical methods for kinetic studies. The primary reason for this attitude is the difficulty associated with the precise measurement of voltammetric peak potentials. One of the primary advantages of phase selective second harmonic AC voltammetry over cyclic voltammetry for the measurement of reversible potentials for electrode processes cited by Bond and Smith¹ is the fact that the potentials are measured on the rapidly changing slope of the voltage time curve as the current passes through zero. Perone and co-workers have improved the

reliability of peak potential measurements by employing the first derivative of the analog signal which passes through zero at the current maximum.^{2,3} While the potential of the latter method has been demonstrated,^{2,3} applications to kinetic studies are limited. In this paper we describe the precise measurement of peak potentials by cyclic voltammetry, compare kinetic results with those obtained by AC techniques and point out the problems involved in the selection of the magnitude of the IR compensation.

EXPERIMENTAL

Reagents, electrodes and cells. Standard purification procedures were employed on the aromatic compounds used in this study. The supporting electrolyte, tetrabutylammonium tetrafluoroborate was prepared from the hydrogen sulfate and aqueous fluoroboric acid. *N,N*-Dimethylformamide (DMF) was passed through a column of active neutral aluminium (ICN, W200 neutral, super grade 1) before use.

A stock solution of tetrabutylammonium tetrafluoroborate (0.1 M) in DMF was prepared and passed through a column of active aluminium. The latter was done to ensure that the composition of electrolyte solutions was the same for all of the compounds studied. Solutions of the aromatic compounds (3.0 mM) were prepared from a fresh electrolyte solution on the same day that measurements were made. The DMF solutions are not stable for long periods due to the decomposition of the solvent.

* To whom correspondence should be addressed.

The working electrode was a 0.6 mm platinum wire sealed in glass and polished to a planar surface before electrolytically covering the surface with mercury. Reference electrodes were Ag/AgNO₃ (0.01 M, Bu₄NBF₄/0.1 M) in acetonitrile constructed in the manner described by Moe.⁴ Leakage from the reference electrode was negligible as was the current consumed using the small electrodes for short pulses which enabled us to use a single compartment cell consisting of a cylindrical tube (25 ml volume) fitted with a joint to accommodate a teflon electrode holder equipped with a tube for the inlet of purified nitrogen.

Instrumentation. The potentiostat was a PAR model 173D driven by a PAR 175 function generator. Reversible electrode potentials were obtained by phase selective second harmonic AC voltammetry using a PAR 5203 lock-in amplifier with built in oscillator as the phase sensitive detector. A PAR 189 selective amplifier operated in the band pass mode was used to differentiate the cyclic voltammograms. The data were digitized by a Nicolet 1090 AR digital oscilloscope interfaced to a Hewlett Packard 9825A desk computer. The oscilloscope has a time resolution of 0.5 μ s/point with 12-bit precision.

Data collection. Data initially stored in the oscilloscope memory, 0.2 mV/data point, were taken into the computer memory. The computer was programmed to find the potential where the derivative of the current-voltage curve passed through the zero current line.

RESULTS

The applied voltage-time and current-voltage response along with the corresponding differentiated wave forms for the cyclic voltammetric reduction of nitrobenzene in DMF are shown in Fig. 1. The curves illustrate the application of the PAR 189 selective amplifier as a highly accurate differentiator. The response of the instrument can be adjusted exactly by fine tuning of the bandwidth. For a sweep rate of 100 V s⁻¹ a 3 DB bandwidth of about 5 kHz was used to give a 3.5 mV lag in the differentiated signal. At higher frequency ranges the lag could be eliminated with a corresponding increase in the noise level. We elected to use the noise free signal and apply the known correction.

An empirical method, using the known heterogeneous rate constant for the reduction of nitrobenzene as a standard, was used to adjust the level of IR compensation on the potentiostat. The most reliable data for the charge transfer kinetics

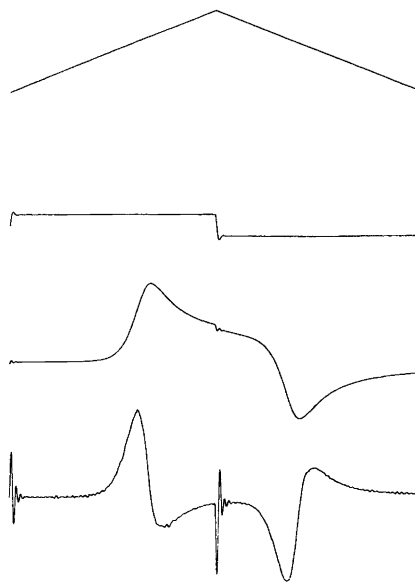


Fig. 1. Cyclic voltammetry waveforms; (a) potential-time, (b) differentiated potential-time, (c) current-potential and (d) differentiated current-potential.

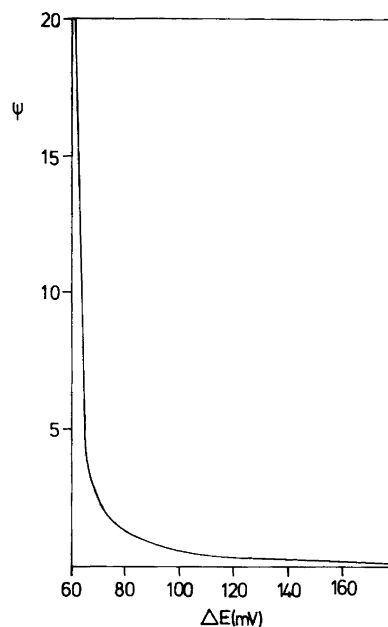


Fig. 2. Working curve for the determination of heterogeneous charge transfer rate constants from cyclic voltammetric peak separations. Data from Ref. 9.

for the reduction of aromatic compounds in DMF appear to be those reported by Kojima and Bard.^{5,6} Their data, reported for a supporting electrolyte concentration of 0.5 M, was adjusted to correspond to an electrolyte concentration of 0.1 M by using the known relationship, $k_s \sim C^\alpha$,⁷ where C is the concentration and α is the transfer coefficient. The proportionality had previously been found to hold for the reduction of cyclooctatetraene in DMF.⁸ The working curve shown in Fig. 2 was constructed from the theoretical data reported by Nicholson.⁹ The function ψ is defined by eqn. (1) in which γ ($\sqrt{D_O/D_R}$) was taken to be equal to unity, v is the voltage sweep rate and the other symbols have

$$\psi = \gamma^\alpha k_s / (\pi D_O n F v / RT)^{1/2} \quad (1)$$

their usual significance. The expected peak separation, ΔE^P , the difference in the potentials of the oxidation and reduction peaks during cyclic voltammetry, for the reduction of nitrobenzene at a sweep rate of 100 V s^{-1} was obtained from the working curve. The IR setting of the potentiostat was then adjusted so that ΔE^P corresponded closely with the calculated value. This IR setting was then used for the entire series of measurements on solutions prepared from the same stock solution.

Data for the reduction of the aromatic compounds are gathered in Table 1. The peak separations listed are the average of ten determinations on the same

solution and the error is the standard deviation. Both *p*-dinitrobenzene and *m*-dinitrobenzene gave erratic results when the voltammograms were recorded in the normal manner. However, reliable potential measurements could be made by pulsing the electrode to about 1 V negative of the peak potential just before initiating the cyclic scan. The most significant feature of the data is the precision. The maximum standard deviation was $\pm 0.9 \text{ mV}$ observed for *p*-dinitrobenzene. On the average, the error in ΔE^P is of the order of $\pm 0.5 \text{ mV}$. This error involves the measurement of two peak potentials indicating even higher precision for the measurement of a single potential.

DISCUSSION

The greatest drawback to the use of cyclic voltammetry, for that matter any DC sweep method, is the difficulty associated with the accurate compensation of solution resistance. A number of studies have dealt with calculating the uncompensated resistance^{10,11} and promising results have recently been reported using convolution sweep voltammetry.¹² However, peak potential measurements are so sensitive to the precise IR compensation setting that even a very small error in the calculated setting would be expected to give a significant error in the potential measurement. In our opinion, methods which involve corrections as large as 100 mV cannot be expected to give precision of the order of $\pm 0.5 \text{ mV}$ in potential measurements. To illustrate our point we call attention to the comprehensive study of Savéant and Tessier¹² in which a correction of more than 100 mV was made for IR during the cyclic voltammetric reduction of fluorenone which was assumed, in analogy to anthracene, to have a heterogeneous rate constant of 5 cms^{-1} and an α value of 0.5 as reported by Kojima and Bard.^{5,6} After making the correction, the convoluted potential data indicated diffusion control even at 2278 V s^{-1} . The authors overlooked the fact that k_s for anthracene was measured with a supporting electrolyte concentration of 0.5 M while their measurements were at 0.1 M which requires a significant correction. The rate constant for the reduction of fluorenone was determined in this study to be of the order of 1 cm s^{-1} (Table 2) and considerable deviation from reversibility is predicted at 2278 V s^{-1} . This forces the conclusion that the calculated correction was

Table 1. Cyclic voltammetric peak potential separations for reductions of aromatic compounds in dimethylformamide obtained by signal differentiation.^a

Compound ^b	$\Delta E^P/\text{mV}^c$	Standard deviation
Nitrobenzene ^d	72.00	0.20
4-Cyanopyridine	94.10	0.59
Benzonitrile	92.80	0.37
Perylene	67.80	0.30
Anthracene	69.67	0.48
<i>trans</i> -Stilbene	75.65	0.82
<i>m</i> -Dinitrobenzene	71.60	0.58
<i>p</i> -Dinitrobenzene	70.05	0.90
Fluorenone	69.33	0.20

^a Voltage sweep rate = 100 V s^{-1} , supporting electrolyte = Bu_4NBF_4 (0.1 M). ^b Concentration = 3.0 mM. ^c Difference in zero crossing potentials for the first derivative of the reduction and oxidation cycles. ^d Standard compound used to set the IR compensation.

Table 2. Heterogeneous charge transfer rate constants calculated from cyclic voltammetric peak separations for the reduction of aromatic compounds in dimethylformamide.^a

Compound ^b	k_s (this work ^c)/cm s ⁻¹	k_s (Ref. 5, 6 ^d)/cm s ⁻¹
Nitrobenzene ^e	0.71(3)	0.71(1)
4-Cyanopyridine	0.21(1)	0.18(8)
Benzonitrile	0.27(1)	0.22(1)
Perylene	0.82(10)	2.2(9)
Anthracene	0.75(3)	2.1(12)
<i>trans</i> -Stilbene	0.54(2)	0.47
<i>m</i> -Dinitrobenzene	0.63(6)	1.21(2)
<i>p</i> -Dinitrobenzene	0.72(3)	0.35(4)
Fluorenone ^f	0.74(3)	

^a Based on voltammetric data from Table 1. ^b Diffusion coefficients for the compounds used in the calculations are those given in Refs. 5 and 6. ^c Calculated from the data used in the construction of the working curve shown in Fig. 2 from Ref. 9. ^d Values from Refs. 5 and 6 adjusted for the concentration difference. ^e Standard compound. ^f Calculated assuming the same diffusion coefficient as anthracene.

considerably too large. The empirical method used here seems to be preferred. A just criticism to this method is that kinetic data reported for at least one compound must be taken as a standard and must be accepted as being precise. An error in these data will bring about comparable errors in the parameters calculated for other compounds.

Heterogeneous charge transfer rate constants, k_s , obtained using the data in Table 1 along with Fig. 2 constructed from Nicholson's data⁹ for the reduction of several aromatic compounds are summarized in Table 2 along with the data of Kojima and Bard^{5,6} adjusted for the difference in electrolyte concentration. The errors listed for our data are based upon the standard deviation of the peak potential difference measurements and do not take into account any possible error in either the calculated data⁹ or extrapolations using the latter. Linear extrapolation between data points was used with ψ then being calculated at 0.2 mV intervals of ΔE^p .

There is a very close correspondence between our data and the literature values.^{5,6} Noticeable deviations are found in the rate constants for anthracene and perylene which are significantly lower than the reported values but still within the large error limits assigned for these two compounds.

The rate constants for the two dinitrobenzenes deviate significantly from the reported values and we find the parameters for the two to be quite similar while Kojima and Bard report the rate constant for the *meta* isomer to be nearly four times that of the *para* isomer. Due to the difficulty associated with these measurements, presumably due to adsorption of the reduction products, we suggest that our values should be considered to be more reliable since the shorter times used in our experiments should minimize such problems. We also point out that the rate constant measured for fluorenone is very close to that for anthracene as previously presumed.¹²

The need for very accurate potential measurements using the cyclic voltammetric method to determine heterogeneous rate constants for fast processes can readily be seen from a consideration of the working curve shown in Fig. 2. The ψ values for the rapid charge transfers fall on the very steep portion of the curve where a small error in ΔE^p gives a significant error in k_s . For slower reactions where ψ falls on the flatter portion of the curve, the precision in potential measurements is not so critical.

In conclusion, we point out that accurate IR compensation along with signal differentiation allows for very precise potential measurements to be made using cyclic voltammetry. The empirical method for adjusting the IR compensation gives an accuracy dependent upon the validity of the model substance data. The results obtained by cyclic voltammetry are as internally consistent as AC data and since the technique is so rapid the method gives superior results in cases where absorption is a problem or where the charge transfer is coupled to homogeneous chemical reactions. Furthermore, rate studies can now be extended to oxidation processes at platinum or other solid electrodes for which the mercury electrode cannot be used. Further studies are in progress.

Acknowledgement. We thank the Norwegian Research Council for Science and the Humanities for support for E. A.

REFERENCES

1. Bond, A. M. and Smith, D. E. *Anal. Chem.* 46 (1974) 1946.
2. Perone, S. P. and Mueller, T. R. *Anal. Chem.* 37 (1965) 3; Evins, C. V. and Perone, S. P. *Anal. Chem.* 39 (1967) 309.

3. Perone, S. P. In Mattson, J. S., Mark, H. B., Jr. and MacDonald, H. C., Jr., Eds., *Computers in Chemistry and Instrumentation, Electrochemistry*, Dekker, New York 1972, Chapter 13.
4. Moe, N. S. *Anal. Chem.* 46 (1974) 968.
5. Kojima, H. and Bard, A. J. *J. Electroanal. Chem.* 63 (1975) 117.
6. Kojima, H. and Bard, A. J. *J. Am. Chem. Soc.* 97 (1975) 6317.
7. Conway, B. E. *Theory and Principles of Electrode Processes*, Ronald Press, New York 1965.
8. Jensen, B. S., Ronlán, A. and Parker, V. D. *Acta Chem. Scand. B* 29 (1975) 394.
9. Nicholson, R. S. *Anal. Chem.* 37 (1965) 1351.
10. Nemeč, L. J. *Electroanal. Chem.* 8 (1964) 166.
11. Smith, D. E. *Crit. Rev. Anal. Chem.* 2 (1971) 247.
12. Savéant, J. M. and Tessier, D. J. *Electroanal. Chem.* 77 (1977) 225.

Received July 19, 1979.