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DEDICATED COMPUTER CONTROL OF CHEMICAL INSTRUMENTATION

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Research in the area of computer controlled instrumentation is described. This involved the development of a hierarchical computer network to acquire data and control chemical experiments. Experiments involving electrochemical generation of transient intermediates and the study of chromatographic surfaces are presented.

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Introduction

In our original proposal of November 1970, the small, high speed digital computer was identified as an important tool for chemical research, particularly as it related to the development and use of chemical instrumentation. Prior to this time "small" computer use was, in general, restricted to data acquisition and did not involve two way communication between computer and experiment and/or computer and experimentalist particularly where an intervening decision is required. The impressive technological developments which have led to the microprocessor/microcomputer revolution have made such capability widely accessible due to significant cost reduction. The advantages of these developments cannot be fully realized unless and until corresponding improvements have occurred in programming techniques and software development. For this reason, a substantial part of our effort has been devoted to the development of a computer system utilizing software which is easy to use and maintain. The effort required to program a computer is usually justified by its subsequent use in performing repetitive operations such as routine data handling and process control. Chemical research calls for constant software modification in response to changing requirements. If the software is sophisticated such modifications are difficult and time consuming particularly for someone who is not an experimental programmer.

From the standpoint of the development of the computer as a tool in the chemical laboratory our efforts were directed in three major areas: 1. Experimental control and data processing, 2. Experiment simulation and 3. Interactive graphics. As will be described subsequently, this capability was then directed toward the solution of a variety of problems involving electrochemistry of transient intermediates and the characterization of chromatographic surfaces.

Our efforts were greatly aided by the acquisition in June 1972 of a Hewlett-Packard 2100 computer system with 16K core, 2.5 million word disk storage, line printer, photoreader, punch and interactive graphics terminal.

This project involved the collaboration of two (and later three) research groups with diverse interests. We used the individual research problems within each group to define priorities for broadly based improvements in computer utilization.

I. Software Development

At the time this project was initiated, we did not have on-campus interactive computer capability (we now have a DEC-10 system with numerous terminals within the Chemistry Department). Consequently we identified the development of interactive graphics as an important priority. Graphics software, particularly that designed to utilize our interactive graphics terminal, is quite complicated. A large part of the complexity results from the desire to accommodate a wide variety of options within a subroutine structure. The so-called Plot-10 advanced graphics software provided by Tektronix is designed to operate on a large computer (DEC-10). With the help of Mr. Thomas Sargent this package was rewritten with a series of overlays so that it could run on a 16K x 16 bit computer with a disk. This software, written in Fortran IV is available to interested users. This software was augmented with another routine HDCOP which generates an ASCII compatible paper tape. This tape can drive a digital plotter to generate a hard copy of the graphics terminal record.

A number of applications, particularly those involving large arrays, (simulations, for example) could not be accommodated in 16K of core. Dynamic memory allocation software was developed so that the disk could be used to effectively expand core by 64K obviously at some expense in computation time.

By early 1973 it became apparent that we were expending considerable effort on the development of software. At this point we began serious consideration of how we might best make utility software, in particular, readily available to a variety of users. We experimented with a macro-assembler and a modified Super Basic to see whether these approaches would facilitate the rapid synthesis of complete programs. A more promising approach appeared to be FORTH, a programming language developed by astronomers and in extensive use at Kitt Peak National Observatory. The simplicity of program development and maintainability was very attractive and we had great need for an operating system which could be conveniently modified to meet our changing needs. In attempting to modify the Hewlett-Packard Disk Operating System (DOS), we discovered that changing one driver could modify the characteristics of the entire system. Because of this, we decided to develop our own operating system based on some of the concepts of FORTH. The characteristics of FORTH and a comparison with the system we ultimately developed have been presented elsewhere (1) and will not be discussed in detail here. In addition to facilitating the development and maintenance of software, we wished to interconnect several "slave" computers (having the primary function of controlling an experiment) with a central system having superior data processing and storage capability. The configuration of the system is shown in Figure 1. Such a system imposed the requirement of some form of real time data acquisition. Since the system must possess computational as well as control capability, we felt that this could be best accomplished by incorporating multilevel programming. For example, the programmable microprocessor in the Hewlett-Packard 2100 was used, in effect, to expand the instruction set to convert to "stack" operation and to handle specialized I/O procedures. The operating system, for example, can accomodate simultaneously programs at the microprogram, assembly and Fortran levels. In addition and more importantly, the use of threaded programming techniques (2) makes possible the creation of a laboratory oriented language designed for specialized purposes. The operating system called Hierarchical Interactive System Sharing (HISS) is hierarchical with respect to both hardware and software. Though the system described in Figure 1 was designed prior to the development of the microcomputer, it anticipates its use. Data collected on "slave" systems can be conveniently transferred to the central system thus reducing the need for the still relatively expensive bulk storage devices.

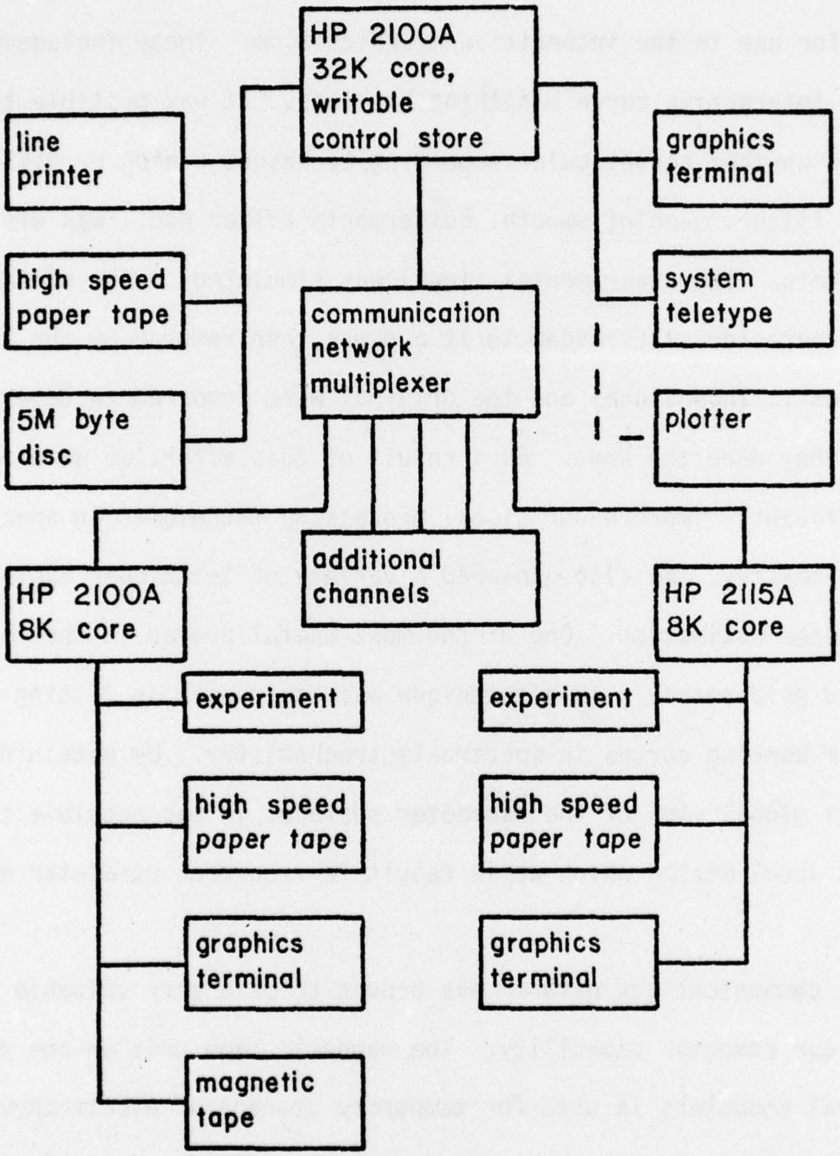


Figure 1. Hierarchically structured computer system hardware.

Several problems of general interest in data processing were developed for use in the interactive graphics mode. These included, for example, interactive curve smoothing routines. It was possible to determine whether a particular smoothing technique analog or digital (Fourier filter, n-point smooth, Butterworth filter etc.) was distorting the data. The experimental signal was simulated, noise of the correct characteristics added to it and was then removed by the filtering process. This signal and the original were compared to determine whether they were the same. As a result of this effort we were able to significantly improve our signal processing techniques in spectroelectrochemistry. We also explored a variety of techniques applicable to parameter estimation. One of the most useful proved to the interactive organized grid search. This technique was again used in fitting multiparameter working curves in spectroelectrochemistry. By obtaining a graphical global view of the parameter surface, it was possible to avoid choosing local minima which would result in incorrect parameter estimation.

The communications network has proven to be a very valuable addition to our computer capability. The magnetic tape unit on one of the peripheral computers is used for temporary storage of electrochemical data collected on that system. Thus real time electrochemical experiments can be performed without imposing critical timesharing requirements on the central system. The magnetic tape unit is also used as an peripheral for the central system as a supplement to disk storage. For rapid experiments where there is insufficient time to access the magnetic tape, the data can be transferred directly to the central system from the experiment at a rate of about 250 KHz (16 bit words). We are therefore able, to an increasing extent to enjoy the advantages of a distributed system. We expect in the future to connect several microcomputer based experiments into the communication network.

II. Electrochemistry and Spectroscopy of Transient Intermediates

Computer control of electrochemical instrumentation is greatly simplified by the fact that the experiment can be controlled entirely by electrical means. Proper control of potential and/or current makes it possible to selectively electrogenerate various molecular oxidation states and at controlled rates. Electrochemical techniques provide the dual advantage of control as well as additional information in the form of either current or potential variation which allows elucidation of reaction kinetics.

A particularly powerful approach to the study of fast reactions involves the combination of the advantages of electrochemical control with the valuable diagnostic capability of spectroscopy. This task was greatly facilitated by the development and construction (in collaboration with Harrick Scientific Corp.) of a rapid scan spectrophotometer with a resolution of about 5Å and a scan rate of 3. x 10^6 Å/sec. It was readily realized that the resolution of this instrument was limited at the highest scan rates not by the optics but rather by the throughput rate of the data acquisition system. Consequently it was necessary to keep the I/O overhead as low as possible. To do this a controller for the wavelength drive was constructed which could run synchronously with data acquisition but without constant computer control. Prior to the start of the experiment pertinent experimental parameters (scan rate, wavelength increment and range, for example) are transferred from the computer to controller memory. Thus until the parameters are updated, the controller will continue to operate under those conditions. This procedure also greatly simplified wavelength calibration and compensation of the non-ideal characteristics of the galvanometer wavelength scanner. It is easily possible to obtain 5-15 spectra with wavelength resolution and reproducibility of better than 1 nm and photometric accuracy exceeding 0.002. This instrument and a newer prototype using entirely front surface optics are being used to measure spectra of transient intermediates generated electrochemically and by stopped flow techniques.

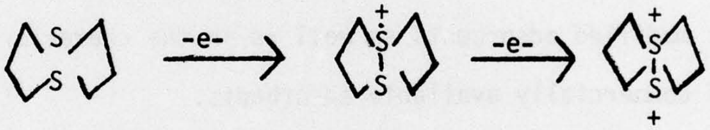
The principal spectroelectrochemical experiment carried out involves the observation of transients generated by a potential step perturbation at an optically transparent electrode. Design considerations and electrochemical characteristics of spectral cells with optimal response have been described elsewhere (3). Prior to our efforts no systematic examination of time dependent spectra generated by a potential step perturbation had been made. Previous studies were confined to the observation of a single wavelength where only one species absorbs. Since we were interested in obtaining spectra of intermediates rather than just rate constants, it was necessary to fully account for all time dependent spectral changes of all species at all wavelengths. This work resulted in a publication (4) in which we systematically examined a variety of common electrode mechanistic schemes accounting for all species present. Clearly it is necessary in analyzing data to choose the correct model in order to obtain the correct parameters. For this reason we have given continuing attention to the development of diagnostic criteria which will enable us to distinguish a priori closely related mechanisms (5). Most potential step chronoabsorptometry boundary value problems involving reversible and/or second order reactions cannot be solved in closed form. Consequently it is necessary to resort to digital simulation techniques (explicit finite differences). The technique has the advantage that it is very general and can be readily adapted to minor changes in mechanistic schemes. There are, however, two serious limitations which must be clearly appreciated. 1. It is relatively easy to obtain erroneous or unstable solutions if a certain relatively narrow range of rate constants is exceeded. 2. The functional relationship between variables must be deduced by performing a large number of simulations followed by empirical correlation of parameters. Regarding the latter point, it became clear that a versatile simulation routine coupled to our interactive graphics capability would greatly aid in interpreting experimental results. Suitable software has been developed so that a chemist can sit at the graphics terminal and input pertinent parameters such as rate constants, molar absorptivities, and diffusion coefficients for incorporation into a particular model. Within several minutes a simulation of an experimental response curve appears on the screen. The actual experimental results are then directly superimposable. An organized grid search can then be used to systematically adjust all parameter until an optimum fit is obtained between the experimental and theoretical curves. Goodness of fit is established using a reduced chi square function.

We have been able to demonstrate, using the two electron reduction of a porphyrin diacid as a model system for testing our techniques (5,6). As our approach became more sophisticated we were able to detect more subtle system perturbations. Further the complementary nature of the cyclic voltammetric and potential step experiments should be noted. The former method is not sensitive to a sequence of irreversible chemical steps, the latter does not permit facile evaluation of the $E^{0'}$ values for the individual electron transfer steps. A combination of the two methods leads to the conclusion that the mechanism must be

$$\begin{array}{ll} A + e^- \gtrless B & E \\ 2B \gtrless C + A & D \\ B + e^- \gtrless C & E \\ C \gtrless D & C \\ D \gtrless e & C \end{array}$$

Species B is stable to further chemical reaction, C is not. Therefore the effect of the disproportionation (reproportionation) reaction is to siphon off C that would otherwise react to form D. Using parameter estimation techniques we are able to obtain complete transient spectra of B, C and D. Detailed discussion of these results will appear in a subsequent technical report, a preliminary version of which is attached.

Using the above described techniques, we have also examined the spectral and electrochemical characteristics of numerous electron deficient sulfides. The epr spectral properties of the dication of tetramethoxythianthrene was the subject of a collaborative study with Dr. Ira B. Goldberg (7). From epr measurements, it was possible to demonstrate a triplet ground state for the dication. In the course of looking for other stable electron deficient sulfides, we have examined also a series of mesocyclic dithioethers (4-10 membered rings), the most noteworthy of which is dithiacyclooctane (DTCO). The cyclic voltammogram appears, nominally, to be a quasi-reversible two-electron oxidation. More careful examination of digitally acquired data using interactive graphics, reveals two one-electron steps having nearly the same formal potentials. The heterogeneous rate constants are fast. The observation of a stable cation radical and dication is novel because such aliphatic species are ordinarily not stable even in aprotic solvents. Among the series examined, DTCO is unique even among isomeric dithiocyclooctanes in its unusual stability and ease of oxidation. We are attempting to understand the reasons for this behavior by carrying out electrochemistry in a variety of organic solvents (with temperature variation) and by several different spectroscopic techniques as well. This work will shortly be the subject of technical reports dealing with the chemistry of these compounds and the systematic parameter estimation for the EE case cited above (8).



III. Chromatographic Studies

A. Methodology

Computer control of a gas chromatographic experiment has involved controlling the pneumatically driven switching valve used to introduce the sample, electric motors to set the column temperature and carrier gas flow rate, as well as taking data from the flame ionization detector, temperature sensor and flow sensor. Control of these parameters, however, has made it possible for us to make considerable progress in the development of chromatographic methodology to obtain information about the interaction of gaseous molecules at the gas-solid interface. This information has proven to be very useful in our program to synthesize chemically modified adsorbents as well as in the characterization of a variety of commercially available adsorbents.

During the course of this work, we have used the computer-controlled instrumentation to implement a variety of experiments. Using standard elution chromatography of a sample pulse we can obtain thermodynamic data concerning the gas-solid interaction from the peak position and kinetic data, which is a function of the physical nature of the surface, from the broadening of the solute peak as a function of temperature and flow rate. The precision of the data, as well as the magnitude of the signals measured, has been described elsewhere (9). Similar experiments using frontal analysis chromatography have been developed and used to determine the surface available to a given adsorbate on a particular surface (10).

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In addition to the standard, single pulse elution chromatography experiments, use of the computer-controlled system has made it possible to develop chromatographic methodology which cannot be done without the interaction of a computer. The first of these experiments involved the use of the computer to inject multiple pulses of the sample on to the column and then to obtain the desired information from the complex output signal by means of cross-correlation techniques. This work is described in an earlier report (11) and represents the first time that information concerning both linear and non-linear chromatographic behavior have been studied using basic information theory techniques.

The successful application of the cross-correlation of the injection series and the detector output has given impetus to the development of chromatographic experiments which involve the use of an input profile of the sample other than a single pulse. The possibility of modulating a continuous flow of sample being introduced to the column raises the opportunity of investigating the properties of a chromatographic column in terms of a transmission channel. A concentration signal generating system has been described (12) which allows the development of a variable frequency sine-wave or square-wave of sample concentration to be introduced onto the column. An alternative approach to the development of such a concentration modulated flowing stream, which is based on high-speed fluidic logic under computer control, is currently being developed by Mr. Dan Villalanti and will be the subject of a future publication at a later date.

In summary of this area of our work, it can be said that the use of computer-controlled instrumentation has allowed the development of more precise means of using conventional gas chromatographic experiments for study of gas-solid interactions as well as the development of new and unique methodology for obtaining information of these systems.

B. Adsorbent Studies

The development of adsorbents with improved selectivity and efficiency has been and remains one of the major goals of our work. This work has involved the characterization of commerically available adsorbents such as the Porapak series (Waters Associates) and the Century series (Johns-Manville). The work described earlier by Gearhart (13) demonstrated that the chromatographic information was useful in determining both the chemical nature of the adsorbents and the physical homogeniety of the porous beads. This was followed by the development of a systematic method of evaluating the sampling capacity and efficiency of these porous beads for use as preconcentration devices in atmospheric and head-gas sampling systems (14).

The data from the characterization of the totally porous beads was then used to define the synthetic scheme for the development of pellicular polymer adsorbents. The surface of silica particles were modified so as to allow the development of polystyrene (cross-linked with divinyl benzene) as a thin film bonded to the glass surface (15). This work has been extended by Mr. Larry Butler and a future technical report (16) on his work will be submitted.

The work carried out under this grant has established a basis for work which is being extended to surface modification being done on open tubular (capillary) columns as well as adsorbents for liquid chromatography.

C. Digital Simulation

The increased sophistication of the chromatographic experiments allowed by the use of the computer system as well as the increase in our knowledge concerning the interaction occurring on the surface has greatly increased the need for a means of simulating the chromatographic processes. The work by John Phillips in the development of a discrete event approach to the simulation of the adsorption and desorption processes (17) is a large step forward in separation chemistry. The development of the threaded code programming technique which allowed the implementation of the simulation technique has already been discussed.

The simulation system has been used to investigate the role two adsorption sites of unequal energy (as is often thought to occur on modified silica surfaces) in the peak position and peak broadening in single pulse elution chromatography under non-linear conditions.
It is this area of non-linear chromatography that this type of simulation can be most useful. It is hoped that similar simulation experiments

which help to determine the best means of interpreting the data which is obtained from the modulated continuous input chromatography discussed earlier.

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11. Chromatographic Simulation, J. B. Phillips and M. F. Burke
12. Final Technical Report, G. S. Wilson and M. F. Burke.
13. Cyclic Voltammetric Studies of the EE Mechanism: A Porphyrin Diacid Reduction, D. L. Langhus and G. S. Wilson, to be submitted to Analytical Chemistry.
14. Dynamic Spectroelectrochemistry - Identification of Porphyrin Transient Intermediates, D. L. Langhus and G. S. Wilson, to be submitted to Analytical Chemistry.

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17. Pellicular Adsorbents for Preconcentration Columns, L. D. Butler and M. F. Burke.

Preliminary Technical Report

Cyclic Voltammetric Studies of the EE Mechanism: A Porphyrin Diacid Reduction

by

David L. Langhus and G. S. Wilson

An organized method for obtaining information about complex reaction mechanisms from cyclic voltammetric data has been developed. Each step is illustrated by an application to the study of the reduction of *meso*-tetra(N-methyl-p-pyridyl) porphyrin in 1*M* HCl.

It is important in such an investigation to make maximum use of all data available on the system of interest, particularly that obtained *via* independent experiments. In the case of the porphyrin, these included coulometric and spectroelectrometric studies which established the reduction as a two-electron process and showed that the mechanism included an irreversible chemical step at some point following reduction. Inspection of cyclic voltammetric data at a variety of pH values indicated that the reduction itself did not involve hydrogen ion and revealed a separation of roughly 80 mV between the two single electron transfers--just sufficient to observe a small broadening in the leading edge of the wave. This latter point is very important as it eventually allows us to eliminate several possible mechanisms.

To obtain the maximum amount of information from the cyclic voltammetric experiment, however, it is necessary to compare the data more precisely with the theory. This is most conveniently done by selecting several diagnostic features of the current potential curve and plotting each as a function of scan rate. Similar theoretical plots can be prepared by simulating on the computer the data corresponding to an assumed mechanism and making the appropriate measurements with the help of interactive graphics. The experiment and theory may then be compared directly with respect to the chosen characteristics. Four features which have proved useful for data of the type obtained from the porphyrin system are:

a. The normalized peak current. This is approximated by

$$i_n = \frac{i_p}{\sqrt{v}}$$

where i_p is the peak current, v is the scan rate, and i_n is the resulting normalized value. When plotted as log i_n vs. scan rate, the shape and scale of the curves are identical to the theoretical normalized current although the absolute magnitude of the numbers vary. This feature is expected to remain constant regardless of scan rate unless the product of the electrode reaction is consumed causing it to rise at scan rates sufficiently low for this process to become important.

b. The peak potential. In the simple case, this will remain constant with scan rate except for any anomalies due to uncompensated resistance at the higher values. Shifts, primarily at low values of scan rate, are due to consumption of the electrode product following electron transfer or to competing equilibria.

c. $E_p - E_{p/2}$. This measurement is made by measuring the difference between the peak potential and the potential at the point where the current assumes half its peak value on the leading edge of the wave. For uncomplicated electron transfer, this will also be affected only by uncompensated resistance at high scan rates. Following chemical reactions will cause significant narrowing of the peak at low scan rates; whereas, a homogeneous reaction interposed between two electrochemical steps which occur at roughly the same potential will cause considerable broadening at higher scan rates.

d. The ratio of anodic to cathodic peak current. For simple electron transfer, this ratio is unity. Any perturbation which modifies the concentrations of either member of the couple will change this ratio accordingly. This is a very sensitive indication of homogeneous processes.

To use these features, an overall reaction mechanism for the system is postulated which includes all heterogeneous processes as well as chemical effects. Simulations are performed over a range of scan rates for several values of the mechanistic parameters. Measurements are then made on the simulated curves and plotted for comparison with the data. If no consistent fit is possible for parameter values, that supposed mechanism is considered unreasonable and another postulated. If the curve shapes do agree, it may then be possible to estimate the values of the parameters assuming that mechanistic scheme.

Several mechanisms have been examined in conjunction with the porphyrin system. The cyclic voltammetry behavior for each will now be discussed.

EEC Case

$$A + e^- \gtrless B \quad (E)$$

$$B + c^- \gtrless C \quad (E)$$

$$C \rightarrow D \quad (C)$$

Examination of the peak position versus scan rate for the data showed a cathodic shift with increasing scan rate up to roughly 0.1 V/sec after which the peak remained constant. This plateau was interpreted as the region in which kinetic complications no longer had a significant effect on the peak potential. The $E_p - E_{p/2}$ plot indicated similar characteristics. The I_a/I_c plot rose with increasing scan rate assuming the value unity at roughly 1 V/sec. The normalized current decreased to a plateau at around 0.1 V/sec. The simplest mechanism which is likely to give similar results consists of the two electrochemical steps followed by a single, irreversible chemical step.

Simulation of the theoretical EEC case for several values of the rate constant yields a family of curves for each feature which are roughly comparable to those for the data. The shapes of the curves, however, are somewhat different, particularly in the I_a/I_c case as shown in Figure 1. Also, the estimate of the value of k obtained from the E_p data is more than an order of magnitude different than that obtained from the I_a/I_c data. The irreversible EEC case, therefore, does not fit well and must be abandoned.

While the case for which the chemical step is made reversible was not considered especially pertinent to the porphyrin system (the reduction of which is known to be quite irreversible), it is appropriate here to consider what effects such a system would have on the diagnostic features. At high scan rates, the four features do not change appreciably with v as noted before. As v is decreased, at some point corresponding to the value of the forward rate, I_a/I_c begins to decrease, followed by a simultaneous shift of E_p in the anodic direction and a contraction of $E_p - E_{p/2}$. These, as well as the normalized current, follow roughly the same pattern as the irreversible EEC case initially. Depending then upon the value of the reverse rate, I_a/I_c again returns to near unity and remains there for the slowest scan rates, E_p assumes a constant value shifted anodically approximately $.059 \log_{10}(1 + k_f/k_b)$ Volts. The other parameters assume constant values at roughly the same time.

<u>EECC Case</u>

$$
\begin{array}{ll}
A + e^- \gtrless B & (E) \\
B + c^- \gtrless C & (E) \\
C \gtrless D & (C) \\
D \gtrless E & (C)
\end{array}
$$

Clearly, the situation in which two successive chemical steps are both irreversible behaves identically from the point of view of electrochemistry to a situation in which only the first chemical step takes place. The same is true for the case in which the second chemical step only is reversible. If the EEC case did not give satisfactory results, then the only EECC mechanisms of interest are those in which the first chemical step is reversible and the second either reversible or irreversible.

The second situation is the more interesting from the point of view of the porphyrin system in that the overall mechanism is irreversible. Two major classes of perturbation are observed: that where the reversible chemical step is much faster than the succeeding irreversible step and that where it is much slower. These are shown in Figures 2 through 4. In the first case, the diagnostic features exhibit a combination of the characteristics of reversible and irreversible following chemical reactions. At high scan rates, as usual for this type of mechanism, the four features assume constant values. As the scan rate is decreased, the characteristics, discussed in the previous section, corresponding to the reversible chemical step become evident; that is, the peak potential shifts anodically toward a stable value and the other parameters exhibit their respective changes. As the scan rate is further decreased to the point where the irreversible step becomes important, the features take on the characteristics appropriate to the irreversible case. The interval over which reversible chemical reaction characteristics are observed is related directly to the difference in rate between the first and second forward rates. As this distance decreases to zero and, in fact, as the second rate becomes faster than the first, we would expect the reversible behavior to disappear entirely. This is indeed what happens in the second class of reactions for which the second irreversible rate is significantly greater than the first reversible forward rate. Looked at another way, under these conditions the reverse reaction does not really have much of an opportunity to take place since the intermediate between the two reactions does not accumulate. The result is essentially an irreversible EEC case with rate constant equal to the forward rate of the first chemical step.

This mechanism yields many more possibilities for adjusting curve shape than EEC and, as a result, gives a more satisfying looking fit to the porphyrin data. The parameters predicted by the E_p and I_a/I_c features, however, are still an order of magnitude apart. Examination of the chronoabsorptiometric behavior, assuming this mechanism resulted in gibberish, confirmed the likelihood that this is not a reasonable candidate.

The EECC case corresponding to two reversible cases was not examined. It would, no doubt, consist of a mixture of the two reversible situations separately convolved together in a way similar to the previous.

<u>ECE Case</u>

$$A + e^- \gtrless B \quad (E)$$

$$B \rightarrow D \quad (C)$$

$$D + e^- \gtrless E \quad (E)$$

The situation where a chemical reaction is situated between the two electron transfers was not examined in detail since it was clear that this mechanism could not obtain in the porphyrin system. For the case where the potentials of the two electron transfers are closely spaced, the intermediate chemical reaction causes the peaks to separate with increasing scan rate. In fact, we observe that $E_p - E_{p/2}$ for the porphyrin assumes a constant value as scan rate is increased. The curve shape is completely wrong and, therefore, this mechanism is rejected.

EDEC Scheme

$$A + e^- \gtrless B \quad (E)$$

$$2B \gtrless C + A \quad (D)$$

$$B + e^- \gtrless C \quad (E)$$

$$C \gtrless D \quad (C)$$

Whenever the potentials of the two successive electron transfers become close and especially when the second is easier than the first, homogeneous electron transfer in the form of disproportionation of the one electron intermediate into the starting material and the two electron reduction product becomes an important consideration. In the case of a simple system with two electron transfers and no kinetic complications, the path by which reduction takes place is not significant and the shapes of the current potential curves are not greatly affected. When homogeneous chemical processes other than this are introduced, however, the additional pathways for perturbation of species concentrations can make effects due to disproportionation visible under certain conditions. If the electrochemistry is reversible and the separation between the two one-electron steps can be measured, a reasonable value for the k_f/k_b ratio for disproportionation should be chosen for theromodynamic consistency using the relation

$$E_2^o - E_1^o = .059 \log_{10}(k_f/k_b)$$

For the case where the homogeneous chemical step is irreversible, slow disproportionations, having rates on the order of the chemical step, show only the most minor of differences in the diagnostic features compared with the EEC case. When the disproportionation is made very fast, however, a change is noted which is significant only for the I_a/I_c plot. In this case, the apparent first order rate, as inferred from the shape of the I_a/I_c versus v curve, is shifted toward lower values by nearly an order of magnitude as shown in Figure 5. In the case of the porphyrin data, the fit is much superior and mechnaisms of the EDEC type require serious consideration.

Clearly, a reasonable fit of the cyclic voltammetric data does not constitute proof that a given mechanism obtains. It does, however, eliminate a significant number of other possibilities, presents a reasonable candidate for further examination, and suggests appropriate kinetic parameter values. In the case of the porphyrin, the next step is to see if the spectroelectrochemical data fit this mechanism. While this procedure is not yet complete, preliminary fits at a number of wavelengths indicate excellent agreement.

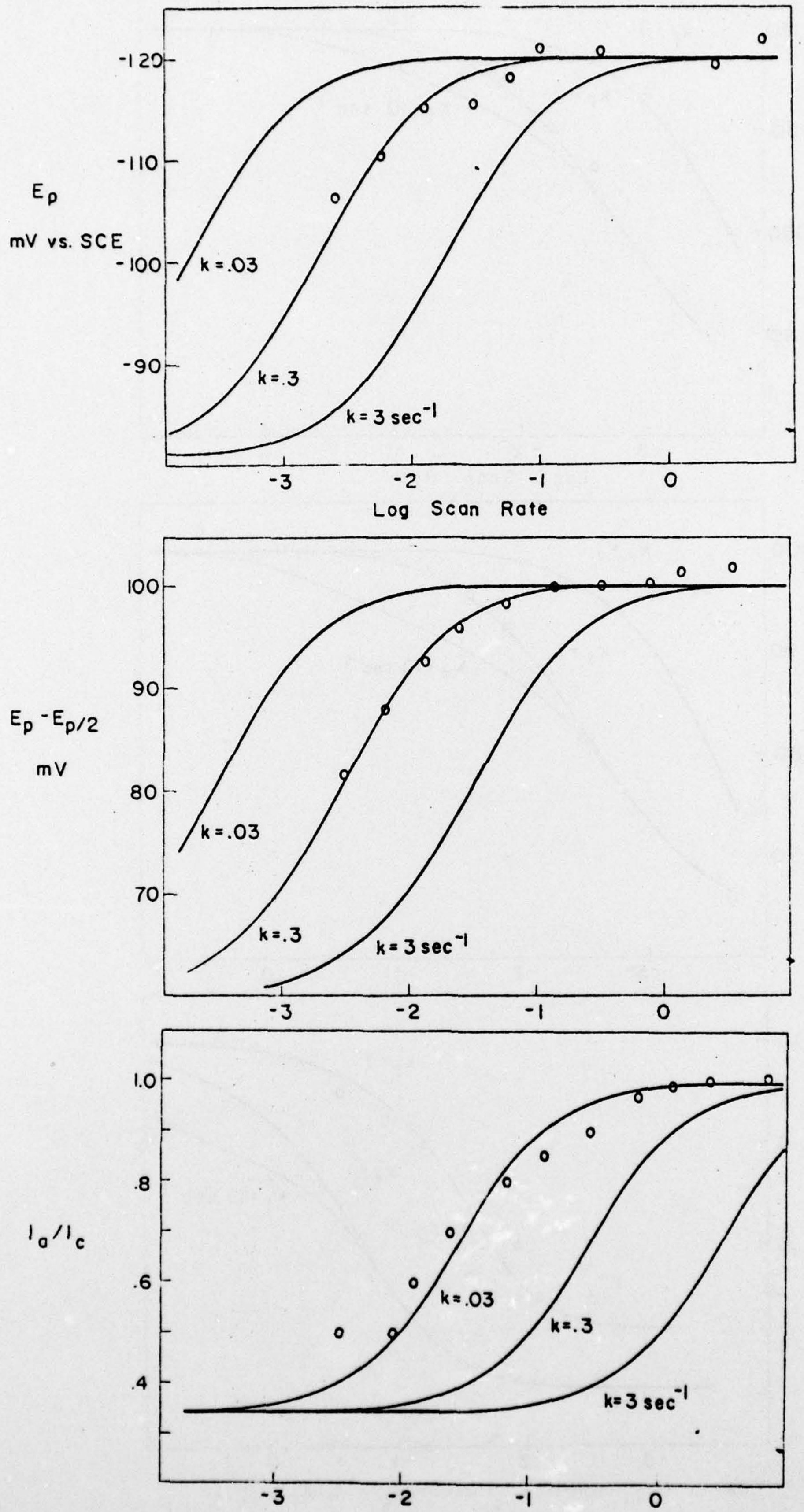

Figure 1: EEC_I Mechanism $E_1^{\circ\prime} = -0.025v$, $E_2^{\circ\prime} = -0.105v$ vs SCE.
Rate Constant at Chemical Step = k.

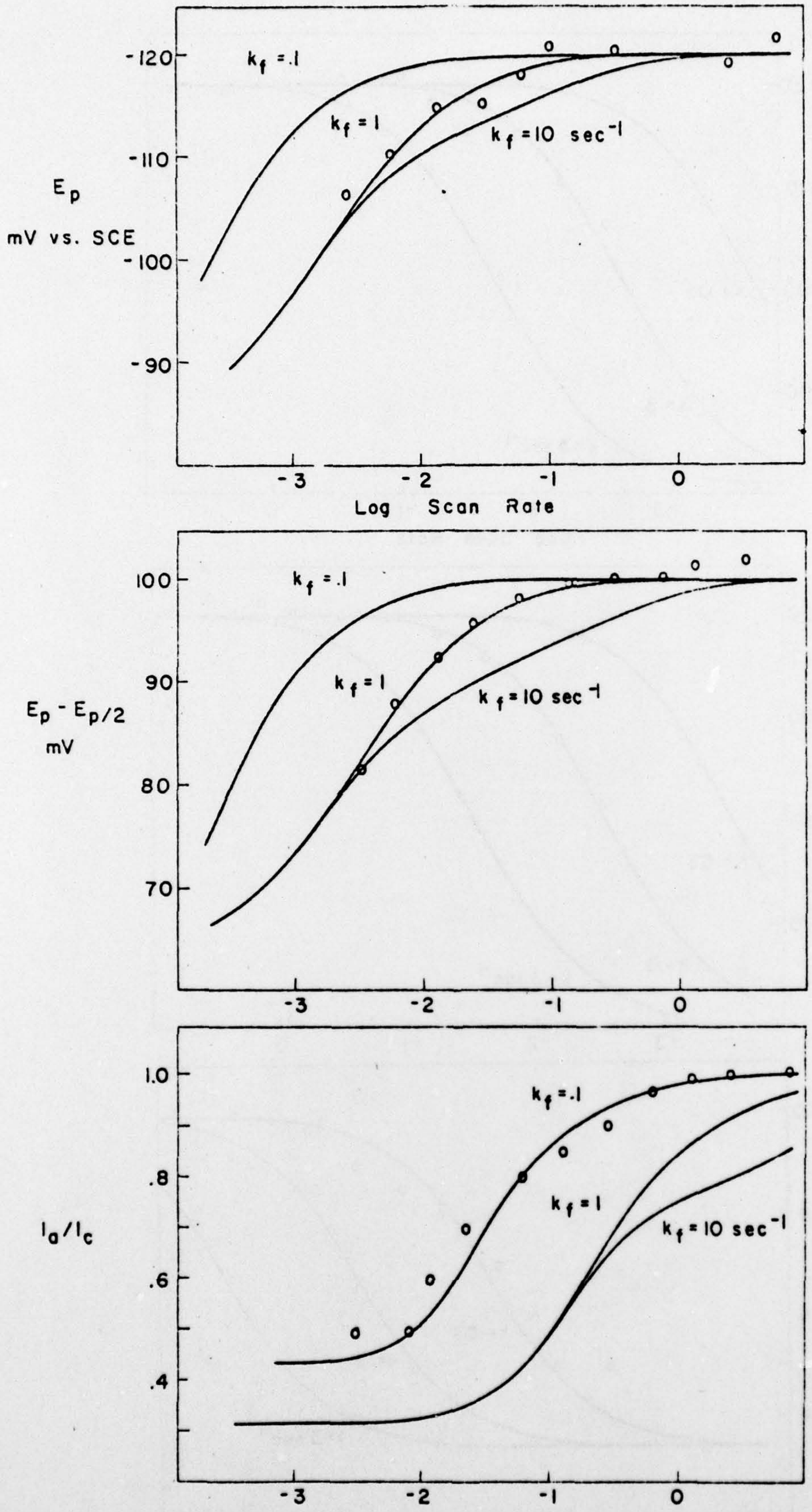

Figure 2: EEC_RC_1 Mechanism E_1' = -0.025v, E_2' = -0.105v vs SCE.
Rate Constant ratio $\frac{k_f}{k_b}$ = 0.3, k = 3 sec^{-1} (Variable k_f).

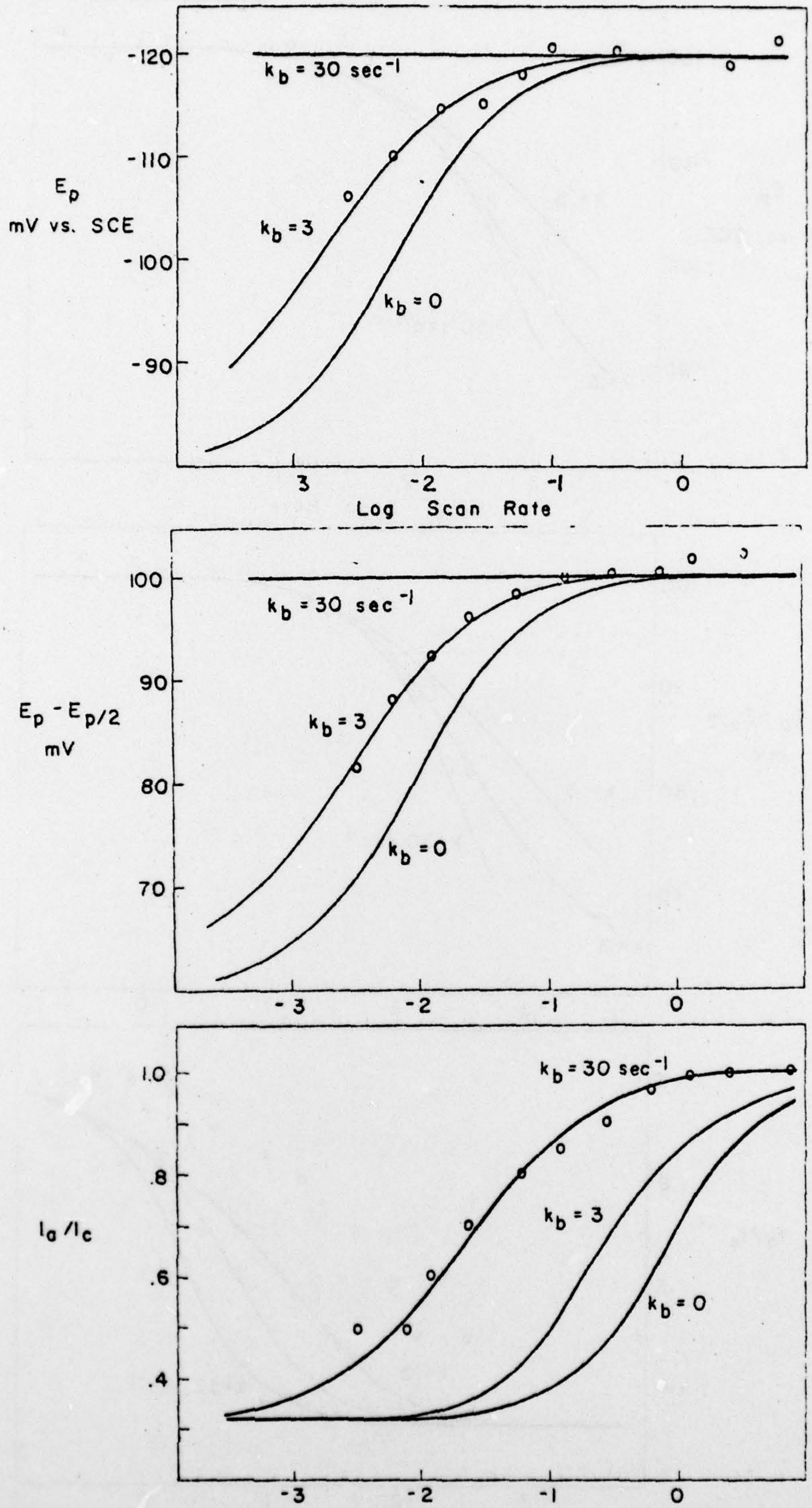

Figure 3: EEC_RC_I Mechanism $E_1^{\circ\prime}$ = -0.025v, $E_2^{\circ\prime}$ = -0.105v vs SCE.
Rate Constants: k_f = 1 sec^{-1}, k = 3 sec^{-1}. (Variable k_f/k_b).

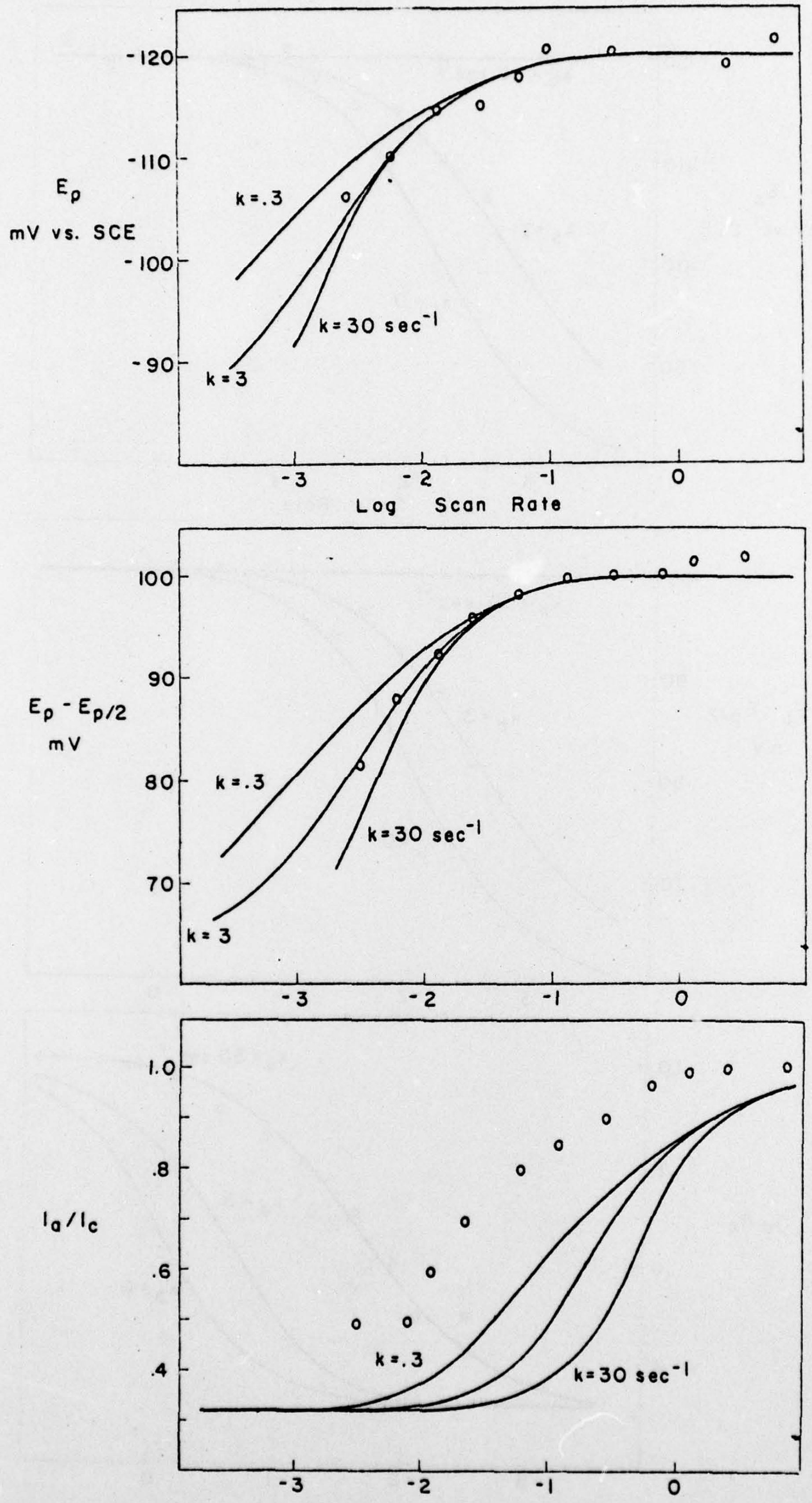

Figure 4: EEC_RC_I Mechanism $E_1^{\circ\prime} = -0.025$v, $E_2^{\circ\prime} = -0.105$v vs SCE.

Rate Constants: $k_f = 1$ sec^{-1}, $k_b = 3$ sec^{-1} (Variable k).

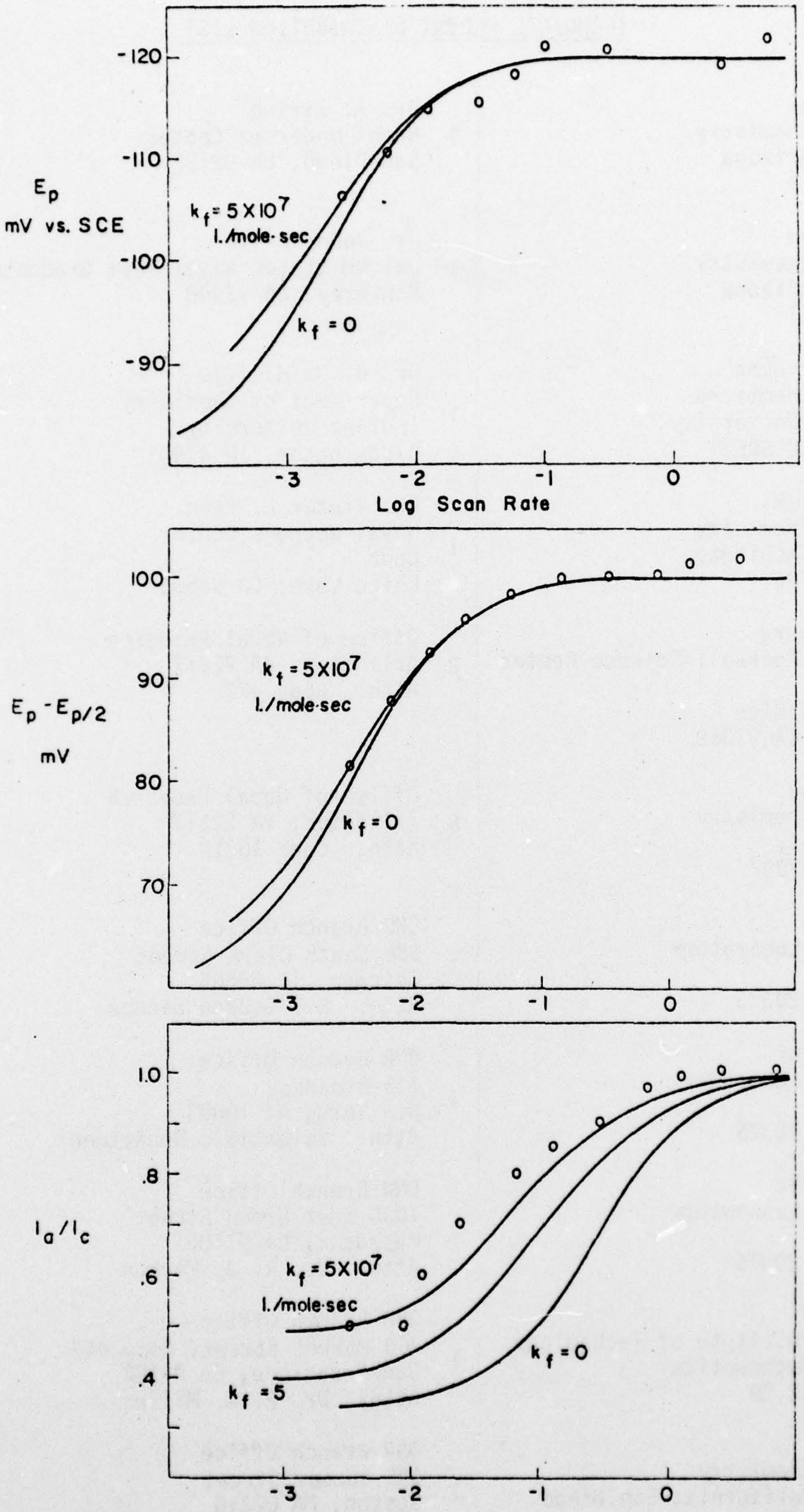

Figure 5: EDEC$_1$ Mechanism $E_1^{\circ\prime} = -0.025$v, $E_2^{\circ\prime} = -0.105$v vs SCE.

Rate Constant Ratio $\frac{k_f}{k_b} = 0.05$, $k = 0.3$ sec^{-1} (Variable k_f).