AN A.C. TECHNIQUE FOR DETERMINING THE RATES OF RAPID ELECTRODE REACTIONS OF AROMATIC COMPOUNDS IN APROTIC MEDIA

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ABSTRACT

An a.c. technique for measuring the rate constants for rapid electrode reactions in aprotic solvents using commercially available instrumentation with applied a.c. frequencies of 425 to 4250 Hz is described. A.c. phase sensitive detection using a lock-in amplifier and a hanging mercury drop electrode was employed. Electrode kinetic parameters are given for phthalonitrile, terephthalonitrile, *t*-stilbene, nitrobenzene, *m*-dinitrobenzene, anthracene and perylene in N,N-dimethylformamide. Experimental details and the comparisons with previously reported results are discussed. The technical simplicity and good precision of this method makes it suitable for studying rapid electrode reactions in nonaqueous systems.

INTRODUCTION

One of the simplest electrode reactions is that involving the outer sphere single electron transfer to an aromatic compound in an aprotic solvent to form the radical anion. This kind of reaction is particularly amenable to theoretical treatment, and a number of models for the processes, predictions, and correlations have been proposed, for example by Marcus[1], Hush[2], Levich and Dogonadze[3], and others. On the other hand there have been relatively few reported experimental rate constants for these systems. This can be attributed to the difficulty in making measurements on these rapid systems, especially in nonaqueous solvents where the uncompensated resistance may be large.

Aten and Hoytink[4] first applied the a.c. impedance bridge method to studies of aromatic hydrocarbons in N,N-dimethylformamide (DMF). Peover and co-workers also obtained kinetic data using an impedance bridge technique for aliphatic and aromatic nitrobenzenes[5] and stilbene and its derivatives[6].

Recently, Geiger and Smith[7] reported data obtained by a.c. polarographic methods for metal sandwich compounds in acetonitrile.

We present here an a.c. technique for kinetic measurements in non-aqueous systems employing a lock-in amplifier and a hanging mercury drop electrode. The technique utilizes only commercially available components, is relatively simple, and allows precise measurement of kinetic parameters even for rapid electrode reactions.

In this paper we will deal with the experimental details and discuss the comparisons of our data to previously reported results.

EXPERIMENTAL

Apparatus

A block diagram of the apparatus is shown in Fig. 1. Its main components are a potentiostat (Wenking Model 61RH, G. Bank Electronik, F.R.G.) and a lock-in amplifier (PAR Model HR-8, Princeton Applied Research Corporation, Princeton, N.J., U.S.A.). The d.c. voltage is adjusted by the potentiostat. An a.c. voltage of 5 mV amplitude is fed into the potentiostat from the reference oscillator of the lock-in amplifier. The cell current is fed to the lock-in amplifier from the potentiostat. Its amplitude and phase are measured with respect to the lock-in amplifier reference oscillator. The potentiostat is used in a simple two-electrode configuration to avoid phase shifts in it. The d.c. potential of the working electrode is monitored with respect to a reference electrode with a digital voltmeter (Digitec Series 200, United System Corp., Dayton, Ohio, U.S.A.; input impedance 2.2 MΩ).
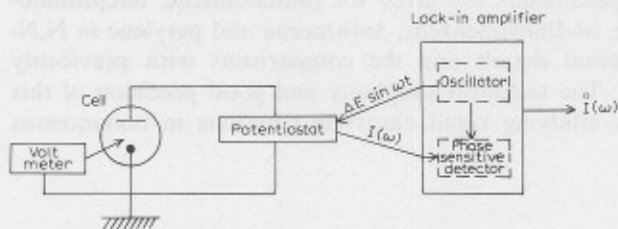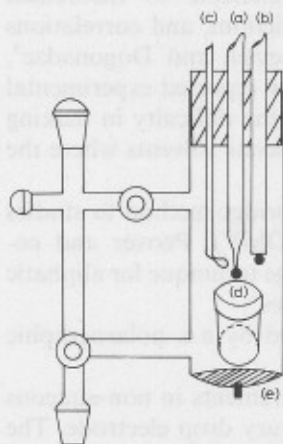

Fig. 1. Block diagram of apparatus.

Fig. 2. Cell configuration. (a) Hanging mercury drop electrode, (b) dropping mercury electrode, (c) glass spoon, (d) reference electrode, (e) counter electrode.

Cell

The cell design is shown in Fig. 2. There are four electrodes in the cell: a hanging mercury drop electrode (HMDE) is the working electrode, a dropping mercury electrode (DME) provides a mercury drop for HMDE, a mercury pool is the counter electrode, and an aqueous saturated calomel electrode (SCE) is the reference electrode. The HMDE consists of a platinum disk of 0.1 mm diameter, sealed in glass and electrolytically plated with gold. One or two drops of mercury, taken from the DME, are caught on a glass spoon and fixed to the gold-plated platinum electrode. To minimize frequency dispersion the working electrode must be drawn to a fine tip. With this electrode, variations of measured R and C values were below 2% for frequencies of 425 to 12500 Hz; the independence of solution
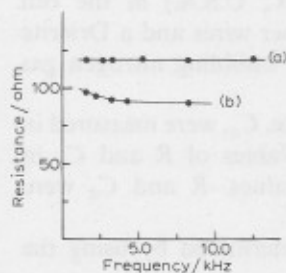

Fig. 3. Dependence of the solution resistance on a.c. frequency. (a) HMDE with fine tip, (b) HMDE with blunt tip. The solution was 0.5 M TBAP+DMF at -1.25 V *vs.* SCE. The electrode areas for (a) and (b) were different.
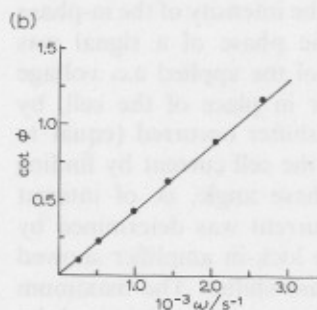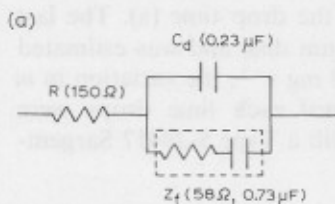

Fig. 4. Result with dummy cell equivalent circuit of the Randles type. (a) Equivalent circuit, R, C_d and Z_f correspond to the solution resistance, the double layer capacitance and the faradaic impedance with the values indicated. (b) Cotangent ϕ of Z_f, points are observed values, line is theoretical behavior.

resistance with a.c. frequency is shown in Fig. 3. With blunt-tipped HMDE's, large variations in R and C with frequency were noticed. The reference electrode was separated from the solution by two medium porosity fritted glass disks and an agar salt bridge.

Procedure

Solutions were prepared under a helium atmosphere in a glove box (Model MO-40-1, Vacuum Atmosphere Co., Calif. U.S.A.). The preparation involved weighing the depolarizer and supporting electrolyte, and diluting to 25 ml with DMF; the concentrations of the supporting electrolyte and a depolarizer were 0.5 M and about 0.5 mM, respectively. Measurements were made with a positive pressure of nitrogen (extra pure grade, Big 3 Industries Inc., Tx., U.S.A.) in the cell. The nitrogen was prepurified by passing it through hot copper wires and a Drierite column. Dissolved oxygen in the solution was removed by bubbling nitrogen gas through the solution.

The solution resistance, R, and double layer capacitance, C_d, were measured in the non-faradaic regions on both sides of the a.c. wave. Values of R and C_d in the faradaic region were estimated by averaging these values. R and C_d were typically about 130 Ω and 0.16 μF, respectively, at -1.50 V.

The electrode area, A (cm^2), of the HMDE was determined by using the equation for the DME:

$$A = 0.852 \, m^{\frac{2}{3}} t^{\frac{2}{3}} - a$$

where m is the flow rate of mercury (g s^{-1}) and t is the drop time (s). The last term, a, corrects for the area of contact with the platinum disk and was estimated to be 0.03×10^{-2} cm^2. The average value of m was 0.613 mg s^{-1}; the variation in m over a two month period was 0.7%. t was determined each time drops were collected for the HMDE and was usually about 11 s with a Type S-29417 Sargent-Welch capillary.

Measurement of phase angle

The phase angle, ϕ, of the a.c. polarographic current is defined as the difference in phase between the a.c. current and the applied a.c. voltage. The lock-in amplifier gives an output which is proportional to the intensity of the in-phase component with respect to the reference oscillator. The phase of a signal was determined as follows. First, we measured the phase P_0 of the applied a.c. voltage with respect to the reference oscillator using a resistor in place of the cell, by determining where the null output point of the phase shifter occurred (equal to $P_0 + 90°$). Secondly, we determined the phase $P + 90°$ of the cell current by finding the null point with the real cell in the circuit. The phase angle, ϕ, of interest is thus given by $\phi = P - P_0$. The amplitude of the cell current was determined by shifting the phase of the reference oscillator by 90°. The lock-in amplifier showed a slight non-linearity in both the amplifier and the phase shifter. The maximum overall deviation from linearity was about 2%. This error was minimized by calibrating with standard resistors of values near the cell impedance at each a.c. frequency.

Chemicals

N, N'-dimethylformamide (DMF) was used as the solvent. It is purified by the following procedure. Reagent grade DMF was stored over anhydrous cupric sulfate and Linde Type 4A molecular sieves for a week. It was then decanted and distilled over new anhydrous cupric sulfate at a reflux ratio of 5 under vacuum. The purified solvent was stored in the glove box under a helium atmosphere. No appreciable decomposition of the solvent was found for over a month under these conditions. Tetra-n-butylammonium perchlorate (TBAP) and tetra-n-butylammonium iodide (TBAI) (Southwestern Analytical Chemicals, Austin, Tx., U.S.A.), used as supporting electrolytes, were dried under vacuum at 100°C for 2 days. Phthalonitrile, terephthalonitrile, *trans*-stilbene (Eastman Organic Chemicals), anthracene, *m*-dinitrobenzene, and perylene (Matheson, Coleman & Bell) were purified by recrystallizations first from benzene and then from methanol, followed by drying under vacuum. Nitrobenzene was distilled at atmospheric pressure.

Dummy cell

The precision of the apparatus was checked using a series RC circuit, with values selected to cover the whole region encountered in real systems. The measured R and C-values agreed with the known values with maximum errors of 2%. The larger errors were found for measured phase angles near 90°. The precision was also checked by using an equivalent circuit of the Randles type as shown in Fig. 4a. The values of R and C_d were first measured in the absence of the faradaic impedance, Z_f. Then the impedance of the whole circuit was measured. The values of cot ϕ in the presence of Z_f was calculated after correction for R and C_d for frequencies of 425 to 4250 Hz. The results are shown in Fig. 4b, where the calculated values are given by a solid line and the observed values are given by the points. These results demonstrate that the precision of determining cot ϕ by this method was better than 6%, for values of R, C_d, and Z_f found in these electrochemical studies.

RESULTS

Determination of kinetic parameters

When a system is quasireversible with $k_s > 0.02$ cm^{-1} so that the process appears nernstian in d.c. polarography, the diffusion polarization resistance, R_{dp}, is given by the eqn.[8]

$$R_{dp} = \frac{4RT \cosh^2(j/2)}{n^2 F^2 A c_0^*(2D_O\omega)^{\frac{1}{2}}} \tag{1a}$$

$$j = (nF/RT)(E_{dc} - E_{\frac{1}{2}}^r) \tag{1b}$$

where ω is the frequency of the a.c. voltage, D_O is the diffusion coefficient of the oxidized form, c_0^* is the bulk concentration of the depolarizer, A is the electrode area, n is the number of the electrons transferred, E_{dc} is the d.c. potential, and $E_{\frac{1}{2}}^r$ is the reversible half-wave potential. At $E_{\frac{1}{2}}^r$ R_{dp} has its minimum value, $R_{dp}{}^m$, given by

$$R_{dp}{}^m = 4RT/(n^2 F^2 A c_0^*(2D_O\omega)^{\frac{1}{2}}) \tag{2}$$
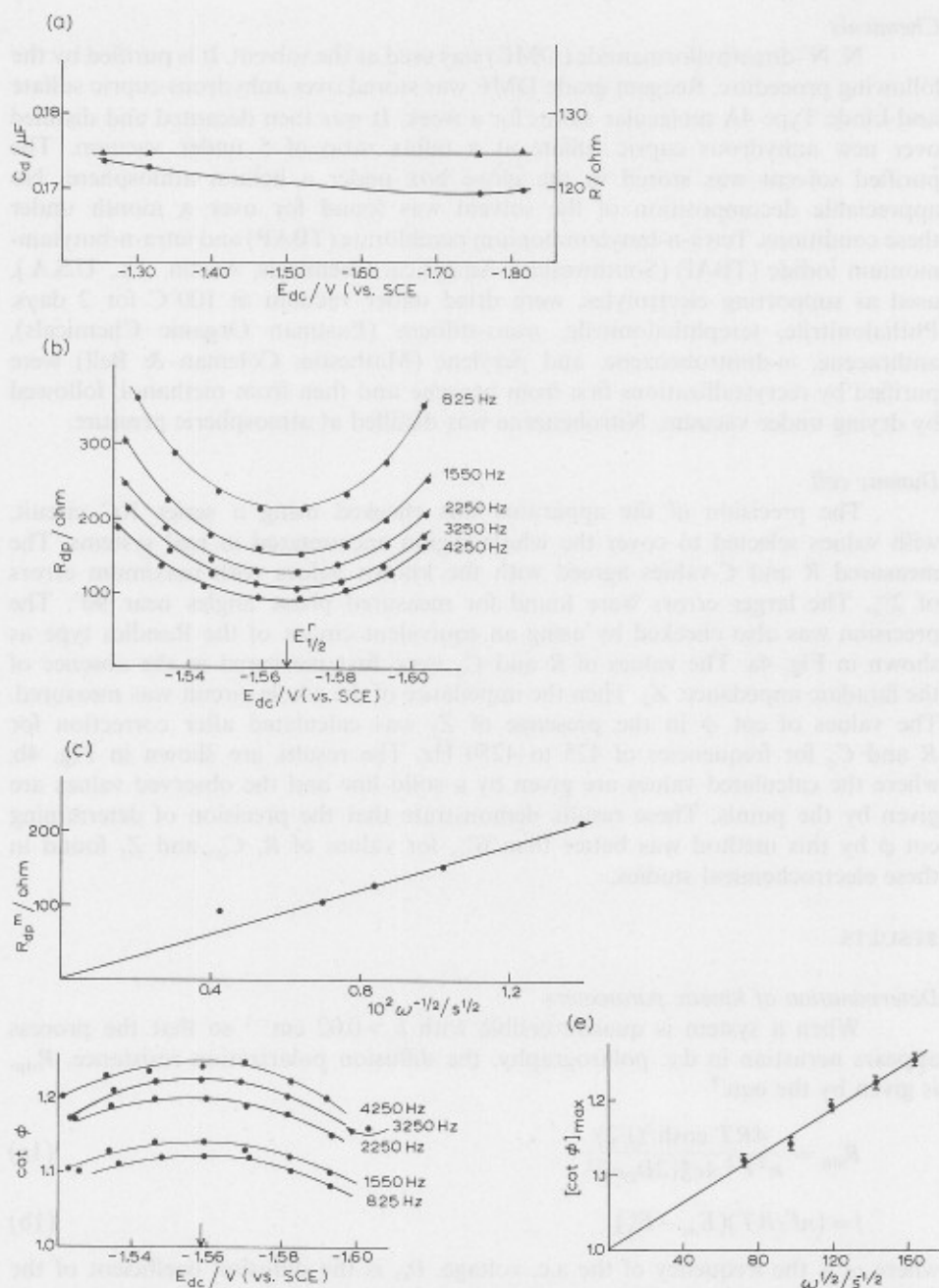
(a)

(b)

(c)

(e)

Fig. 5. Experimental results for a.c. measurement of phthalonitrile in DMF + 0.5 M TBAP. Conditions: $c_0^* = 5.13 \times 10^{-4}$ M, $t = 11.1$ s, $m = 6.34 \times 10^{-4}$ g s^{-1}, $A = 3.14 \times 10^{-2}$ cm^2, frequency = 825–4250 Hz. (a) Double layer capacitance and the solution resistance near the potential of faradaic region. ($\triangle$) Solution resistance, ($\bigcirc$) double layer capacitance. (b) Diffusion polarization resistance, R_{dp}, vs. E_{dc}. (c) R_{dp}^m vs. $\omega^{-\frac{1}{2}}$. (d) cot ϕ vs. E_{dc}. (e) [cot ϕ]$_{max}$ vs. $\omega^{\frac{1}{2}}$.

The diffusion coefficient was determined from the slope of $R_{dp}{}^m$ vs. $\omega^{-\frac{1}{2}}$ plots using eqn. (2). The cot ϕ of the a.c. faradaic current can be expressed by[8]

$$\cot \phi = 1 + (2\omega)^{\frac{1}{2}}/\lambda \tag{3a}$$

$$\lambda = (k_s/D^{\frac{1}{2}})(e^{-\alpha j} + e^{(1-\alpha)j}) \tag{3b}$$

where k_s is the rate constant for the electron transfer, α is the transfer coefficient and D is related to the diffusion coefficients D_O and D_R of the oxidized and reduced form by eqn. (4). In this work we assume $D_O \simeq D_R$, so that $D \simeq D_O$. Cot ϕ has its maximum value, $[\cot \phi]_{max}$ at $E_{dc} = [E_{dc}]_{max}$, where[8]

$$[\cot \phi]_{max} = 1 + \{(2\omega D)^{\frac{1}{2}}/k_s[(\alpha/1-\alpha)^{-\alpha} + (\alpha/1-\alpha)^{1-\alpha}]\} \tag{4}$$

$$[E_{dc}]_{max} = E_{\frac{1}{2}}^r + (RT/nF)\ln(\alpha/1-\alpha) \tag{5}$$

The α-value can be determined from $[E_{dc}]_{max}$ using eqn. (5) and the $E_{\frac{1}{2}}^r$ found from R_{dp} vs. E_{dc} plots. The rate constant k_s is determined from $[\cot \phi]_{max}$ vs. $\omega^{\frac{1}{2}}$ plots, using the measured D and α-values.

In Fig. 5, typical examples of these measurements are shown for the phthalonitrile—TBAP system. Figure 5a shows the double layer capacitance and the solution resistance at potentials before and after the faradaic region (-1.35 V to -1.70 V). This allows estimates of C_d and R in the faradaic region for use in determination of Z_f from the measured overall impedance. Note that the variation of C_d with E_{dc} is taken into account. In Figs. 5b, c, d, and e, plots of R_{dp} vs. E_{dc}, R_{dp}^m vs. $\omega^{-\frac{1}{2}}$, cot ϕ vs. E_{dc} and $[\cot \phi]_{max}$ vs. $\omega^{\frac{1}{2}}$ are shown for a.c. frequencies of 825 to 4250 Hz after correction of the data for R and C_d.

Reproducibility

The precision of the method was determined by making measurements on two different solutions which were prepared independently. The results are quite reproducible, as shown in Table 1. However, not all systems show such good precision. The systems in Table 1 are particularly well-behaved ones. Sometimes a system will show an irregular variation in solution resistance, of about 2 to 3 Ω in the non-faradaic region near the a.c. faradaic region. This variation is very sensitive to the experimental conditions and is perhaps caused by an interaction of a solution species with the mercury surface. This ambiguity in the solution resistance causes

TABLE 1

REPRODUCIBILITY OF INDEPENDENT DETERMINATIONS[a]

Compound	$k_s/cm\ s^{-1}$	α	$10^3\ D^{\frac{1}{2}}/cm\ s^{-\frac{1}{2}}$
Phthalonitrile	1.43	0.63	3.20[b]
	1.42	0.60	3.15
Stilbene	1.66	0.58	2.77
	1.55	0.58	2.82
Terephthalonitrile	0.670	0.50	3.09
	0.681	0.54	3.03

[a] DMF solutions were 0.5 M TBAP for phthalonitrile and terephthalonitrile and 0.5 M TBAI for t-stilbene at HMDE. Frequencies of 825 to 4250 Hz.
[b] Determined from d.c. polarogram by Ilkovic equation; all others determined from R_{dp}^m vs. $\omega^{-\frac{1}{2}}$ plot.

a large error in the non-faradaic correction involving R and C_d. This error becomes very significant for a system showing rapid electron transfer and in such cases, the reproducibility is quite poor. For example, a $[\cot \phi]_{max}$ vs. $\omega^{\frac{1}{2}}$ plot for m-dinitrobenzene system is shown in Fig. 6a, with the variation of $[\cot \phi]_{max}$ given by uncertainty bars. The measured k_s-value for this system shows a poorer precision (see Table 2). Systems in which the a.c. wave occurs at potentials more positive than -0.7 V or more negative than -2.2 V also show poorer reproducibility. In these potential regions, the double layer capacitance changes sharply with potential.
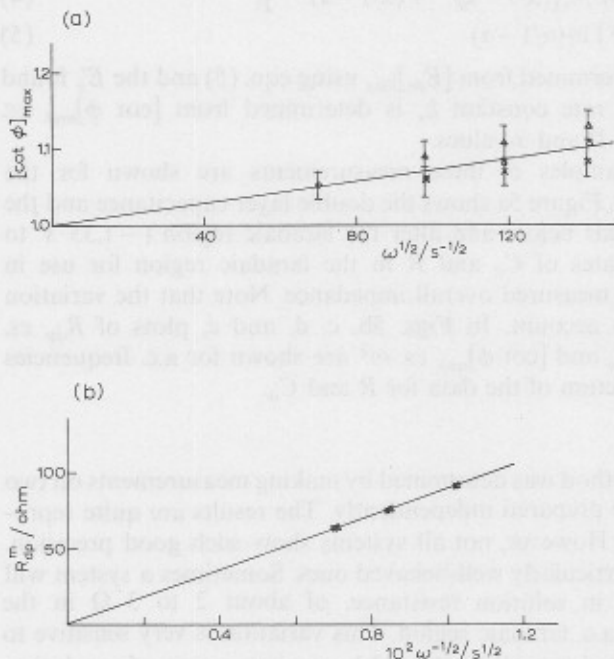

Fig. 6. Experimental results for m-dinitrobenzene in DMF $+0.5$ M TBAP and the effect of adding small amounts of water. Conditions: $c_0^* = 6.43 \times 10^{-4}$ M, $A = 4.62 \times 10^{-2}$ cm^2, frequency $= 1550$–3250 Hz. ($\bigcirc$) Without water, ($\triangle$) 10 mM of water, ($\times$) 20 mM of water. (a) $[\cot \phi]_{max}$ vs $\omega^{\frac{1}{2}}$, (b) R_{dp}^m vs. $\omega^{-\frac{1}{2}}$.

On the other hand, measurements of the diffusion coefficients almost always give good reproducibility, since the major error in the measurement probably comes from the determination of the concentration rather than from the electrochemical measurements. As shown in Table 2, the values of D usually agree with each other within 5%.

Diffusion coefficients determined from the d.c. diffusion current at the DME, using the Ilkovic equation, are always slightly larger than those determined by the a.c. method (see, for example, the first entry in Table 1). The effect of additions of small amounts of water to the solution on the measurements is shown in Figs. 6a and 6b. As shown in Fig. 6b, the diffusion coefficient changes very little, becoming perhaps very slightly smaller with the added water. The value of k_s does not change beyond the range of the experimental error (Fig. 6a).

Comparison with previous measurements

Comparison of the kinetic parameters determined in this study with previous measurements in DMF solution is given in Table 2. Both the Hoytink group[4] and the Peover group[5,6] employed the a.c. impedance bridge method, with applied a.c. frequencies of up to 60 Hz[4] and up to 3000 Hz[5,6]. Adams et al.[9] employed a d.c.

TABLE 2

COMPARISON OF RESULTS OF THIS METHOD WITH PREVIOUS DETERMINATIONS

Compound	Reference	$k_s/cm\ s^{-1}$	α	$10^3\ D^{\frac{1}{2}}/cm\ s^{-\frac{1}{2}}$	Conditions[a]
Stilbene	This work	1.6 ± 0.1	0.58 ± 0.03	2.82	0.5 M TBAI, 22°C, HMDE
	Dietz and Peover[6]	1.84	0.58	2.87	0.44 M TBAI, 30°C, DME
	Aten and Hoytink[4]	2.5	—	2.88	0.1 M TBAI, 25°C, DME
Anthracene	This work	5 ± 3	0.55 ± 0.04	2.62	0.5 M TBAP, 22°C, HMDE
	Aten and Hoytink[4]	4	—	2.77	0.1 M TBAI, 25°C, DME
m-Dinitrobenzene	This work	2.7 ± 0.6	0.50 ± 0.04	2.71	0.5 M TBAP, 22°C, HMDE
	Peover and Powell[5]	5	0.50	3.5	0.1 M TBAI, 30°C, DME
Nitrobenzene	This work	2.2 ± 0.3	0.70 ± 0.05	3.29	0.5 M TBAP, 22°C, HMDE
	Adams et al.[9]	0.03	—	—	0.1 M TBAP[b]
o-Nitrotoluene	Peover and Powell[5]	1.65	0.50	3.4	0.1 M TBAI, 30°C, DME
p-Nitrotoluene	Peover and Powell[5]	2.7	0.54	3.4	0.1 M TBAI, 30°C, DME
Perylene	This work	5 ± 2	0.50 ± 0.10	2.43	0.5 M TBAP, 22°C, HMDE
	Adams et al.[9]	0.07	—	—	0.1 M TBAP[b]
	Aten and Hoytink[4]	4	—	2.56	0.1 M TBAI, 25°C, DME
	Aoyagi et al.[11]	1.0	—	2.0–2.4	0.4 M TBAI, 20°C, Pt[c]

[a] All measurements were by an a.c. method unless noted otherwise. HMDE, hanging mercury drop electrode; DME, dropping mercury electrode.
[b] Measured at mercury plated rotating platinum disk electrode at −40 to −60°C and extrapolated to 25°C.
[c] Galvanostatic double pulse method.

method of measurement utilizing a rotating disk electrode of amalgamated platinum. Because the electrode reactions were too rapid to be measured at room temperature by this method, their measurements were made at a temperature below the freezing point of mercury (−40 to −60°C), and the rate constants at 25°C were obtained by extrapolation of Arrhenius plots of log k_s vs. $1/T$. Aoyagi's group[10–12] employed the galvanostatic double-pulse method with a platinum spherical electrode. Following

a controlled potential electrolysis at the half-wave potential, they measured the potential–time response using current pulses as short as 2 μs in length. Because the only previous measurement for nitrobenzene[9] is significantly different from the value found in this study, data for the analogous compounds, o- and p-nitrotoluene, are given in Table 2. Although estimates of the error of measurement have not been given in the previous studies, the error in k_s for these rapid systems must be fairly large. On the other hand, diffusion coefficients should be in better agreement with each other because there is less error in the measurement. We might note that the values obtained by d.c. measurements at the DME seem too large, perhaps because of convective effects (maxima) which occur at the DME. For example, m-dinitrobenzene is reported to have a larger diffusion coefficient than o- or p-nitrotoluene[5] although the former molecule is larger in size and D is almost proportional to the reciprocal of molecular diameter when there is no interaction with the solvent.

An overestimation of D is closely related to an overestimation of k_s as shown by eqn. (3).

DISCUSSION

Comparison to previous a.c. methods

The fundamental difficulty in a.c. measurements of rapid electrode reactions can be ascribed to the large nonfaradaic currents which arise because of the use of the high a.c. frequencies. The main a.c. methods that are employed are the impedance bridge method[6,8], methods involving measurements of in-phase and out-of-phase currents[13,14], and Fourier transform methods[15,16]. The latter two methods have the virtue of being automatic or semi-automatic but at the expense of greater instrumental complexity, the need for positive feedback iR compensation circuits, etc. The advantage of the conventional impedance bridge is that it is a null point detection method, so that cell parameters can be determined with high precision, independent of amplifier linearity. However, balancing the impedance bridge is tedious, since two variables, the resistive and capacitive components, must be adjusted[6,8]. Even when tuned amplifiers are used in the detector circuit of the bridge and a Wagner earth is employed to minimize stray capacitance to ground, problems of noise pick-up remain in making measurements in highly resistive organic solvents. Thus Peover and Powell[5] found it necessary to shield the entire bridge, cell, and operator in a Faraday cage. The proposed method, which employs null detection, can be viewed as a compromise between the bridge and the phase selective a.c. methods. The null point can be detected with high sensitivity, since very high amplifications can be employed. While manual balance must still be used in the lock-in amplifier mode, the balance can be easily attained with a high sensitivity by adjusting only the phase shifter, with the amplitude obtained directly by shifting the phase by 90°. The error in the amplitude which is accompanied with any error in the phase is diminished, because the intensity is insensitive to variation in phase when the signal is almost in phase with the reference. Interference by noise is very small because of the use of a signal tuned amplifier prior to introducing the signals into the mixer of the lock-in amplifier. Important problems which remain in the measurement are (a) instability of the signal zero

level, (b) lack of linearity of the amplifier, and (c) lack of linearity of the phase shifter. Of these problems, (a) can be minimized by frequent switching off of the applied a.c. voltage and readjustment of the zero level. Problems (b) and (c) are the weak points of the lock-in amplifier. The latter is not very serious unless a phase region too close to 0° or 90° is used. The former depends upon the characteristics of a mixer circuit which involves parallel balanced circuits for signal and reference. Even with careful adjustment of the mixer circuit, it is hard to get very good linearity over the whole phase range. To reduce this error, we compared the signal found with standard resistors to that of the cell and made appropriate corrections.

Hanging mercury drop electrode

The advantage of HMDE over the DME has been discussed by several authors[17,18]. There is no change of the electrode surface area with time, so that synchronization of measurements with a certain time in the mercury drop life, which often leads to a significant error, is not necessary. Both the double layer capacitance and the solution resistance are functions of the electrode area, so that the variation of the electrode area can cause a serious error in the determination of cot ϕ via the correction for the nonfaradaic effect. It has been reported that gold may contaminate the mercury of a HMDE in anodic stripping experiments[17], but this effect is probably negligible for a.c. measurements of k_s. A significant difference between the HMDE and the DME is that the surface concentration is not renewed throughout the measurement. Moreover irregular mass transfer because of the formation of large diffusion layer thickness and the onset of natural convection due to the formation of a density gradient[19] could occur.

The effect of a depleted concentration would appear as a function of time; we would not expect the a.c. phase to be affected directly, since it does not depend on time. Although diffusion polarization resistances might be affected, the time dependence of a.c. currents was shown to be very small when $k_s > 0.02$ cm s^{-1} by Delmastro and Smith[20].

A more serious time-dependent effect involves the continual contamination of the electrode surface by adsorption of impurities or reduction products[21]. This could affect the value of cot ϕ through changes in C_d, R, or λ. Such effects were noticed, for example, when measurements on pyromellitonitrile and p-benzoquinone were attempted. The phase angle was seen to change with time and did not attain a steady value. With the systems under consideration here, however, we did not find any appreciable change of a.c. impedance with time for measurements made over a period of several minutes.

Treatment of data

The present procedure of obtaining the k_s, α, and D-values from the experimental measurements is based on the assumption that an equivalent circuit of the Randles-type (Fig. 4a) can be applied to actual systems; this applicability is generally not known *a priori*[21]. Necessary conditions for the application of this model are that the diffusion polarization resistance and cot ϕ values satisfy the relations which are predicted by eqns. (1) through (5), after the proper correction for the nonfaradaic components. Of these conditions, the diffusion polarization resistance almost always satisfies the relations of eqns. (1) and (2). However, in

some cases, the cot ϕ values do not give a maximum value at a constant E_{dc} at different frequencies or $[\cot \phi]_{max}$ does not have a linear relation to $\omega^{\frac{1}{2}}$ with a unity intercept. The systems cited in Table 1 and 2 all show some irregular behaviour, except for phthalonitrile and stilbene. Systems with anthracene, perylene, m-dinitrobenzene, nitrobenzene and terephthalonitrile show a 2 to 3 Ω variation of the solution resistance with E_{dc}, although they show well-defined d.c. polarograms. This irregularity is certainly beyond the instrumental errors. While the effect is rather minor for a slower system such as terephthalonitrile, it is very significant for a rapid one. The agreement between the results reported here and similar previously reported a.c. measurements is moderately good; the differences can probably be ascribed to variations in solvent purity, solution preparation, etc. The d.c. rotating disk electrode results appear much smaller than the others and we suspect that either the extrapolation from low temperatures was not valid or that complete resistance compensation was not attained. The experimental difficulties in the measurement make comparison of the results with theoretical predictions somewhat uncertain and requires investigation of a large number of systems. The results of such an investigation, the correction of the measured rate constants for double layer effects, and a correlation of these k_s values with rate constants for homogeneous electron transfer reactions will be given elsewhere.

ACKNOWLEDGMENTS

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