dc method. The use of phase-selective detection with these techniques is therefore strongly recommended.

The second harmonic ac voltammogram obtained at a DME is shown in Figure 8c. The system exhibits a virtually flat base line compared with the dc or fundamental harmonic ac techniques because little or no charging current is present (22). The resolution is also excellent and this technique would therefore appear to be more attractive than with the fundamental harmonic or dc methods. It should be noted, of course, that the present work has been applied to reversible electrode processes and analytically applications will generally be restricted to this class of electrode process. However, this means that discrimination against nonreversible electrode processes should be considerable and this technique should be highly specific.

AC Cyclic Voltammetry at a DME. DC cyclic voltammetry consists of applying a triangular dc voltage to the electrochemical cell and reading out the resultant dc current as a function of the applied voltage. This technique enables both the forward and reverse steps of the redox reaction to be studied. This method has been extended to the ac format at stationary electrodes by superimposing an ac voltage onto the dc triangular ramp and either the fundamental (15, 24, 25) or second harmonic (15) ac response is recorded as a function of the applied dc potential. As would be expected, this gives considerable advantage in readout format because of both wave shape and discrimination against charging current. Obviously, the ac technique can now be applied to the DME.

Figure 8a, 8b, and 8c show dc, fundamental, and second harmonic ac cyclic voltammograms at a DME for the reduction $Cd(II) + 2e \rightleftharpoons Cd(Hg)$. For the dc case, the peak-to-peak separation is 30 mV compared to the normal reversible peak-to-peak separation of 29 mV when both species are soluble in the solution. The difference between those values and other departures from ideality can be attributed to amalgam formation (26).

Although no quantitative theory is presently available for ac cyclic voltammetry, Bond (15) has suggested that for a totally reversible system, the forward and reverse scans should be identical, assuming linear diffusion and equal diffusion coefficients of the reduced and oxidized species.

This does not take into account influences of amalgam formation and spherical diffusion. Figures 8b and 8c show the severe influence of amalgam formation in the ac cyclic experiment. In the fundamental harmonic ac mode, the peak separation of the forward and reverse scans is approximately 8 mV, with a scan rate of 50 mV/sec, and the waves are not equal to heights. (The "peak heights" referred to in this section have been corrected for drop area growth.) The second harmonic ac mode has a separation of inflection potentials of 7 mV, with a scan rate of 50 mV/sec, and the peak-to-peak heights of the forward and reverse scans are also not equal. At very much faster scan rates, the peak height of the reverse scan decreases in height and approaches the height of the forward scan. Also the separation of the forward and reverse scan peaks increases with increasing scan rate. This may indicate a departure from reversibility or may be due to amalgam formation or both. The considerable scan rate dependence observed seems to point to the amalgam formations as the major factor contributing to these observations. Obviously cyclic ac voltammetry should provide a powerful technique in investigating electrode processes, and work is in progress to obtain a quantitative theory (27). Presumably, the linear sweep theory in this work needs to be modified to take into account amalgam formation. In the present work, slight departures in wave shape from that theoretically predicted on the linear diffusion model result from amalgam formation in the forward linear sweep scan as is the case in ac polarography (14, 28–30). However for the reverse scan of the cyclic or stripping experiment, in particular, considerable scan rate dependence of peak heights, peak potential, or inflection potential, and wave shape is observed indicating considerable complexity arises from amalgam formation as indicated recently by Moorhead and Davis (31).

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Steady State Current Analysis for Kinetic Studies Using Twin Packed Graphite Electrodes

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A twin electrode flow cell has been developed which is applicable for kinetic studies of electrode coupled reactions having half-lives ranging from 1.3 seconds to several hundred seconds. Steady-state current analysis was employed to determine rate constants for two pseudo-1st-order systems. A new technique of allowing only a small portion of the solution to be in the reactive form is used to determine rates which would ordinarily be too short lived to be studied by conventional steady-state systems. Reproducibility and convenience are also added improvements over other steady-state electrochemical systems.
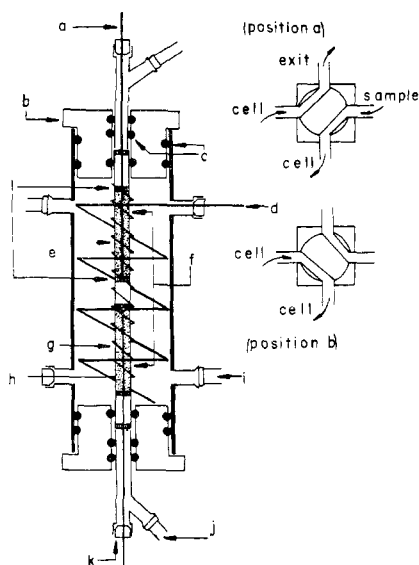
Figure 1. Twin electrode cell

(a) Graphite pencil lead, (b) Teflon plug, (c) O-rings, (d) Counter electrode, (e) Graphite electrode-I, (f) Porous Vycor glass, (g) Graphite electrode-II, (h) Ag–AgCl reference electrode, (i) Electrolyte entrance, (j) Sample entrance, (k) Silicone rubber plug, (l) Teflon disc. Position a: sample introduction and cell rinsing; position b: recycling sample through cell

Thin layer electrochemistry applications to kinetic studies have been discussed in several prior papers (1–4). These methods include chronoamperometry (1), cyclic voltammetry (2), and steady-state current analysis (3, 4). This paper will concern itself with a modification of one of these methods, that of steady-state current analysis.

The study of reaction kinetics by thin layer electrochemistry has been applied to reactions of the type

$$O + ne^- \rightleftharpoons R \xrightarrow{k} P \qquad (1)$$
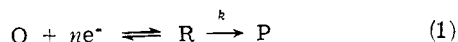
O and R being an electrochemically reversible couple, and P a non-electroactive species formed by a homogeneous solution reaction of R with rate constant k. This method involves generation of a quasi-steady state between the two electroactive species formed at different working electrodes, and subsequent monitoring of the concentration decay as one of the species reacts chemically to form an electrochemically nonreactive product.

In such systems, the currents needed to maintain the steady state are used to directly follow the progress of the chemical reaction. McDuffie, Anderson, and Reilley (3, 4) have successfully applied this method to follow pseudo-1st-order and 2nd-order reactions following the production of a chemically reactive species at one of the working electrodes.

In previous thin layer systems (planar platinum electrodes), determinable reaction rates were limited by the speed at which the reactants could diffuse from one electrode to the other. When the progress of the chemical reaction becomes significant with regard to diffusion rates between electrodes, kinetic decays dependent on the chemical reaction alone are not obtained. Under these reaction conditions ($t_{1/2} < 3$ sec), the inclusion of diffusion terms into the rate expression makes extraction of pure kinetic data difficult.

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(2) W. M. Schwarz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).
(3) B. McDuffie, L. B. Anderson, and C. N. Reilley, *Anal. Chem.*, **38**, 883 (1966).
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The procedure now being discussed handles mass transport between electrodes differently. The use of two granular graphite electrodes which are contained in series in a tubular piece of porous glass (Figure 1) allows solutions to be flowed past the electrodes. The thin layer characteristics of the granular graphite make it possible for samples to be electrolyzed quantitatively while flowing past the electrodes (5, 6). In this way, transfer of material is accomplished by pumping the sample from one electrode to the other. As the sample leaves one electrode, it is passed directly into the 2nd electrode. Upon leaving the 2nd electrode, it is then recycled back into the 1st electrode. The cell can now be thought of as similar in principle to previous planar electrode thin layer cells, except that chemical reaction will now be occurring as chemically reactive material flows between the electrodes. In previous thin layer cells, chemical reaction occurs as material diffuses from one electrode to the other. By maintaining relatively fast recycling rates, diffusional limitations are somewhat overcome and reaction rates with shorter half live ($t_{1/2} > 1.3$ sec) can be handled by this new method. Convenience is also an advantage of the graphite twin electrode cell.

METHOD

Quasi-steady-state conditions are generated in the following manner. Using the example in Equation 1, an oxidized form of the reactant, O, is introduced into the twin electrode cell in Figure 1. The potentials of the two graphite electrodes are controlled such that O is converted totally to the chemically reactive form, R, at Electrode 1 and R is completely oxidized to O at Electrode 2. The sample is flowed through the two electrodes by means of a peristaltic pump. As the material flows from the top of the cell, it is routed back to the bottom by means of silicone tubing. After the sample is recycled for a short time, a steady state is established and the currents needed to maintain this condition are constant. If R chemically reacts in solution to form some non-electroactive species, P, the steady state current will decrease as the concentrations of electroactive species, any change in O and R is reflected in the steady state currents. Thus, by continuously monitoring the steady state current, changes in concentration of R as the chemical reaction progresses can be observed.

The steady state current, i_{ss}, is related to the concentration of electroactive species by the following equation

$$i_{ss} = nFsC \qquad (2)$$

where i_{ss} is the steady state current in milliamperes, n is the number of electrons transferred per molecule, F is the Faraday number, s the flow rate of the solution in ml sec^{-1}, and C the concentration of electroactive species in mole ml^{-1} of solution. Therefore, i_{ss} being directly proportional to the concentration of the electroactive species, affords a method of directly following the rate of the chemical decay of R.

Derivation of 1st-Order Rate Expression. In deriving a suitable rate expression for reactions which are 1st-order in nature, three assumptions are made. First, the rate of the chemical reaction must be slow compared to the time required to recycle the sample. If recycling time is too slow, a true steady state is never achieved. Second, electrolysis reactions must be fast relative to the chemical decay rate so that any change in current is due to the overall homogeneous solution reaction of R producing P. Third, the electrolysis of the sample is considered to be a point electrolysis with the location of this point at some effective distance

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(6) R. L. Bamberger and J. H. Strohl, *Anal. Chem.*, **41**, 1450 (1969).

through the granular graphite electrode. Actually, the electrolysis is a function of the distance the sample travels through the electrode, with essentially 100% electrolysis being achieved over a small distance.

For 1st-order and pseudo-1st-order reactions, the reaction rate is independent of initial concentration and the general rate expression can be written in terms of total amounts of reactants. Therefore, for a 1st-order-reaction of the type in Equation 1, the rate expression is:

$$\frac{dA_P}{dt} = -\frac{dA_T}{dt} = kA_R = k'A_T \qquad (3)$$

where A_R is the total amount of R, A_T the total amount of O and R, and A_P the amount of P at any time, t. The specific rate constant k is determined from k' which is the net rate constant for the system and is determined from the decay of the total amounts of electrochemical species, $(A_O + A_R)$.

From Equation 3:

$$k'A_T = kA_R \qquad (4)$$

and definition states:

$$A_T = A_O + A_R \qquad (5)$$

Equation 4 can be rewritten as

$$k' = \frac{k}{1 + (A_O/A_R)} \qquad (6)$$

Substitution of Equations 6 and 2 into Equation 3 followed by integration yields the following rate expression:

$$\ln \frac{i_{ss}}{i_{ss}^{\circ}} = \left[\frac{-k}{1 + (A_O/A_R)}\right] t \qquad (7)$$

where i°_{ss} is the initial steady state current and i_{ss} the current at any time, t, during the reaction.

A similar expression has been derived for conventional thin layer cells (3) with the ratio A_O/A_R being replaced by the ratio of the diffusion rates for O and R, respectively (e.g., D_O/D_R). Diffusion rates can only be controlled indirectly by changes in temperature and viscosity, and the ratio of D_O/D_R is essentially constant.

The value A_O/A_R, however, provides a unique physical method for controlling the net decay of the reactive system. This ratio can be represented as the relative portion of the solution which is in the inactive oxidized form, O, compared to that portion which is in the chemically reactive form, R. The major requirement being that in order for this representation to be valid, the recycling time must be fast compared to the decay rate of R. In plotting log i_{ss} vs. time from data obtained from conventional thin layer steady-state analysis, reactions having half-lives less than 3 seconds exhibit decays which are rapid, often nonlinear, and difficult to extract pure kinetic information. By making the ratio, A_O/A_R, large, the net decay of the system is slower and the slopes of log i_{ss} vs. t become smaller and more linear. In this work, values of 0.134 and 7.45 were used for the values of A_O/A_R to optimize the net decay rates. Using this method of parameter variation, the greatest limiting factors become the recycling time for the reactive species, which must always be fast relative to the rate of reaction, and the limits necessary for 100% efficiency of electrolysis.

For a 1st-order reaction, a plot of log i_{ss} vs. time will yield a straight line with a slope and rate constant relation as follows:

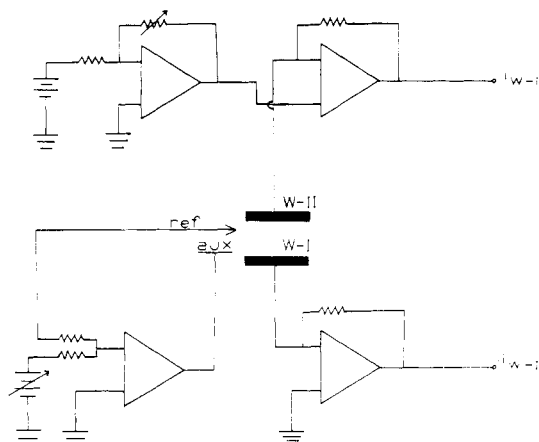$$(2.303) \text{ slope} = -\frac{k}{1 + (A_O/A_R)} \qquad (8)$$

Figure 2. Operational amplifier circuit for separate potential control of twin electrodes

The constant A_O/A_R must be known in order to calculate rate constants by this method. This ratio has been determined by two methods which will be described in the experimental section of this paper.

EXPERIMENTAL

Cell. The cell (Figure 1) was constructed of an outside jacket of Pyrex glass with openings for electrolyte and also for counter and reference electrodes. A smaller piece of 7930 porous Vycor obtained from Corning Glass works was fitted inside the Pyrex jacket by means of Teflon plugs and O-rings. The porous glass contained the two graphite working electrodes which were separated by perforated Teflon disks and glass wool. Outlets at the top and bottom of the cell were constructed to allow the sample solution to be recycled through the cell. Cole-Parmer "Silicone" tubing (No. 6411-43) was used for recycling the samples. A Cole-Parmer Model WZ1R031 peristaltic pump was used to recycle the solutions. Also by use of a 4-way stopcock in the recycling "loop," sample introduction and cell rinsing were accomplished conveniently. Contact to the graphite working electrodes was made with Eagle Turquoise Pencil Leads (No. T2375). The working electrodes consisted of 0.20 gram of 100/150 mesh Asbury graphite (Asbury Graphite Mills, Asbury, N.J.) extracted three times with concentrated NH_4OH. A Ag–AgCl reference was coiled around the porous glass and a Ag wire counter electrode was coiled around the perimeter of the reference.

Operation of Cell. Samples were freshly prepared and then transferred to the sample reservoir where they were thoroughly deaerated with nitrogen. The system contained a 4-way stopcock which was turned to position a (Figure 1), and the pump turned on to introduce the sample into the cell and the tubing. After the cell and tubing were flushed thoroughly with sample, the stopcock was put in position b (Figure 1) so the solution could then be recycled.

In all cases, the 1st electrode turned on was the electrode at which the reactive species was converted to the nonreactive starting material, to ensure that there was no reactive material present before electrolysis. The initial current for this electrode quickly decayed to essentially background (<0.5 mA). The second electrode was then turned on and the rise and decay of i_{ss} was monitored simultaneously on a strip chart recorder and a log recorder. At the termination of the experiment the solution could easily be pumped out of the cell and new sample introduced by correctly adjusting the stopcock.

Potentiostat. An operational-amplifier system similar to that used by Anderson and Reilley (7) for individual control of twin working electrodes was used. However, independent current measurement of both working electrodes was made by the circuit in Figure 2. Working electrode II was used as a regular potentiostat, then a potential difference between E-I and E-II was established such that both electrodes were at the desired potentials. Burr-Brown 3043 operational amplifiers and a Burr-Brown 524 power supply were used to construct the circuit. A Sargent SRL log recorder was used along with a regular strip chart recorder to monitor log i_{ss} and i_{ss}, respectively, as a function of time.

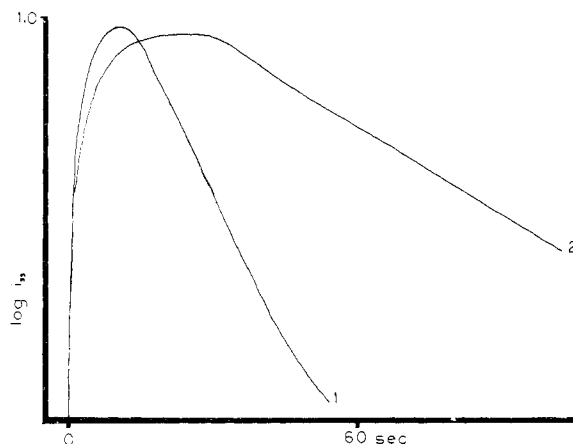(7) L. B. Anderson and C. N. Reilley, *J. Electroanal. Chem.*, **10**, 295 (1965).

Figure 3. Comparative representation of the effect of the values of A_O/A_R

(1) $0.150M$ $HClO_4$ and $2.5 \times 10^{-4}M$ azobenzene $A_O/A_R = 0.134$; (2) $0.150M$ $HClO_4$ and $2.5 \times 10^{-4}M$ azobenzene $A_O/A_R = 7.45$

Loop Ratio. In the system being described, the rate of chemical decay is proportional to the fraction of the total amount which is in the reactive state. This means that the relative magnitude of the slope of log i_{ss} vs. time will be proportional to the fraction of the total electroactive material which is in the reactive form.

The "outer loop" in denoted as the section of the cell contained from the point of electrolysis of electrode-II (going in a clockwise cycle in Figure 1). The section from electrode-II to electrode-I is known as the "inner loop." If R, the reactive species, is contained within the outer loop and O within the inner loop, the ratio of the inner loop volume to the outer loop volume will be A_O/A_R, provided that the rate of recycling is fast compared to the rate of chemical decay. With this arrangement, A_O/A_R will be less than unity, and linear decays are observed for 1st-order reactions with rate constants less than 0.030 sec^{-1}.

For reactions with faster decays, the electrodes are reversed and R is now in the inner loop. Now the former value of A_O/A_R is inverted and the ratio takes the new value of the outer loop to the inner loop. This ratio is some value larger than unity, and dependent on the relative sizes of the outer and inner loops. The magnitude of A_O/A_R will now have a greater effect on the decay of the system and, for faster reactions, steady state is obtained more readily.

Determination of Loop Ratios, A_O/A_R. *Coulometric Determination of A_O/A_R.* A standard iron sample is pumped into the cell, the system is recycled and steady state set up between Fe^{3+} and Fe^{2+}. After the system reaches equilibrium, the pump is stopped. The oxidizing electrode is turned off and the Fe^{3+} in the loop is quantitatively reduced at the cathode and the number of coulombs, Q_O, is determined. The procedure is reversed and the value of Q_R is determined. Q_O/Q_R is the ratio of the two loop volumes and is equal to A_O/A_R.

Comparison of k'. This method involves determining the slope of the log i_{ss} vs. t plot of a sample solution which has a decay rate that can be determined with the reactive species in either the inner loop or the outer loop. The ratio is then determined by solving simultaneous rate expressions (Equation 8). Figure 3 shows the type of relative decays obtained when a system is run with the reactive species first in the outer loop and then again in the inner loop.

Optimum Flow Rate. The minimum flow rate which can be used is controlled by the relative rate of the chemical decay of the system. If the flow rate is not fast enough to transport the reactive species from one electrode to the other before appreciable decay has occurred, the quasi-steady state will not be achieved and plots of log i_{ss} vs. t will be nonlinear. Ideally, the flow rate should be the fastest obtainable. However, the graphite working electrodes do not totally electrolyze samples at very high flow rates (>25 ml/min). This limitation is believed to be the greatest limiting factor in determining fast reaction rates.

The optimum flow rate was determined coulometrically with a standard iron sample. Using the steady state $Fe^{3+} \rightleftharpoons Fe^{2+}$, several flow rates were run and a plot of current vs. flow rate was made to determine the flow at which the efficiency of the working electrodes decreased from 100%. The maximum flow rate with which 100% quantitative electrolysis could still be maintained was always

Table I. Determined Rate Constants for the Benzidine Rearrangement

$HClO_4$ concn, M	A_O / A_R	$-$ slope $\times 10^3$	$k \times 10^3$ sec^{-1}
0.250	7.45	3.5 ± 0.2	68.1
0.150	7.45	2.0 ± 0.2	38.9
0.100	0.134	6.0 ± 0.2	17.4
0.075	0.134	3.4 ± 0.4	8.9
0.35	7.45	6.4 ± 0.3	122.5
1.00	7.45	33.3 ± 0.3	635.5

used. This rate was kept constant throughout each experiment and was generally 20 ml/min.

Solutions. *trans*-Azobenzene obtained from Eastman Organic Chemicals was recrystallized and used at a constant concentration of $2.5 \times 10^{-4}M$. Standardized $HClO_4$ was used for all acidic variations and ionic strengths were adjusted to 0.25 with reagent grade $NaClO_4$ for all solutions of concentrations less than $0.25M$ $HClO_4$. All solutions of $0.25M$ $HClO_4$ or less were prepared using 35 wt % ethanol.

p-Amino phenol obtained from Eastman Organic Chemicals was recrystallized and used with standardized reagent grade H_2SO_4. Ionic strengths were the same as the H_2SO_4 concentrations. The reaction which was observed for the *p*-amino phenol system is
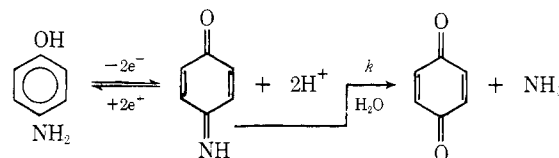
All solutions were deaerated with N_2 while in the sample reservoir. Temperatures of all solutions were 20 ± 1 °C. Inspection of the temperatures of solutions upon leaving the cell showed temperature changes of less than 2 °C.

The oxidizing and reducing potentials used were determined by previous experiments including plots of current vs. applied potentials at constant flow rates. From these plots, the lowest potential at which 100% electrolysis could be maintained was determined. The uncompensated IR drop for these systems was determined to always be less than 0.30 V. For the azobenzene system, potentials were used such that the anodic potential (+0.90 V vs. Ag–AgCl) was enough to convert only hydrazobenzene to azobenzene. The cathodic potential (−0.40 V vs. Ag–AgCl) reduced azobenzene to hydrazobenzene. A variety of potentials higher than those used were also employed with no noticeable difference in decay rates. However, at lower potentials than those used, calculated rate constants were lower due to the efficiency of the working electrodes being nonconstant and less than 100%. Potentials were more limited in the *p*-amino phenol system. In this case, the cathodic potential (−0.40 V) was enough to reduce benzoquinoneimine to *p*-amino phenol selectively. The anode was adjusted to +0.80 V.

RESULTS AND DISCUSSION

Rate constants for the benzidine rearrangement in solutions containing $0.075M$ to $1.00M$ perchloric acid were determined. Typical values for the slopes of plots of log i_{ss} vs. time are shown in Table I. For each experimental run, the slopes used to calculate the rate constants were taken directly from the log recorder. The slopes selected from the experimental decays were linear for a period of at least 10 sec. For solutions with k values of less than 0.030 sec^{-1}, a system which had an A_O/A_R value of 0.134 ± 0.001 was used. This gave plots with a linear portion lasting from 3 minutes to 30 sec for slower and faster reactions, respectively. When faster reactions were studied, anode and cathode were reversed and A_O/A_R became 7.45 ± 0.08. This allowed the log of the decay to be of measurable magnitude and reactions with k values of 0.635 sec^{-1} were run with linearity of the plots lasting 10 sec. Nonlinearity of the plots after several half-lives is attributed to background current and noise becoming more significant at low signal

Table II. Determined Rate Constants for Benzoquinone-imine Hydrolysis

H_2SO_4 concn, M	A_O / A_R	$-slope^a \times 10^3$	$k \times 10^3 \ sec^{-1}$
0.945	0.134	5.6 ± 0.3	14.6
0.472	7.45	2.8 ± 0.2	54.4
0.236	7.45	3.9 ± 0.2	75.1

Rate Constants Determined by Thin Layer Chronopotentiometry (1)

H_2SO_4 concn, F	$k \times 10^3 \ sec^{-1}$
0.510	26.6
1.017	7.4

^{a} Slopes are average of three separate runs plus or minus average deviation.

Figure 4. Comparison of benzidine rate constants with two other electrochemical techniques

○ Steady-state current analysis with graphite electrodes, ⊕ Steady state current analysis with planar electrodes (7) △ Thin layer chronopotentiometry (8)

currents. It is conceivable that if A_O/A_R were made larger, reactions of faster rates could be studied. However, with the system used, recycling rates would have to be increased in order to give attainable equilibrium times for 1st-order reactions with k values greater than 0.635 sec^{-1}.

Plots of i_{ss} vs. t are shown in Figure 3. The initial current increase is due to the initial formation of R when the cathode is first activated. The time required for the log plot to become linear is the time required for the system to reach a steady state. In most cases, this was less than 10 sec. However, relative rates of different reactions did affect equilibration times slightly as can be seen in Figure 3. As expected, the equilibration time was significantly shorter when the inside loop was used to contain the chemically reactive species and was usually on the order of 5 to 10 sec. The attainment of equilibrium depends on the relative decay of R between the electrodes. The less R reacts while being transported, the faster steady state conditions are obtained. This factor limits the range of the method for rate studies.

The calculated rate constants for the benzidine rearrangement are listed in Table I. Reproducibility is expressed in terms of the standard deviation of five consecutive runs. A comparison of the obtained rate constants with rate constants determined by other electrochemical techniques is shown in Figure 4. There is some disagreement in the reported absolute rates, which is due partially to the difference in temperature and reaction conditions; however, relative comparisons due to changes in acid concentration are in good agreement.

Calculated rate constants for the hydrolysis of benzoquinoneimine are shown in Table II. A comparison of these
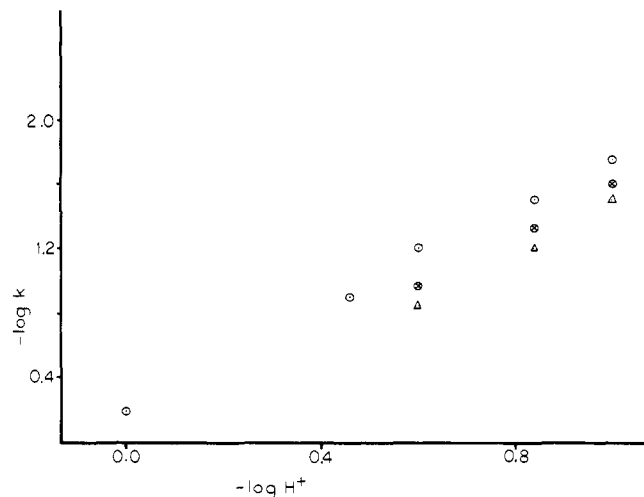
with a thin layer chronopotentiometric method (1) is shown. Differences in temperatures and reaction conditions are consistent with the observed differences in the rate constants.

The system described has two major advantages over other thin layer steady state techniques: the principle of having only a fraction of the total system in the reactive form allows the total progress of the reaction to be of a rate more easily followed and having a mass transport system not totally dependent on diffusion.

At present, the graphite electrode system has extended the limits of steady-state current analysis somewhat. The largest limitation seems to be the maximum velocity at which substances can be flowed through the electrode beds and still be totally electrolyzed. Improvements in this area would definitely increase the range and versatility of the system.

Another possible application of the graphite cell is to that of low temperature kinetic studies. Since high signal currents could be maintained at low temperature, possibilities in this area certainly exist.

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