APPLICATION OF CYCLIC VOLTAMMETRY TO THE STUDY OF DIMERIZATION REACTIONS INITIATED ELECTROLYTICALLY

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ABSTRACT

APPLICATIONS OF CYCLIC VOLTAMMETRY TO THE STUDY OF DIMERIZATION REACTIONS INITIATED ELECTROLYTICALLY

by Paul Joseph Kudirka

Reduction of benzaldehyde in acetonitrile has been used to evaluate steady state theory of cyclic voltammetry for dimerization reactions initiated electrolytically. Qualitative predictions of the theory are in excellent agreement with experimental results, and the rate constant measured for dimerization of benzaldehyde radical anions (log $\underline{k}_{dim}$ = 5.8 ± 0.4) agrees reasonably well with reported photochemical measurements (log $\underline{k}_{dim}$ = 6.2) in buffered 50% ethanol-water solution. Because assumptions of the steady state theory could not be satisfied for dimerization of benzophenone and acetophenone radical anions, an approximate method of estimating these rate constants is described. This method is based on the fact that under conditions where the electrode process is nearly reversible the dimerization reaction can be treated as a small perturbation of the electrochemical equilibrium. In this case it is possible to use cyclic voltammetric theory for the case of first-order reactions initiated electrolytically. The benzaldehyde system was used to

confirm the ideas of the perturbation method, and the rate constant obtained was in exact agreement with the value cited above. The method also was used to estimate the dimerization rate constants of benzophenone (log $\underline{k}_{dim}$ = 3.77) and acetophenone (log $\underline{k}_{dim}$ = 3.64) radical anions in acetonitrile.

$\underline{E}^{o}$ values were estimated for the one-electron reduction of benzaldehyde (-1.614 V *vs* SCE) and benzophenone (-1.393 V *vs* SCE) in water from reported values of $\underline{k}_{dim}$ for these protonated radicals in conjunction with the steady state theory of cyclic voltammetry. Based on these $\underline{E}^{o}$ values, $\underline{E}^{o}$ was estimated for acetophenone (-1.743 V *vs* SCE) in water. The steady state theory was then used to estimate the rate constant for dimerization of the protonated acetophenone radical (log $\underline{k}_{dim}$ = 8.0) in buffered (pH 3.7) aqueous solution.

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INTRODUCTION

Recent literature (see ref. 1 for a review) shows that a large number of electrode reactions of organic compounds occur by stepwise addition (or removal) of electrons with formation of free radical intermediates. In many instances the major reaction of these free radicals is dimerization. Thus, an understanding of the electrochemistry of many organic compounds requires a knowledge of how reactions such as radical dimerization influence electrode behavior.

Although in general modern electrochemical techniques are ideally suited for studying homogeneous chemical reactions initiated electrochemically, when these reactions are higher than first order (or pseudo first order) quantitative studies are complicated for the following reason. Mathematical formulation of an electrochemical experiment requires a description of both the mass transport process (usually diffusion) and any kinetic reactions. Because of the mass transport complication, the entire process is described by partial differential equations. If the homogeneous kinetics are first order, then the partial differential equations are linear and usually amenable to solution. However, if the kinetics are higher than first order, the partial differential equations are nonlinear and extremely difficult to solve. The result of this fact is that quantitative theories of most electrochemical techniques have not been developed for reactions higher than first order. Therefore, in spite of the importance of these higher order processes, they generally cannot be studied quantitatively.

Although the rigorous treatment of second order reactions in electrochemistry is difficult, approximations aimed at simplifying the mathematics obviously can be made. An example of this is a recent treatment of cyclic voltammetry (stationary electrode polarography) for the case of a dimerization reaction following reversible charge transfer (2).

$$O + n\,e \rightleftharpoons R \qquad \text{Ia}$$

$$2\,R \longrightarrow Z \qquad \text{Ib}$$

There Reaction Ia is reversible, and Z is not electroactive at potentials where Reaction Ia takes place.

To make the above problem mathematically tractable, the partial differential equations were linearized by assuming a steady state for the concentration of R at the electrode surface. It was shown that this assumption is equivalent to the rate of dimerization being very rapid with respect to scan rate. Clearly this fact excludes from the theoretical treatment the case of a triangular wave scan during which unreacted R would be oxidized back to O, even though this would be the ideal way to study the dimerization. In other words existing theory applies only to the situation where the succeeding chemical dimerization is so rapid and irreversible that no R remains in the vicinity of the electrode to give an anodic wave on reverse scan of the applied triangular wave. In fact, this absence of an anodic wave is a necessary condition for application of steady state theory.

Results of the steady state theory for cyclic voltammetry are expressed as the following equation that relates peak potential to other experimental parameters (2).

$$E_p = E^{\circ} - (RT/3nF) \ln [(4.78\pi 3D_O)/(2D_R)] - (RT/3nF) \ln [(nFv)/(RT\underline{k}_{dim}C_O^*)] \quad (1)$$

There $\underline{E}_p$ is peak potential, $\underline{D}_O$ and $\underline{D}_R$ are diffusion coefficients, $\underline{E}^{\circ}$ is the formal potential, $\underline{v}$ is scan rate, $\underline{k}_{dim}$ is the second order rate constant of Reaction Ib, $\underline{C}_O^*$ is the bulk concentration of depolarizer, and the other terms have their usual meaning (3).

Equation 1 predicts that peak potential should shift about 20/$\underline{n}$ mV for each decade change of scan rate ($\underline{v}$) or depolarizer concentration ($\underline{C}_O^*$). These shifts are useful diagnostic tests for establishing the presence of a dimerization following charge transfer. However, quantitative determination of $\underline{k}_{dim}$ from Equation 1 requires a knowledge of $\underline{E}^{\circ}$. This fact constitutes a major limitation of the steady state theory (Equation 1) because $\underline{E}^{\circ}$ is the formal potential of Reaction Ia--the case where $\underline{k}_{dim}$ is zero in

Mechanism I. Therefore, for most real systems, it is clear that $\underline{E}^{o}$ cannot be determined polarographically. In fact, the only practical experimental way to determine $\underline{E}^{o}$ is to use cyclic voltammetry under conditions where duration of the cyclic scan is sufficiently small with respect to half-life of the dimerization that the cyclic polarogram is not influenced by Reaction Ib.

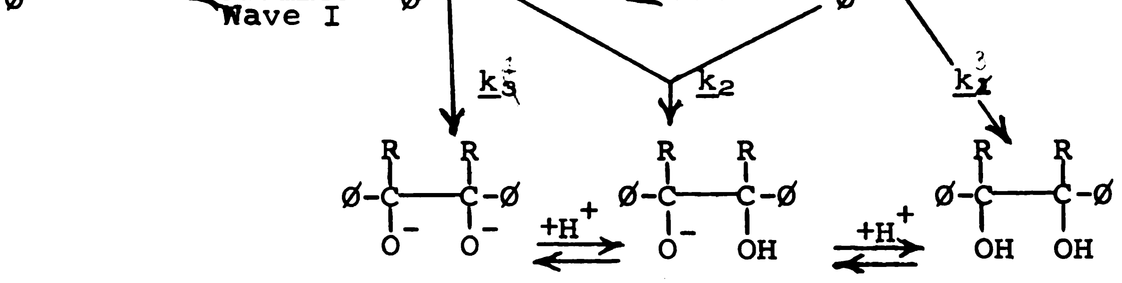
In summary, experimental application of existing steady state theory for cyclic voltammetry (Equation 1) requires scan rates that are slow with respect to the rate of Reaction Ib (no anodic wave). However, quantitative application of Equation 1 requires knowledge of $\underline{E}^{o}$, which can only be obtained by using scan rates that are fast with respect to the rate of Reaction Ib. The result of this is that, depending upon the magnitude of $\underline{k}_{dim}$, an extremely large range of scan rates may be required to study a given system.

In spite of these serious limitations, until a more satisfactory treatment is forthcoming, use of the steady state theory is the only way to characterize processes like Mechanism I with cyclic voltammetry. Therefore, it seemed important to test and evaluate the scope of Equation 1 experimentally, and this task was adopted as the major objective of this research.

Experimental evaluation of Equation 1 requires a system that is reduced according to Mechanism I, and for which the restrictions of Equation 1 can be satisfied. Although a number of systems presumably could be used, the extensive electrochemical literature on reduction of aldehydes and ketones, and the photochemical literature on dimerization of ketyl radical anions indicated that these systems would be a logical choice. Also, it appeared that considerable time could be saved by judicious choice of the compound and experimental conditions based on the existing literature.

Elving and Leone (4) have postulated a mechanism for reduction of aromatic aldehydes and ketones that is consistent with most experimental data. This mechanism is briefly restated here to provide a logical discussion of the selection of experimental conditions for evaluation of Equation 1.

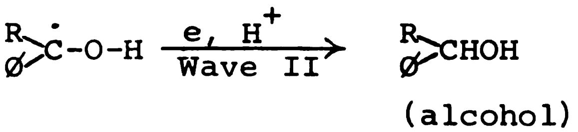
Depending on the specific compound, either one or two polarographic reduction waves are observed in buffered acidic aqueous solutions. The first wave, Wave I, corresponds to a reversible one-electron reduction of the aromatic aldehyde or ketone ($\begin{smallmatrix}R\\ \emptyset\end{smallmatrix}\!>\!C{=}O$) followed by dimerization to the pinacol.



II

None of the rate constants $\underline{k}_1$, $\underline{k}_2$, or $\underline{k}_3$ has been measured by electrochemical experiments. However, for some compounds photochemical measurements have been reported; for example, Table I lists values obtained by Porter, Beckett and Osborne from flash photolysis experiments (5). Clearly from the data of Table I in acidic media the path involving rate constant $\underline{k}_3$ is the important path, and in fact the only one considered explicitly by Elving and Leone.

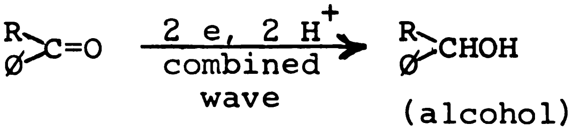
When a second wave, Wave II, is observed in buffered acidic aqueous solutions, it corresponds to a pH independent one-electron reduction of the protonated radical $(\substack{\text{Ø}\\ \text{R}}\!>\!\dot{\text{C}}\text{-O-H})$ to the corresponding alcohol.



$$\substack{\text{R}\\ \text{Ø}}\!>\!\dot{\text{C}}\text{-O-H} \xrightarrow[\text{Wave II}]{e,\ H^+} \underset{\text{(alcohol)}}{\substack{\text{R}\\ \text{Ø}}\!>\!\text{CHOH}} \qquad \text{III}$$

Wave II is irreversible and observed in acidic media only for a few compounds (benzophenone and substituted benzophenones), presumably because it usually is masked by hydrogen discharge (4).

Wave I shifts cathodically with increasing pH ($\Delta E_{\frac{1}{2}}/\Delta pH$ $\sim$60 mV) so that at about pH 6 it overlaps Wave II to give a single two-electron reduction wave with the alcohol as the major product.



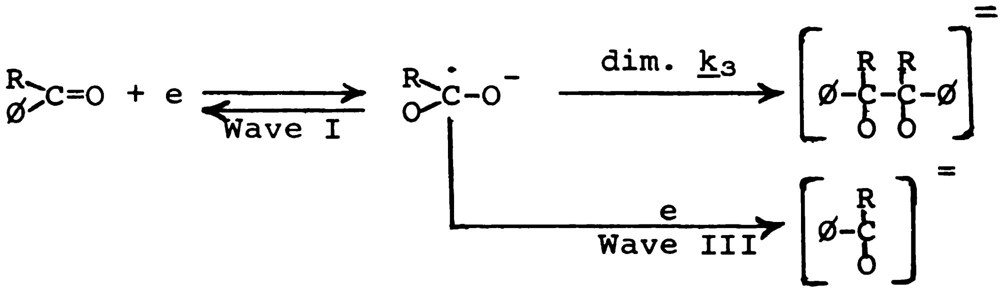
$$\substack{\text{R}\\ \text{Ø}}\!>\!\text{C=O} \xrightarrow[\substack{\text{combined}\\ \text{wave}}]{2\ e,\ 2\ H^+} \underset{\text{(alcohol)}}{\substack{\text{R}\\ \text{Ø}}\!>\!\text{CHOH}} \qquad \text{IV}$$

Table I. Photochemical Data of Porter *et al*. (5).

System	Radical species dimerizing	$\underline{k}_{dim}$ $\underline{M}$-sec^{-1}	pK of Equilibrium ${}^{R}_{\phi}{>}\dot{C}\text{-OH} \rightleftarrows {}^{R}_{O}{>}\dot{C}\text{-O}^{-} + H^{+}$
Benzaldehyde 50% ethanol-water	${}^{\phi}_{H}{>}\dot{C}\text{-O-H}$	6×10^{8}	10.5
	${}^{\phi}_{H}{>}\dot{C}\text{-O}^{-}$	1.6×10^{6}	
Acetophenone 50% isopropanol-water	${}^{\phi}_{H_3C}{>}\dot{C}\text{-O-H}$	---	10.9
	${}^{\phi}_{H_3C}{>}\dot{C}\text{-O}^{-}$	---	
Benzophenone 50% isopropanol-water	${}^{\phi}_{\phi}{>}\dot{C}\text{-O-H}$	5.9×10^{7}	9.2
	$\phi_2\dot{C}\text{-OH}$ + $\phi_2\dot{C}\text{-O}^{-}$	1.1×10^{9}	
	${}^{\phi}_{\phi}{>}\dot{C}\text{-O}^{-}$	$\leq 1.8 \times 10^{5}$	

This combined wave shifts cathodically with pH ($\Delta E_{\frac{1}{2}}/\Delta pH$ is from 15 to 40 mV depending upon the specific system). In addition, this wave generally decreases from a limiting current corresponding to a two-electron reduction at pH from about 6 to 9 to that of a one-electron reduction at pH 13 or greater. For pH 13 or greater the pinacol once again is the predominant reduction product. This behavior is consistent with the above mechanism because in highly alkaline solutions very little protonated radical would be formed and reduced at potentials of Wave II. Thus, in sufficiently basic solutions, the combined wave corresponds to a one-electron reduction, and the mechanism is essentially that of Wave I where dimerization occurs via paths involving rate constants $\underline{k}_1$ and $\underline{k}_2$.

For very highly alkaline solutions, a third wave, Wave III, often is observed at potentials cathodic of Wave I. Wave III probably corresponds to reduction of the radical anion $({}^{R}_{\emptyset}{>}\dot{C}{-}O^{-})$ produced by the process corresponding to Wave I. Hence in essentially aprotic solvent only two waves, Waves I and III, would be expected.



V

Based on the above discussion of the mechanism of reduction of aromatic aldehydes and ketones, it would appear that Equation 1 could be evaluated with these compounds in buffered acidic solutions where Wave I is well defined. In fact, recently Saveant and Vianello attempted to do this for benzaldehyde at pH about 3 (6). These authors showed that Equation 1 adequately described experimental peak potential dependence on scan rate and bulk concentration of benzaldehyde. However, they stated that they were unable to scan rapidly enough to measure $\underline{E}^o$ for the benzaldehyde couple, and hence unable to measure $\underline{k}_{dim}$. The explanation of this fact is readily apparent from the rate constants listed in Table I. Based on the rate constant for benzaldehyde protonated radical, one calculates that scan rates of the order of 10^5 V sec^{-1} are required to obtain an anodic peak on the oxidation scan, whereas the largest scan rate used by Saveant and Vianello was about 10 V sec^{-1}. Even if it were possible to scan 10^5 V sec^{-1} (state of the art equipment permits maximum scan rates of the order of 10^3 V sec^{-1}) charge transfer kinetics probably would prevent determination of $\underline{E}^o$. Hence one concludes that Equation 1 cannot be evaluated quantitatively in acidic aqueous solutions.

The next logical choice of experimental conditions would appear to be basic media where the combined wave has one-electron character, and dimerization of the radical anion is considerably slower than dimerization of the corresponding protonated radicals. However, even in very basic aqueous solutions proton availability is high enough that the combined wave always is complicated by some simultaneous reduction of protonated radicals. To avoid these possible complications the obvious choice is a nonaqueous solvent of low proton availability. There the mechanism is given by Reaction V where Wave I is well defined and easily resolved from Wave III. Moreover, the rate of dimerization between radical anions is considerably slower than the reaction between protonated radicals, especially if the nonaqueous solvent has a low dielectric constant. In fact experiments in DMF (7) indicate that the radical anion of benzophenone is so stable that even for the slowest scan rates possible (ca. 20 mV sec^{-1} determined by onset of convection) an anodic wave still would be obtained with cyclic voltammetric experiments. As would be expected, similar electron spin resonance experiments indicate that the radical anion of benzaldehyde is considerably less stable than those of benzophenone or acetophenone (7). For these reasons reduction of benzaldehyde in a nonaqueous solvent appeared to be the logical system to study. Acetonitrile was chosen as solvent because it is relatively proton deficient, and has a high enough dielectric constant that uncompensated ohmic potential drop in the solution is manageable.

Another important reason for selection of acetonitrile is the fact that recent studies (8) have been made on comparison of standard potentials measured in acetonitrile and aqueous solutions. For example, the liquid junction potenial between acetonitrile solutions and an aqueous SCE has been estimated. Knowing the value of the liquid junction potential makes it possible to estimate the $\underline{E}^{\circ}$ values of benzaldehyde and benzophenone in water. With these values of $\underline{E}^{\circ}$ it is then possible to estimate dimerization rates in acidic aqueous solutions. Although subject to considerable uncertainty, results of these experiments also are included in this thesis.

EXPERIMENTAL

Instrumentation

The instrument was assembled from commercially available units. Basically, it consisted of two different sections, a three-electrode potentiostat (Wenking Potentiostat Model 61RS) and a function generator (Exact, Type 255s). A block diagram of the circuit configuration used is shown in Figure 1.

Cell and Electrodes

The cell and electrodes were of conventional design and are described elsewhere (9).

Chemicals

All chemicals were reagent grade and used without further purification with the following exceptions. Acetonitrile (Fisher, B.P. 81.4-81.7°C) was purified by distillation according to the procedure of Mann (10). The tetraethylammonium perchlorate, which was used as supporting electrolyte, was prepared by metathesis of tetraethylammonium bromide with sodium perchlorate according to the procedure of Kolthoff (11). The product was recrystallized four times from water and dried at 80°C.

Experimental Procedures

For scan rates greater than about 0.25 V sec^{-1} curves were recorded by photographing (Tektronix Type C-12 Camera

Figure 1. Block diagram of circuit configuration.

RE: Reference electrode

CE: Counter electrode

WE: Working electrode

R_L: Load resistor (decade resistance box)

C.A.: Wenking Potentiostat

E_i: Initial potential

F.G.: Exact function generator

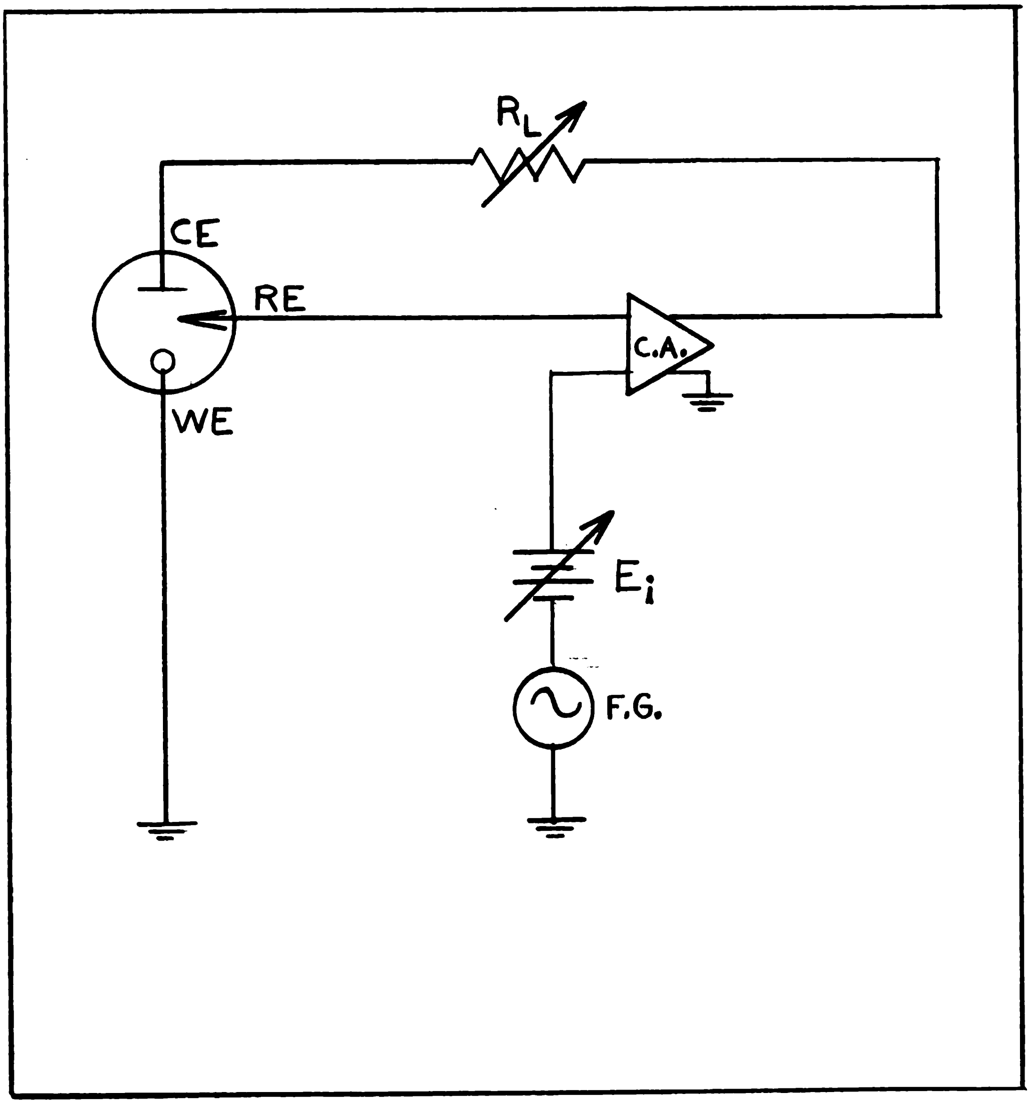


Figure 1

and Polaroid Type 47 Film) an oscilloscopic display (Tektronix Type 564 Storage Oscilloscope using Type 2A63 Differential Amplifiers). For scan rates slower than about 0.25 V sec^{-1}, data were recorded on an x-y recorder (Honeywell Model 520).

Aqueous experiments were run at pH about 3.7 using a potassium acetate-acetic acid buffer system.

REDUCTION OF BENZALDEHYDE IN ACETONITRILE

Estimation of E^o

Benzaldehyde was studied at three depolarizer concentrations (1.18, 2.50, and 5.00 x 10^{-4} $\underline{M}$), and a typical stationary electrode polarogram is shown in Figure 2. For the curve of Figure 2 scan rate is sufficiently large that the electrode process is not influenced by the succeeding dimerization reaction. Evidence for this fact is the well-defined anodic wave, and the peak potential separation of 70 mV. Actually, for a reversible one-electron reduction, the theoretical peak potential separation is about 60 mV (12). The source of the additional 10 mV of overpotential was not determined, but probably is due either to uncompensated $\underline{iR}$ drop, or charge transfer kinetics. Nevertheless, it has been shown (13) that overpotentials of this magnitude correspond to very small perturbations of the electrode process from the reversible case. Moreover, the curve of Figure 2 was recorded oscillographically where the experimental error is about ± 5 mV. Thus, it is possible to use curves like those of Figure 2 to estimate the value of $\underline{E}^o$ for the electrode process. This is accomplished from the fact that for a reversible electrode process, $\underline{E}^o$ occurs $28.5/\underline{n}$ mV anodic of the cathodic peak potential (12). From an average of 8 experiments at all three depolarizer

Figure 2. Stationary electrode polarogram for benzaldehyde in acetonitrile.

$V = 17.04\ \mathrm{V\ sec^{-1}}$.

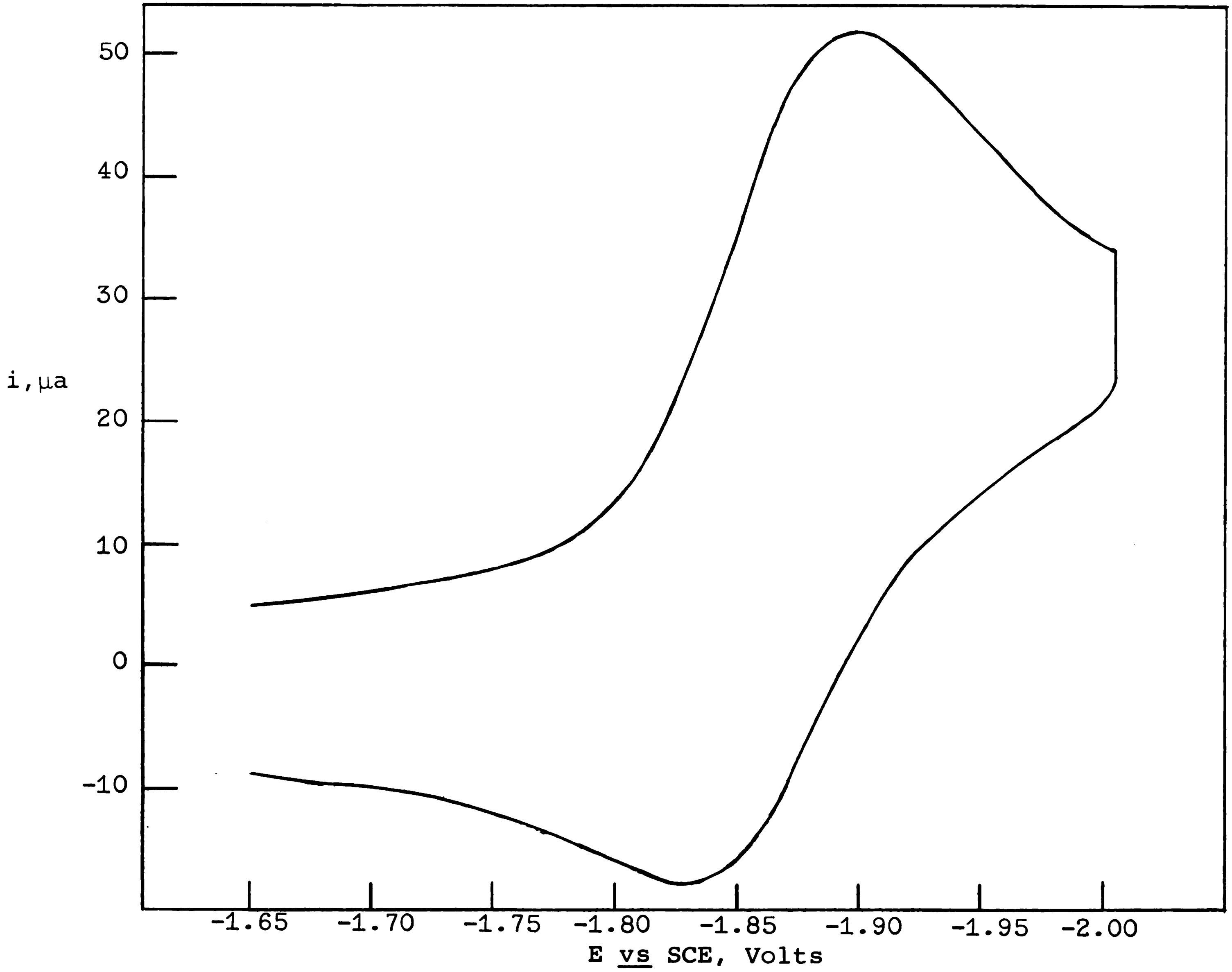
$C_O^* = 2.5 \times 10^{-4}\ \underline{M}$.

$E_i = -1.650$ V vs SCE.

$E_p^c = -1.898$ V vs SCE.

$\Delta E_p = 70$ mV.

Figure 2


i, μa
50
40
30
20
10
0
-10
-1.65
-1.70
-1.75
-1.80
-1.85
-1.90
-1.95
-2.00
E vs SCE, Volts

concentrations a value of $\underline{E}^{o}$ for benzaldehyde equal -1.865 ± 0.005 V *vs* aqueous SCE was obtained.

Influence of the Dimerization Reaction on the Electrode Behavior of Benzaldehyde

When scan rates slower than those of Figure 2 are employed, the presence of the succeeding dimerization becomes readily apparent. Thus the curve of Figure 3 was recorded with a scan rate about a factor of 400 less than that used for Figure 2. The total absence of an anodic wave in this case is proof of the presence of a chemical reaction involving the product of electron transfer. The anodic shift of the cathodic peak potential of about 50 mV also is evidence of a succeeding chemical reaction. The fact that this chemical reaction is dimerization is indicated by the shape of the curve of Figure 3. Thus, Figure 3 also contains data (points) calculated from the steady state theory for a dimerization (2). The good agreement between theory and experiment strongly suggests that the mechanism of reduction of benzaldehyde is the same as Reaction I.

Additional evidence for the presence of the dimerization can be obtained by applying the diagnostic tests discussed in connection with Equation 1. For example, Equation 1 predicts that peak potential should shift cathodically with increasing scan rate. Figures 4 and 5 illustrate the dependence of peak potential on scan rate for two depolarizer concentrations, and the data are contained in Table II.

Figure 3. Stationary electrode polarogram for benzaldehyde in acetonitrile.

$V = 71$ mV sec^{-1}.

$C_O^* = 5.0 \times 10^{-4}$ <u>M</u>.

$E_i = -1.620$ V <u>vs</u> SCE.

$E_p^c = -1.850$ V <u>vs</u> SCE.

Lines, experimental

Points, theoretical.

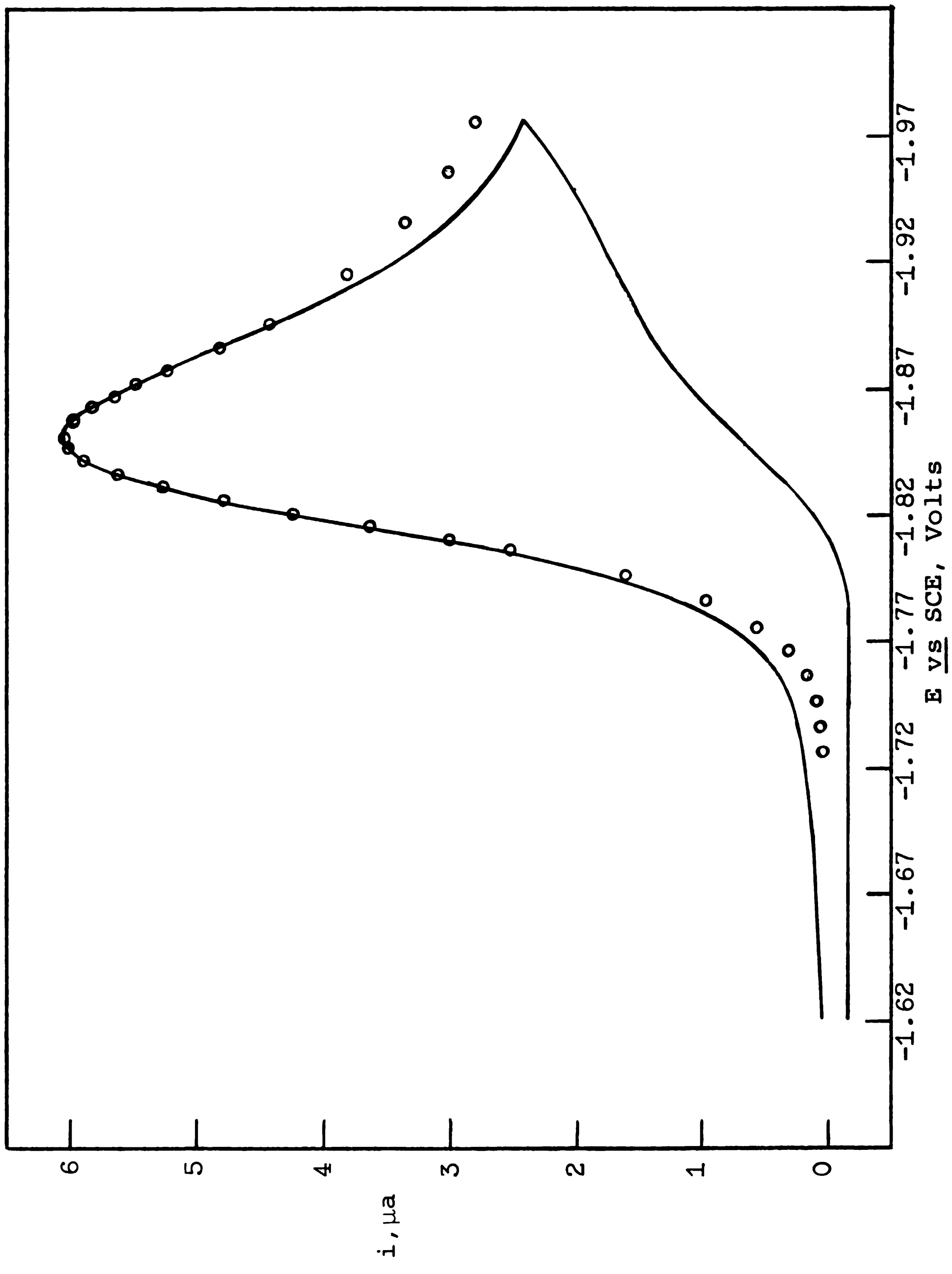


Figure 3

Figure 4. Variation of peak potential with scan rate for benzaldehyde in acetonitrile.

$C_O^* = 5.0 \times 10^{-4}$ M.

Slope = 20 mV/unit log (v).

Log $(k_{dim}) = 5.82$

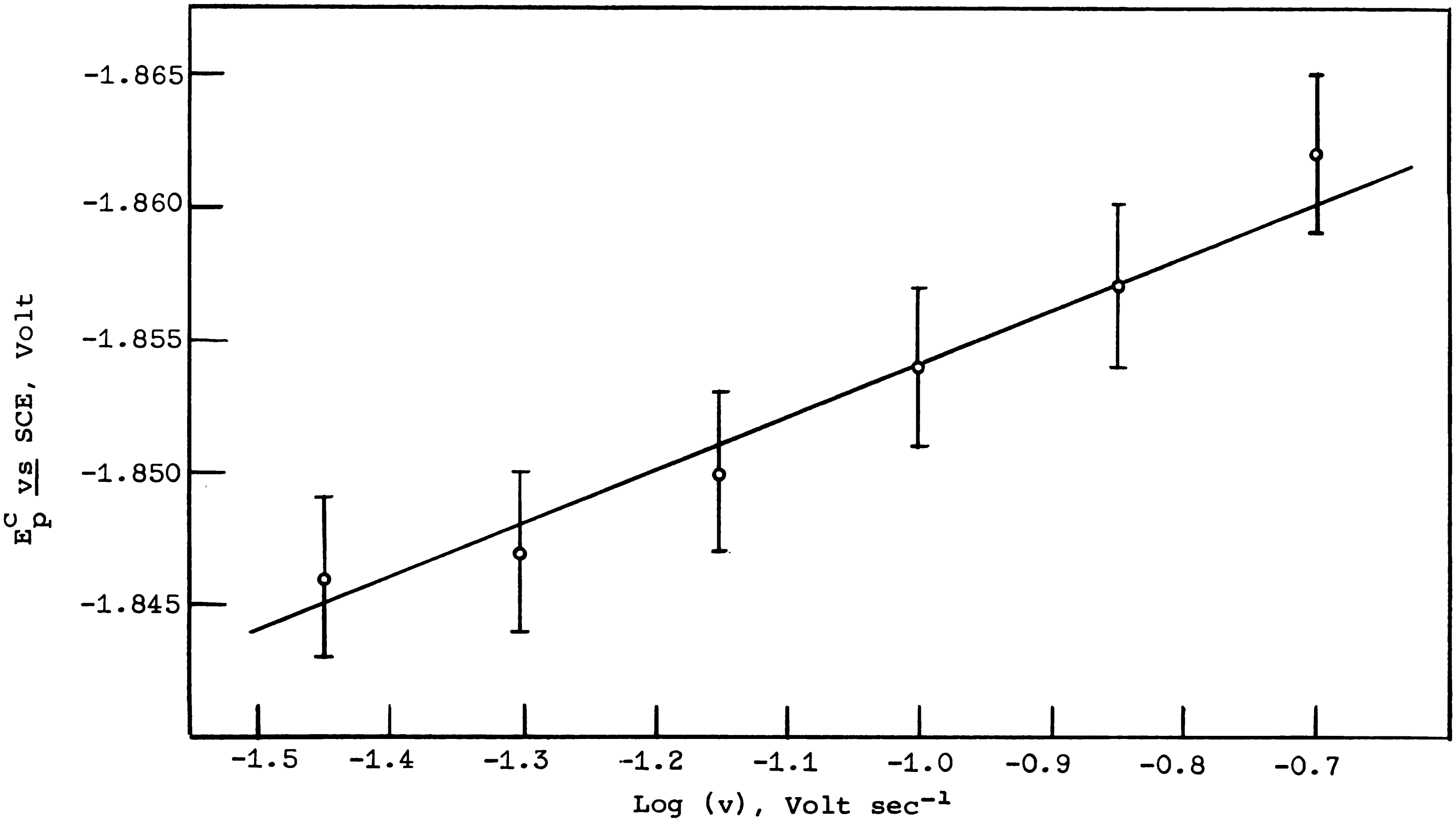

E_p^c vs SCE, Volt
-1.865
-1.860
-1.855
-1.850
-1.845
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
Log (v), Volt sec^{-1}

Figure 4

Figure 5. Variation of peak potential with scan rate of benzaldehyde in acetonitrile.

$C_O^* = 2.5 \times 10^{-4}$ M.

Slope = 20 mV/unit log (v).

Log (k_{dim}) = 5.71

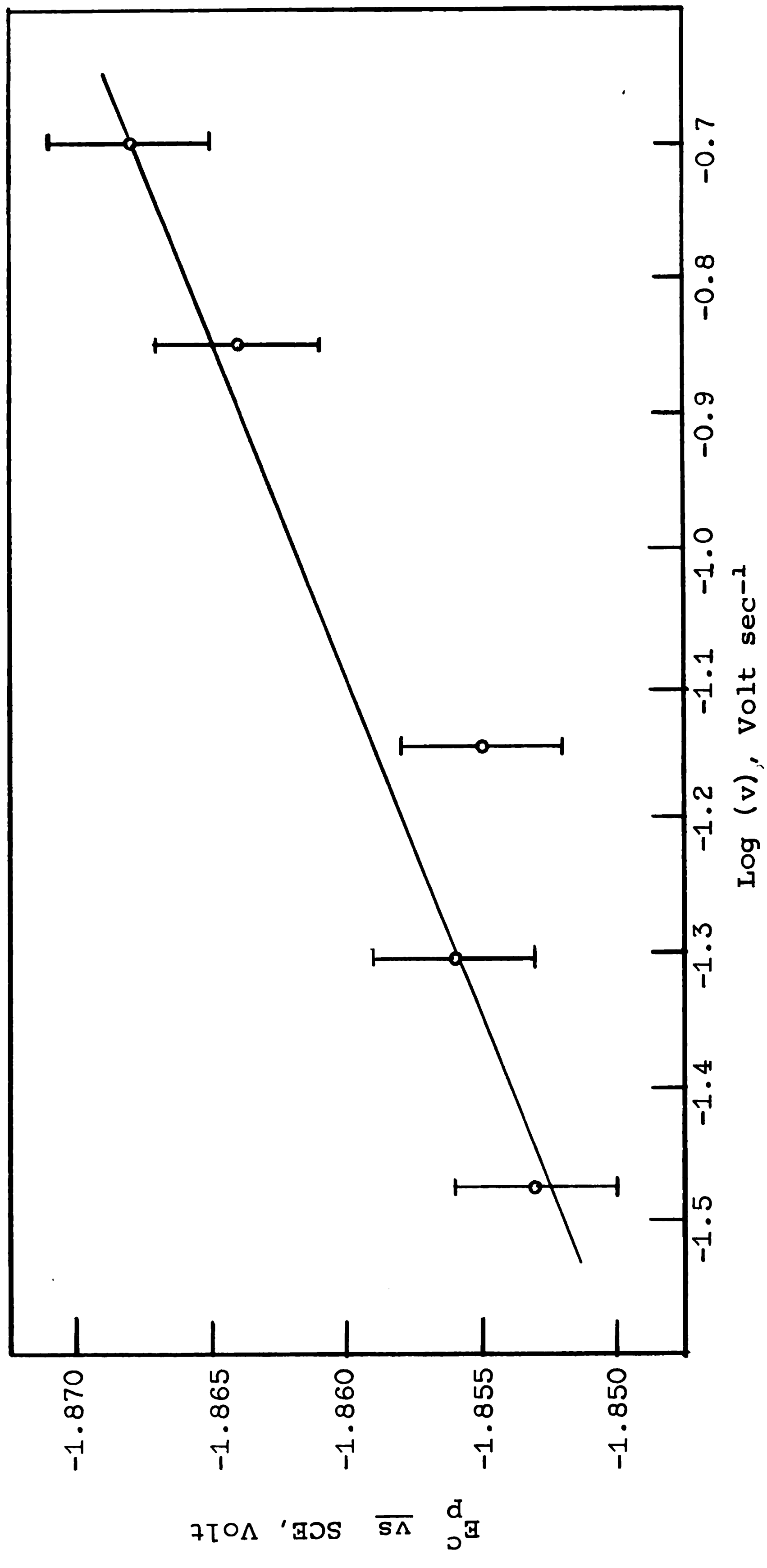

E^c_p vs SCE, Volt
-1.870
-1.865
-1.860
-1.855
-1.850
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
Log (v), Volt sec^{-1}

Figure 5

Figure 5. Variation of peak potential with scan rate of benzaldehyde in acetonitrile.

$C_O^* = 2.5 \times 10^{-4}$ $\underline{M}$.

Slope = 20 mV/unit log (v).

Log ($\underline{k}_{dim}$) = 5.71

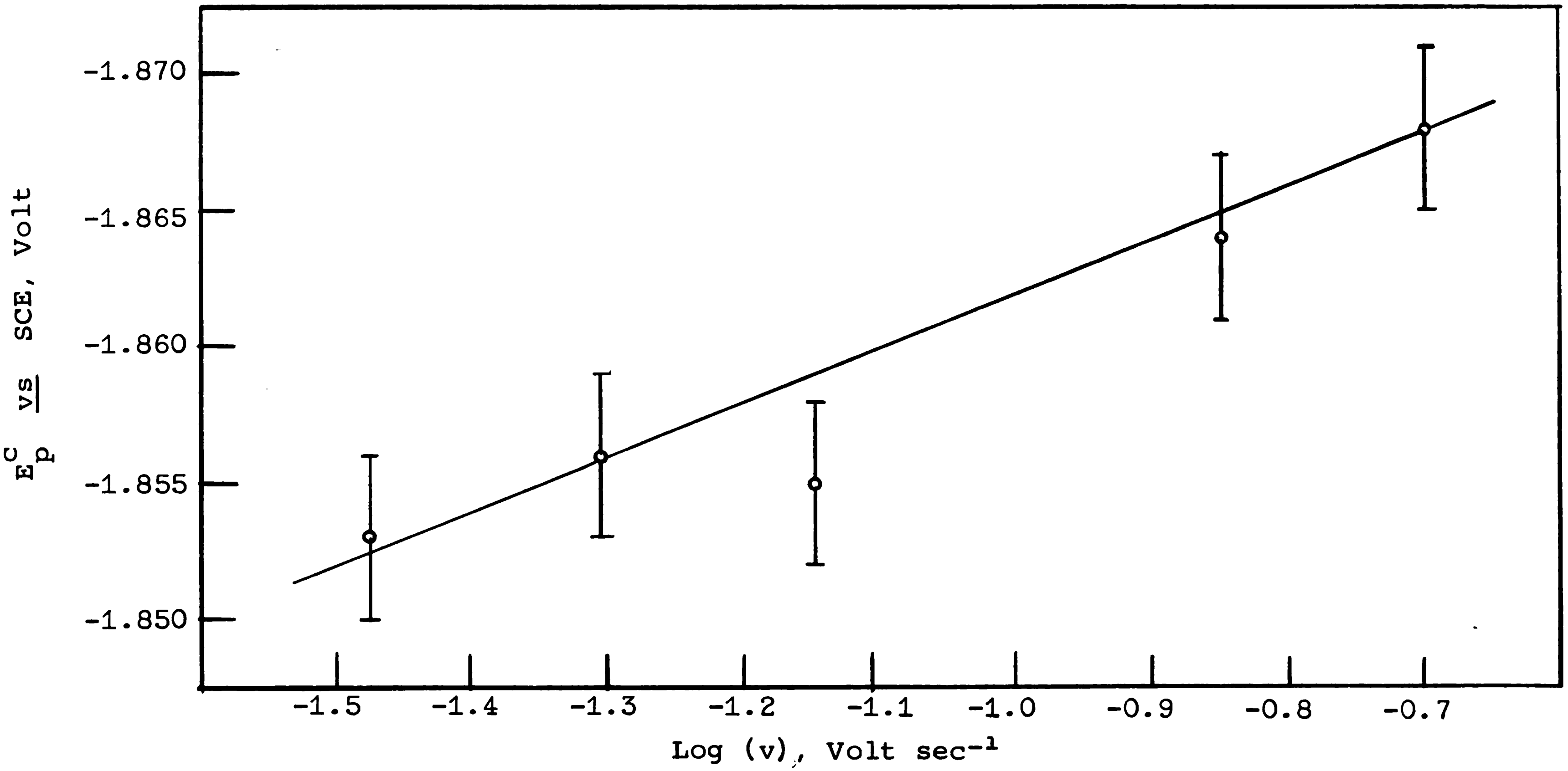

E_p^c vs SCE, Volt
-1.870
-1.865
-1.860
-1.855
-1.850
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
Log (v), Volt sec^{-1}

Figure 5

Table II. Peak Potential _vs_ Scan Rate for Benzaldehyde in Acetonitrile

Scan rate (v) V sec^{-1}	Log (v)	Peak Potential (E_p) V _vs_ aqueous SCE	
		$C_O^* = 5 \times 10^{-4}$ _M_	$C_O^* = 2.5 \times 10^{-4}$ _M_
0.0335	-1.475	-1.846	-1.853
0.0497	-1.304	-1.847	-1.856
0.0710	-1.148	-1.850	-1.855
0.0995	-1.002	-1.854	---
0.142	-0.848	-1.857	-1.864
0.199	-0.701	-1.862	-1.868

Although there is considerable uncertainty in the experimental data, the trends certainly are in agreement with predictions of Equation 1. Moreover, the slopes of the straight lines that have been drawn in Figures 4 and 5 (see figure legends) are in very good agreement with the theoretical slope of 20 mV. All of these data indicate that the mechanism of reduction of benzaldehyde in acetonitrile is the one already postulated (Reaction V).

Estimation of the Rate Constant for Dimerization of Benzaldehyde Radical Anions

Because it is possible to estimate E^o for formation of the radical anion of benzaldehyde (Reaction Ia), it is possible to apply Equation 1 in conjunction with the data of Table II and calculate k_{dim} (Reaction Ib). The average value of the rate constant calculated in this manner is $\log (k_{dim}) = 5.8 \pm 0.4$. The large uncertainty associated with the value of k_{dim} comes primarily from uncertainties in E^o. Because of the logarithmic relationship between k_{dim} and E^o, small errors in E^o correspond to relatively large errors in k_{dim}. The error level assigned to $\log (k_{dim})$ above was calculated on the basis of a 5 mV uncertainty in the value of E^o.

Although the rate constant reported above cannot be compared directly with rate constants determined by an independent method, the value obtained appears to be reasonable. For example, Porter *et al*. (5) report a value of $\log (k_{dim})$

equal 6.2 for the dimerization in buffered 50% ethanol-water (see Table I). The value measured electrochemically is within experimental error of the rate constant measured photochemically. Also, the smaller value obtained in acetonitrile is reasonable in view of the lower dielectric constant. Thus, the electrochemical approach appears to provide a satisfactory means of characterizing dimerization reactions and measuring their rate constants.

DESCRIPTION OF AN APPROXIMATE PERTURBATION METHOD FOR MEASURING SECOND ORDER RATE CONSTANTS

In preceding discussions it was shown that cyclic voltammetry could be used to measure the rate constant for dimerization of benzaldehyde radical anions. It was also pointed out that in aprotic solvents the radical anions of many aromatic ketones (e.g., benzophenone) are too stable to permit application of the steady state equations. Thus, for these systems Reaction Ib apparently is so slow that an anodic wave always is obtained for all scan rates. In other words, in these cases electrochemical equilibrium is nearly maintained, the dimerization causing only small decreases in the anodic peak current. Therefore, it seemed possible that the dimerization reaction could be treated as a perturbation of an equilibrium system. This would be important because rate equations near equilibrium can be linearized, and, moreover, the theory of cyclic voltammetry for first-order reactions is available. Thus, it might be possible to estimate dimerization rate constants with the aid of the first-order theory by selecting experimental conditions where the electrode process is nearly reversible.

Cyclic voltammetric theory for measuring first-order rate constants is presented as a working curve that relates ratios of anodic to cathodic peak currents to $k_f\tau$ (12). In this case k_f is the first-order rate constant, and τ is the time from $E_{\frac{1}{2}}$ to the switching potential. From experimental ratios of peak currents and the theoretical working curve, values of $k_f\tau$ are readily obtained. If this procedure is applicable to measurement of second-order rate constants, then a plot of $k_f\tau$ vs τ should be a curve that approaches linearity as τ is decreased (perturbation from equilibrium is decreased). If this is the case, then clearly the slope of the curve through the origin, $[d\ (k_f\tau)/d(\tau)]_{\tau=0}$, is $k_{dim} \times C_O^*$.

Values of $[d\ (k_f\tau)/d\ (\tau)]_{\tau=0}$ can be obtained by fitting the experimental curve to a polynomial, and then differentiating this polynomial and evaluating it at $\tau = 0$. For example, if the polynomial is second order

$$(k_f\tau) = a\ (\tau)^2 + b\ (\tau) + c$$

then one has $k_{dim} = b/C_O^*$.

RESULTS OF EXPERIMENTAL EVALUATION OF THE PERTURBATION METHOD

Benzaldehyde was used to test the ideas presented in the preceding section because values of $\underline{k}_{dim}$ estimated by the approximate perturbation method could be compared with values obtained by application of the steady state theory (Equation 1). Results of these experiments on benzaldehyde are discussed first, and then application of the perturbation method to systems where the steady state theory cannot be used is illustrated.

Benzaldehyde

Reduction of benzaldehyde in acetonitrile under conditions where the electrode process is nearly reversible already has been discussed (Figure 2). From curves like those of Figure 2, values of $\underline{k_f \tau}$ and $\underline{\tau}$ were obtained for three different benzaldehyde concentrations; plots of these data are shown in Figures 6, 7, and 8. As anticipated these curves all become linear as $\underline{\tau}$ decreases. The straight lines that have been drawn have slopes calculated by the second-order polynomial extrapolation method already discussed. Values of log ($\underline{k}_{dim}$) obtained from Figures 6, 7, and 8 are 5.89, 5.77, and 5.66 respectively. The average value of log ($\underline{k}_{dim}$) = 5.8 agrees exactly with the value obtained from

Figure 6. Variation of $\underline{k}_f\tau$ with τ for benzaldehyde in acetonitrile.

$C_O^* = 1.18 \times 10^{-4}$ M.

$\underline{k}_f = 92.5\ \text{sec}^{-1}$.

Log $(\underline{k}_{dim}) = 5.89$

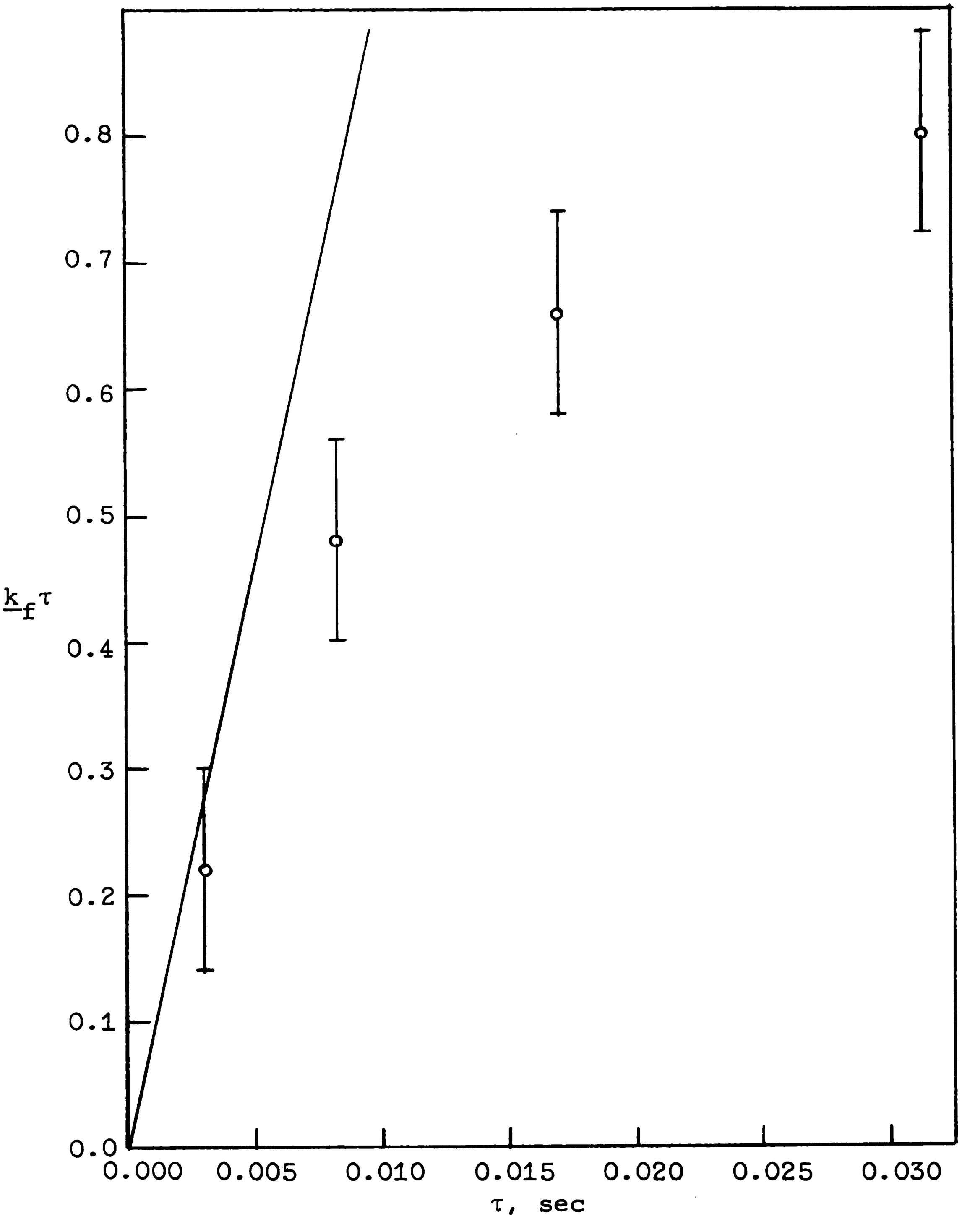

0.8
0.7
0.6
0.5
$\underline{k}_f\tau$
0.4
0.3
0.2
0.1
0.0
0.000
0.005
0.010
0.015
0.020
0.025
0.030
τ, sec

Figure 6

Figure 7. Variation of $\underline{k}_f\underline{\tau}$ with $\underline{\tau}$ for benzaldehyde in acetonitrile.

$C_O^* = 2.5 \times 10^{-4}$ $\underline{M}$.

$\underline{k}_f = 149$ sec^{-1}.

Log $(\underline{k}_{dim}) = 5.77$

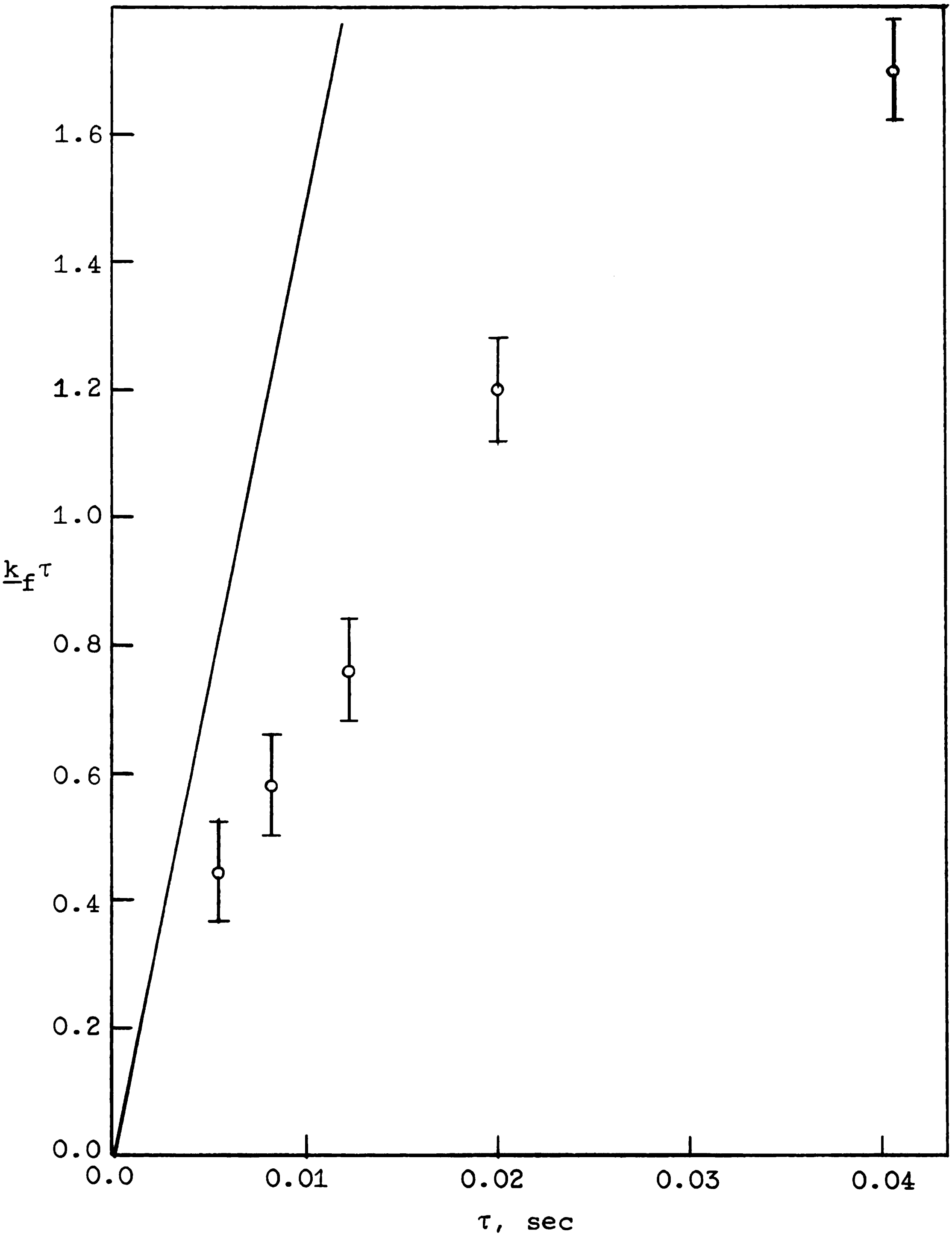


Figure 7

Figure 8. Variation of $\underline{k}_f\underline{\tau}$ with $\underline{\tau}$ for benzaldehyde in acetonitrile.

$C_O^* = 5.0 \times 10^{-4}$ $\underline{M}$.

$\underline{k}_f = 230$ sec^{-1}.

Log ($\underline{k}_{dim}$) = 5.66

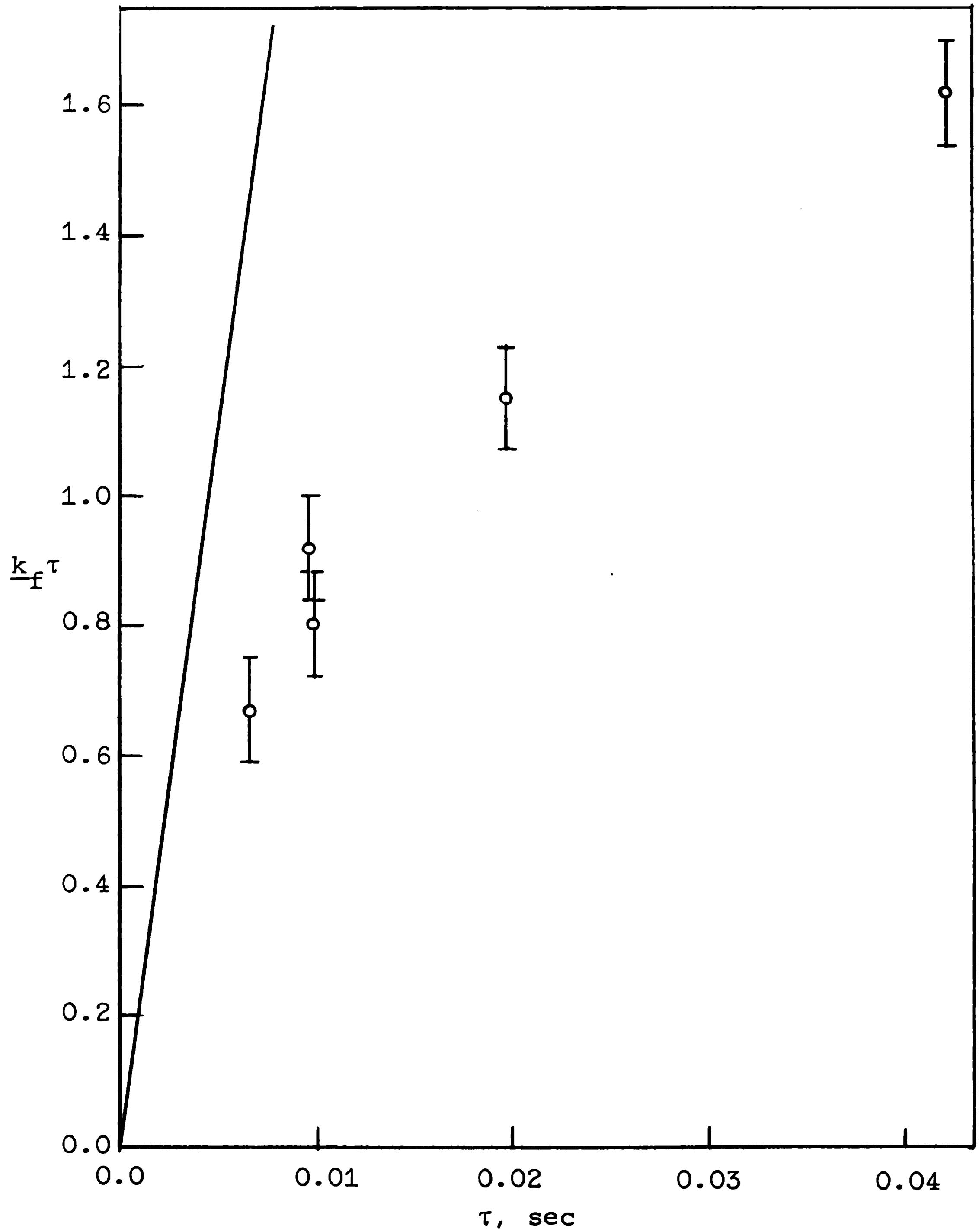


Figure 8

the steady state theory, and therefore the perturbation method apparently is a reliable means of estimating second-order rate constants.

Acetophenone and Benzophenone

The reduction mechanism of acetophenone and benzophenone in acetonitrile is the same as for benzaldehyde, but because the radical anions are more stable, the steady state theory cannot be used to measure rate constants. The perturbation method, however, is ideally suited to these compounds.

Data for acetophenone and benzophenone were treated in the manner described for benzaldehyde; the $k_f\tau$ plots are shown in Figures 9, 10, 11, 12, 13, and 14. The consistency of the values of k_{dim} calculated in each case (see figure legends) lends confidence to the applicability of the perturbation method.

Table III summarizes E^o values, and rate constants measured by the perturbation method for all three compounds. Again, reliability of the rate constants is difficult to assess, but the results are consistent with measurements of Porter *et al*. They also are in qualitative agreement with estimates of radical stability based on electron spin resonance experiments (7).

Figure 9. Variation of $\underline{k}_f\underline{\tau}$ with $\underline{\tau}$ for acetophenone in acetonitrile.

$C_O^* = 1.0 \times 10^{-4}\ \underline{M}$.

$\underline{k}_f = 0.42\ \text{sec}^{-1}$.

Log $(\underline{k}_{dim}) = 3.62$

Figure 10. Variation of $\underline{k}_f\underline{\tau}$ with $\underline{\tau}$ for acetophenone in acetonitrile.

$C_0^* = 2.0 \times 10^{-4}$ $\underline{M}$.

$\underline{k}_f = 0.87$ sec^{-1}.

Log $(\underline{k}_{\mathrm{dim}}) = 3.64$

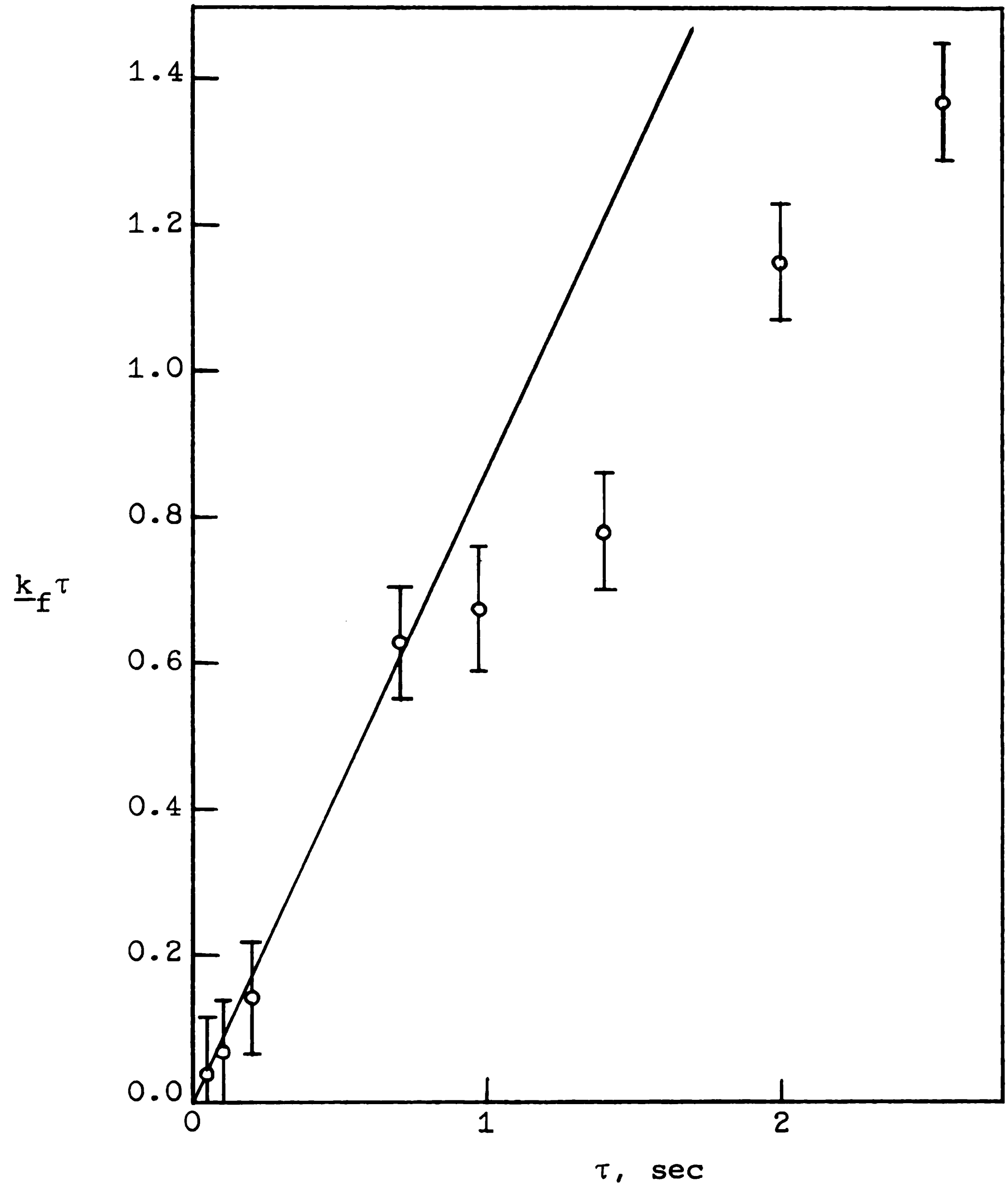


Figure 10

Figure 11. Variation of $\underline{k}_f\underline{\tau}$ with $\underline{\tau}$ for acetophenone in acetonitrile.

$C_O^* = 5.0 \times 10^{-4}$ $\underline{M}$.

$\underline{k}_f = 2.18$ sec^{-1}.

Log $(\underline{k}_{dim}) = 3.64$

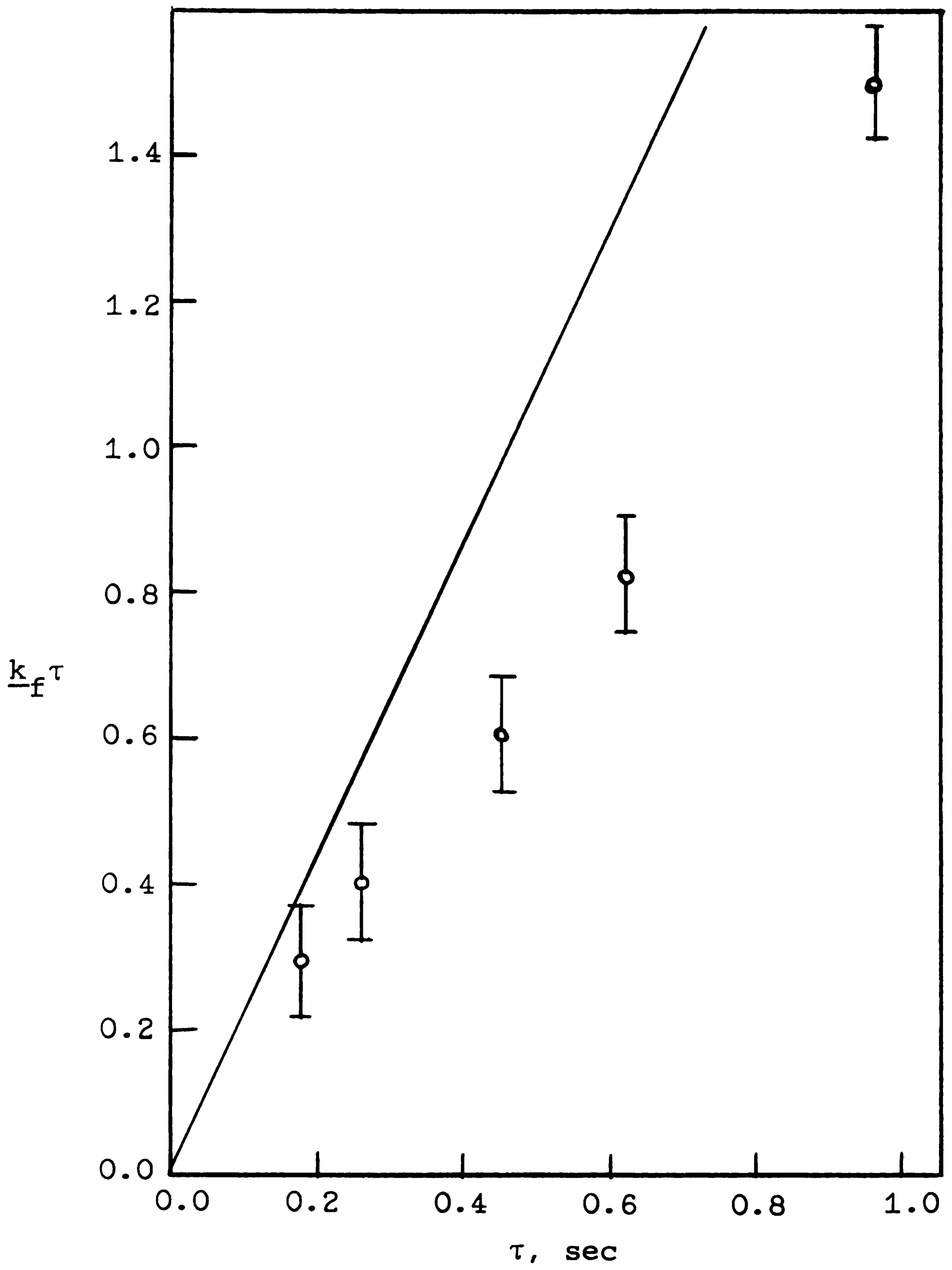


Figure 11

Figure 12. Variation of $\underline{k}_f\underline{\tau}$ with $\underline{\tau}$ for acetophenone in acetonitrile.

$C_O^* = 1.0 \times 10^{-3}$ $\underline{M}$.

$\underline{k}_f = 4.35$ sec^{-1}.

Log $(\underline{k}_{dim}) = 3.63$

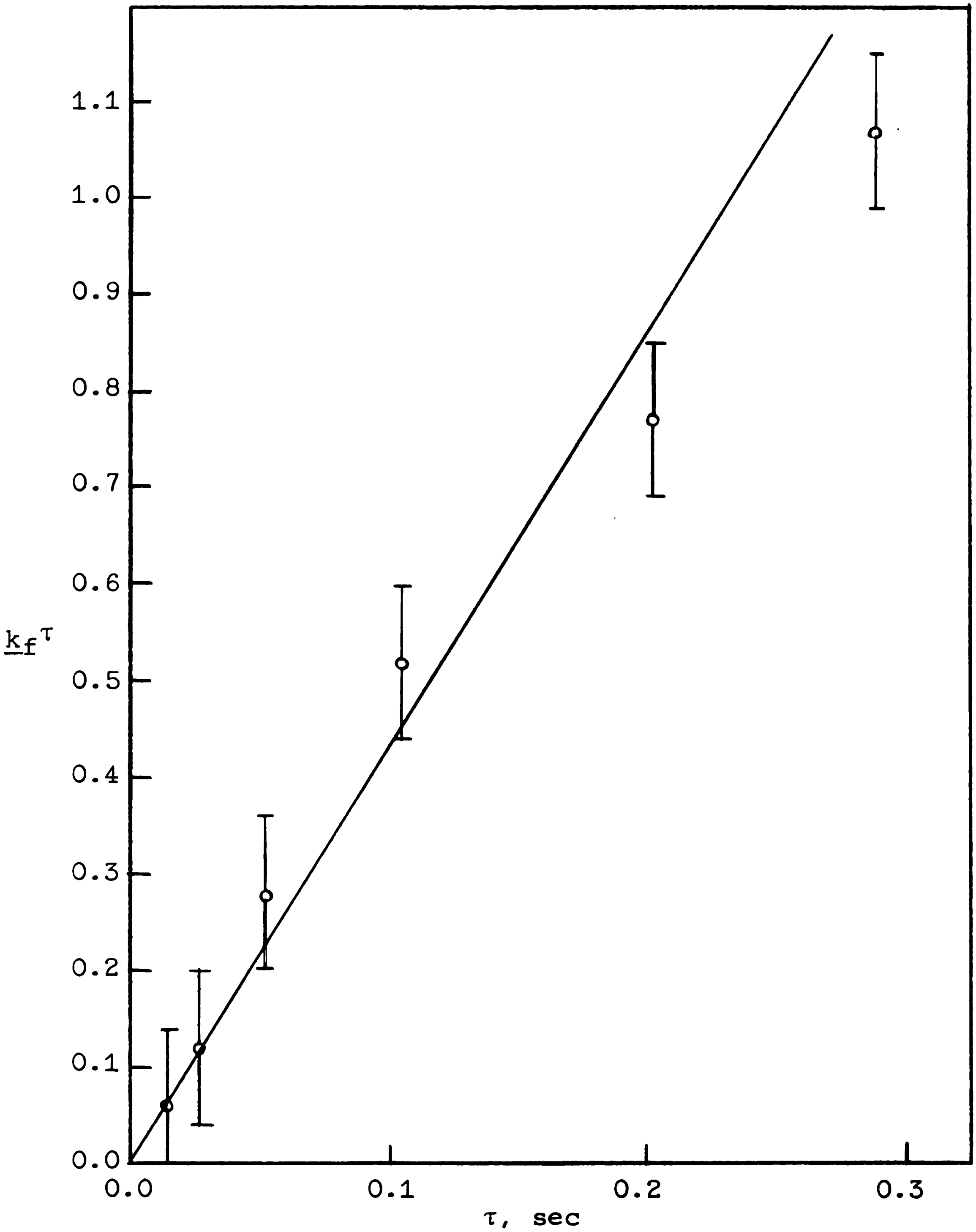

1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
$\underline{k}_f\tau$
0.0
0.1
0.2
0.3
τ, sec

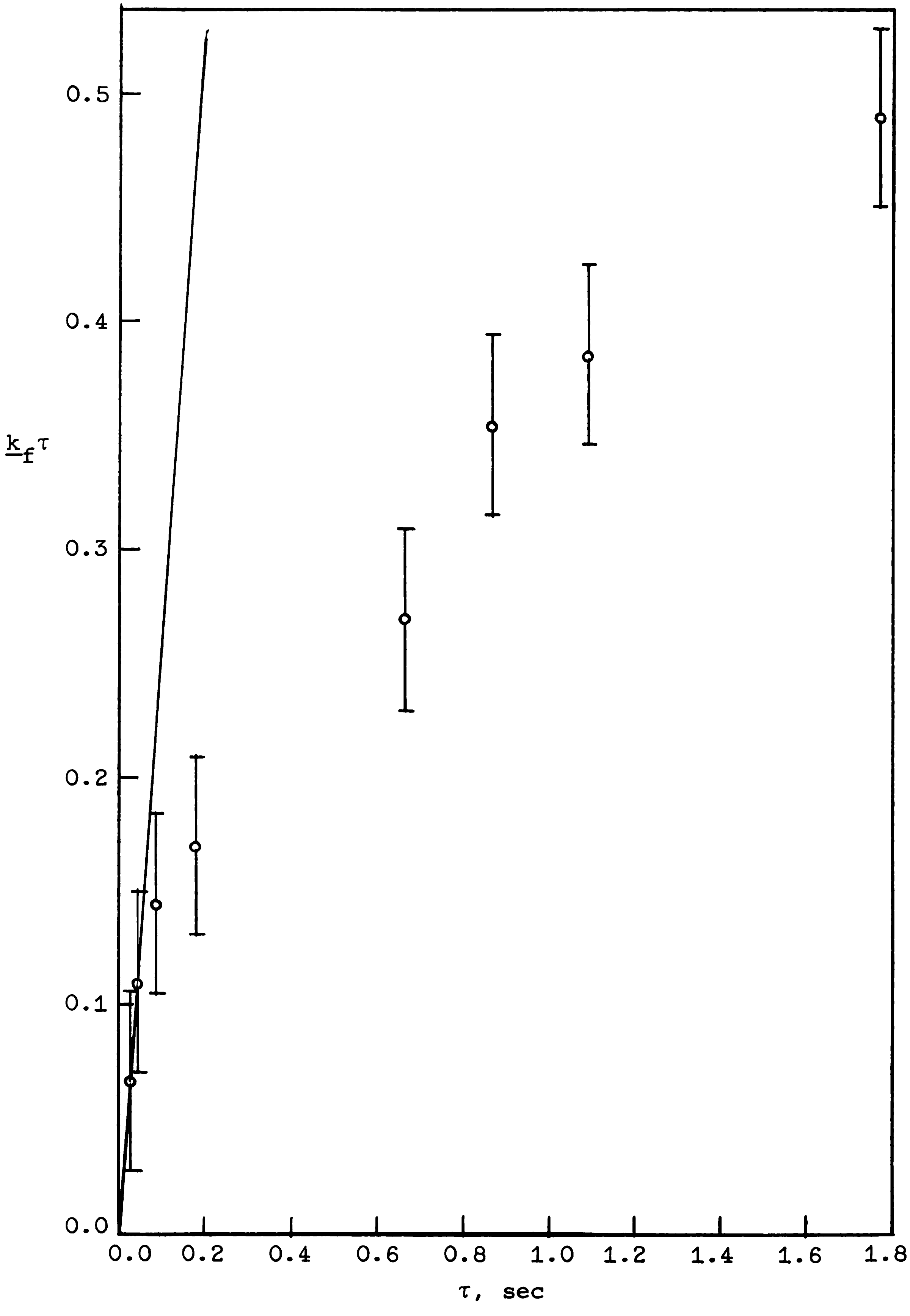
Figure 12

Figure 13. Variation of $\underline{k}_f\tau$ with τ for benzophenone in acetonitrile.

$C_0^* = 5.0 \times 10^{-4}$ M.

$\underline{k}_f = 2.73\ \mathrm{sec}^{-1}$.

Log ($\underline{k}_{dim}$) = 3.75



0.0
0.1
0.2
0.3
0.4
0.5
$\underline{k}_f\tau$
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
τ, sec

Figure 13

Figure 14. Variation of $\underline{k}_f\underline{\tau}$ with $\underline{\tau}$ for benzophenone in acetonitrile.

$C_O^* = 1.0 \times 10^{-3}$ $\underline{M}$.

$\underline{k}_f = 6.0\ \text{sec}^{-1}$.

Log $(\underline{k}_{dim}) = 3.78$

nzophenone in

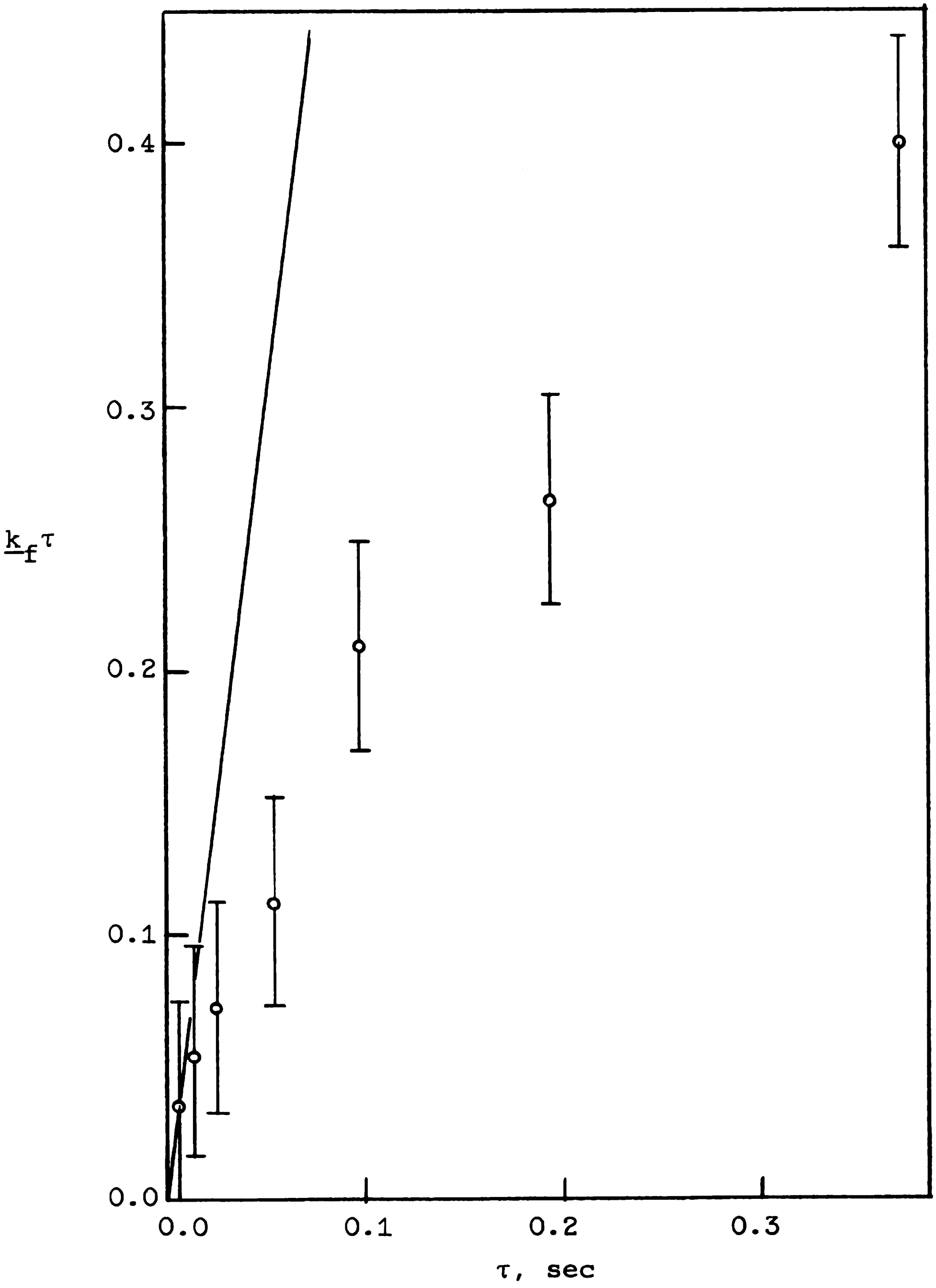


Figure 14

Table III. E^o Values and Values of Dimerization Rate Constants Measured by the Perturbation Method in Acetonitrile

Compound	E^o of couple $O + e \rightleftharpoons R^-$, V *vs* aqueous SCE	Log (k_{dim}) k_{dim} in *M*-sec^{-1}
Benzaldehyde	-1.865	5.77
Acetophenone	-2.055	3.64
Benzophenone	-1.805	3.77

ESTIMATION OF DIMERIZATION RATE CONSTANTS OF PROTONATED RADICALS IN WATER

An acidic aqueous solution of benzaldehyde has already been characterized as a succeeding dimerization reaction by cyclic voltammetry (6). However, as discussed previously, the dimerization reaction is so rapid that reversible cyclic polarograms, and hence $\underline{E}^{o}$ values, cannot be obtained experimentally. Thus, to estimate dimerization rate constants of protonated radicals in acidic aqueous solution, it was decided to attempt to estimate $\underline{E}^{o}$ values for these compounds in acidic aqueous solution from corresponding $\underline{E}^{o}$ values determined in acetonitrile (see Table III). For this reason a brief historical discussion of the estimation of $\underline{E}^{o}$ values in various solvents follows.

Comparison of E^{o} Values in Different Solvents

An exact comparison of electrode potentials in two solvents is impossible because of the presence of an unknown liquid junction potential; this liquid junction potential can be estimated, however. One way this can be done is to use an ion that approaches an ideal ion whose electrode potential is constant in all solvents. The difference in the electrode potentials of such an ideal ion in two solvents would equal the unknown liquid junction potential between these two solvents.

An ideal reference ion should have the same free energy of solvation in various solvents and thus have zero free energy of transfer between these solvents. According to Pleskov (14), a real ion would approach this ideal ion if its free energy of solvation were very small. This would require the ion to exhibit no specific interactions with the solvent, such as the formation of strong complexes. A further requirement is that the ion be as weakly polarizable as possible (14). In addition, the ion should have low charge and a large radius to minimize electrostatic interactions with the solvent. Based on these considerations, Pleskov proposed the use of the rubidium ion, Rb^+, as a standard reference ion (14).

Actually, there are small differences in the solvation energy of the rubidium ion in various solvents. Thus Strehlow (15) was able to improve on Pleskov's method by calculating a correction for this deviation. Strehlow took a certain value for the standard potential of the rubidium couple in water, and was able to calculate this electrode potential in other solvents and relate it to the potential of the standard hydrogen electrode in water. Therefore, especially with Strehlow's corrections, Pleskov's method appears to be a good approximation.

Determination of the Liquid Junction Potential between Acetonitrile and an Aqueous SCE

It was decided to verify the existing value (8) for this liquid junction potential because there is some controversy in recently reported values, and also so that $\underline{E}^{o}$ values of benzaldehyde, acetophenone, and benzophenone measured in acetonitrile could be used to estimate the corresponding $\underline{E}^{o}$ values in water.

Coetzee et al. (16) measured the polarographic half-wave potentials of a number of inorganic cations in a series of solvents, among them water and acetonitrile, using 0.1 M tetraethylammonium perchlorate as supporting electrolyte. They assumed, after the method of Pleskov, that $E_{\frac{1}{2}}$ of rubidium ion ($Rb^{+} + e \rightleftarrows Rb(Hg)$) is constant with solvent change, and thus they were able to use this ion as a solvent-independent reference ion to compare $E_{\frac{1}{2}}$ values for a series of inorganic ions.

Coetzee determined that the difference in $E_{\frac{1}{2}}$ between rubidium and sodium is -0.01 V in water and -0.13 V in acetonitrile (16). Thus, if it is assumed that these $E_{\frac{1}{2}}$ differences for acetonitrile and water are correct, sodium ion also could be used as a solvent-independent reference ion between acetonitrile and water. Thus, to estimate the liquid junction potential between an acetonitrile solution containing 0.1 M tetraethylammonium perchlorate as a supporting electrolyte, and an aqueous SCE, $E_{\frac{1}{2}}$ for sodium was measured both in acetonitrile and water. These measured $E_{\frac{1}{2}}$ values, along with the values reported by Coetzee et al., are given in Table IV.

Table IV. Measured and Reported $E_{\frac{1}{2}}$ Values of Sodium

Solvent	$E_{\frac{1}{2}}$ vs aqueous SCE Measured value (this work)	 Literature value[a]
Water	-2.111 V	-2.12 V
Acetonitrile	-1.847 V	-1.853 V

[a] Reference 13.

The $\underline{E_{\frac{1}{2}}}$ values of rubidium in acetonitrile and water can be determined from reported differences in $\underline{E_{\frac{1}{2}}}$ for rubidium and sodium, in conjunction with measured $E_{\frac{1}{2}}$ values of sodium in Table IV. These values are

$$[(E_{\frac{1}{2}})_{Rb}]_{water} = (-2.111) + (-0.01) = (-2.121)\ V$$

and

$$[(E_{\frac{1}{2}})_{Rb}]_{acetonitrile} = (-1.847) + (-0.13) = (-1.977)\ V$$

According to Pleskov, rubidium ion is considered to be a solvent-independent reference ion. Hence the difference between these two $\underline{E_{\frac{1}{2}}}$ values of rubidium should equal the liquid junction potential between the acetonitrile solution and the aqueous SCE, namely $\underline{E}_{l.j.}$ is about +0.144 V. However, as already discussed, Strehlow was able to calculate solvation energy differences for rubidium ion in some solvents (15) and, thus improve upon the method of Pleskov. Strehlow calculated that the potential of rubidium ion is 106 mV more negative (cathodic) in acetonitrile than in water. In other words, using this correction factor, the $\underline{E_{\frac{1}{2}}}$ value of rubidium ion in acetonitrile should be taken as 106 mV anodic of the measured $\underline{E_{\frac{1}{2}}}$ value, if the rubidium ion is to be considered as a solvent-independent reference ion between acetonitrile and water.

Thus, the corrected $\underline{E_{\frac{1}{2}}}$ value of rubidium ion in this acetonitrile solution is -1.871 V <u>vs</u> an aqueous SCE. The difference between this $\underline{E_{\frac{1}{2}}}$ and the $\underline{E_{\frac{1}{2}}}$ of rubidium ion in water should be a better estimate of the liquid junction potential between the acetonitrile solution and aqueous SCE. This liquid junction potential is $E_{l.j.}$ = (−1.871) − (−2.121) = +0.250 V. This value for $E_{l.j.}$ agrees exactly with the value reported by Kolthoff and Thomas (8).

Estimation of E^o for Benzaldehyde, Acetophenone, and Benzophenone in Water

Based on the E^o values measured in acetonitrile and the liquid junction potential reported above, it was possible to estimate E^o values of aromatic aldehydes and ketones in water, even though very accurate estimations are apparently impossible because exact solvent effects on these reduction potentials are unknown. For instance, a recent study (17) of a series of substituted quinones in acetonitrile and water has shown that E^o differences between the two solvents cannot be accounted for by dielectric constant considerations. The reduction potentials generally are about 0.6 V more anodic in water than in acetonitrile (17). Because of roughly similar structures it might be expected that the E^o differences between acetonitrile and an aqueous solution of quinone and aromatic aldehydes and ketones would be comparable. Thus, E^o for benzaldehyde, acetophenone, and benzophenone in water were calculated on the basis of the assumption that their behavior is comparable to that of reported E^o differences of substituted quinones. These estimated E^o values are given in Table V.

Table V. Estimated E^{o} for Benzaldehyde, Acetophenone, and Benzophenone in water.

Compound	Estimated E^{o} value, V *vs* SCE
Benzaldehyde	$[(-1.865) - (+0.250) + (+0.6)] = -1.5_2 \pm 0.2$
Acetophenone	$[(-2.055) - (+0.250) + (+0.6)] = -1.7_1 \pm 0.2$
Benzophenone	$[(-1.805) - (+0.250) + (+0.6)] = -1.4_8 \pm 0.2$

The E^o values listed in Table V are admittedly very approximate; hence it would be useful to check these estimations. Fortunately, this can be done for two of the compounds by assuming that the values of k_{dim} reported by Porter *et al*. (see Table I) for benzaldehyde and benzophenone are correct. In this way Equation 1 can be used to calculate aqueous E^o values from cyclic voltammetric experiments. However, there are several other considerations with regard to the use of Equation 1 for determining values of E^o (or k_{dim}) in acidic aqueous solution. A discussion of these considerations is given in the following section.

Additional Considerations Necessary for Determination of Values of k_{dim} or E^o in Water

Based on the mechanism given in the Introduction, for experiments in acidic aqueous solutions E^o in Equation 1 corresponds to formation of the protonated radical, i.e., $E^o_{O,RH}$. The E^o values reported in Table V, however, are for formation of the radical anion, E^o_{O,R^-}. These two E^o values clearly differ by an amount proportional to the equilibrium constant, K_{form}, for formation of the protonated radical from the radical anion

$$E^o_{O,RH} = E^o_{O,R^-} + RT/F \ln \{K_{form}[H^+]\} \qquad (2)$$

Hence the form of Equation 1 applicable to experiments in acidic aqueous solutions is

$$E_p = E^o{}_{O,R^-} + 59.1 \text{ mV} \log\{K_{form}[H^+]\} - 19.7 \text{ mV} \log[(4.78\pi D_O 3)/(2D_R)] - 19.7 \text{ mV} \log[(a)/(\underline{k}_{dim} C_O^*)] \qquad (3)$$

Clearly Equation 3 predicts peak potential shifts with scan rate and depolarizer concentration identical with Equation 1. Thus, either Equations 1 or 3 could be used to characterize a system in acidic aqueous solution. Furthermore, if $\underline{E}^o{}_{O,R^-}$ and $\underline{K}_{form}$ values in water are known, Equation 3 can be used to determine quantitatively $\underline{k}_{dim}$ in acidic solution. Obviously Equation 3 also can be used to determine values of $E^o{}_{O,R^-}$, if all of the other experimental parameters are known.

The values of the formation constants ($\underline{K}_{form}$) for the protonation of the three radical anions have been determined by Porter et al. (see Table I) for buffered 50% alcohol-water solutions. To apply these $\underline{K}_{form}$ values to the solutions used in this work, values of Porter were corrected for bulk dielectric constant differences of the solvents (18). These corrected formation constants for benzophenone, acetophenone, and benzaldehyde protonated radical are $10^{8.9}$, $10^{10.5}$, and $10^{10.2}$ respectively.

Since values of $\underline{K}_{form}$ and $\underline{k}_{dim}$ are known for benzaldehyde and benzophenone, cyclic voltammetric experiments were performed in acidic aqueous solution, so that $\underline{E}^o$ could be estimated for these compounds and compared with the values estimated from the quinone behavior comparison (Table V). Cyclic voltammetric experiments also were carried out for acetophenone, even though its $\underline{E}^{o}$ value could not be estimated from Equation 3 since there is no available value of $\underline{k}_{dim}$. Results of these experiments are discussed next.

Results of Experiments in Water

The peak potential vs scan rate data for benzaldehyde, acetophenone, and benzophenone at pH 3.7 are given in Tables VI, VII, and VIII respectively. These data also are plotted in Figures 15, 16, 17, 18, 19, and 20; slopes of all of the straight lines are in good agreement with theory (see figure legends). These results demonstrate that acidic aqueous solutions of all three compounds can be characterized by either Equation 1 or 3 as a rapid dimerization reaction. Hence these data can be used in conjunction with Equation 3 and the $\underline{K}_{form}$ and $\underline{k}_{dim}$ values (Table I) to estimate $\underline{E}^{o}$ values in water for benzaldehyde and benzophenone. Estimated $\underline{E}^{o}$ values of these two compounds, as determined by the steady state theory (Equation 3), are given in Table IX.

A comparison of the $\underline{E}^{o}$ values between Tables V and IX indicates that differences between acetonitrile and water for aromatic aldehydes and ketones follow the same trends reported for the substituted quinones (17), and, furthermore, indicates that the quinone approximation is apparently fairly reasonable in that the estimated $\underline{E}^{o}$ values differ at most by o.1 V. However, the quinone approximation apparently is not good enough to permit very accurate estimations of $\underline{k}_{dim}$ since a 20 mV error in $\underline{E}^{o}$ results in a one order of magnitude error in $\underline{k}_{dim}$.

Table VI. Peak Potential vs Scan Rate for Benzaldehyde in Acidic Aqueous Solution

Scan rate (v) V sec^{-1}	Log (v)	Peak Potential (E_p) V vs SCE $C_O^*=1.19 \times 10^{-3}$ M	 $C_O^*=1.19 \times 10^{-4}$ M
0.021	-1.678	-1.140	---
0.035	-1.456	-1.141	-1.162
0.070	-1.154	-1.146_5	-1.166
0.140	-0.854	-1.152	-1.173
0.210	-0.678	-1.157_5	-1.177
0.700	-0.154	-1.167	-1.186
3.50	+0.544	-1.181	-1.200
7.00	+0.846	-1.189	-1.215

Table VII. Peak Potential *vs* Scan Rate for Acetophenone in Acidic Aqueous Solution

Scan rate (v) V sec^{-1}	Log (v)	Peak Potential (E_p) V *vs* SCE	
		C_O^*=1.02 x 10^{-3}M	C_O^*=1.02 x 10^{-4}M
0.035	-1.456	-1.268	-1.290
0.070	-1.154	-1.272	-1.294
0.140	-0.854	-1.280	-1.300
0.210	-0.678	-1.285	-1.304
0.700	-0.154	-1.293	-1.317
3.50	+0.544	-1.310	-1.330
7.00	+0.846	-1.313	-1.340

Table VIII. Peak Potential *vs* Scan Rate for Benzophenone in Acidic Aqueous Solution

Scan rate (v) V sec^{-1}	Log (v)	Peak Potential (E_p) V *vs* SCE	
		C_O^*=1.20 x 10^{-3}*M*	C_O^*=1.20 x 10^{-4}*M*
0.035	-1.456	-1.024	-1.041
0.070	-1.154	-1.028	-1.048
0.140	-0.854	-1.032	-1.058
0.210	-0.678	-1.039	-1.059
0.700	-0.154	-1.046	-1.069
1.40	+0.146	-1.052	-1.076
3.50	+0.544	-1.060	-1.080
7.00	+0.846	-1.070	---

Figure 15. Variation of peak potential with scan rate for benzaldehyde in water.

$C_O^* = 1.19 \times 10^{-3}$ $\underline{M}$.

0.1 $\underline{M}$ acetic acid.

0.01 $\underline{M}$ potassium acetate.

pH = 3.63

0.1 $\underline{M}$ tetraethylammonium perchlorate as supporting electrolyte.

slope = 20 mV/unit log (v).

Figure 15

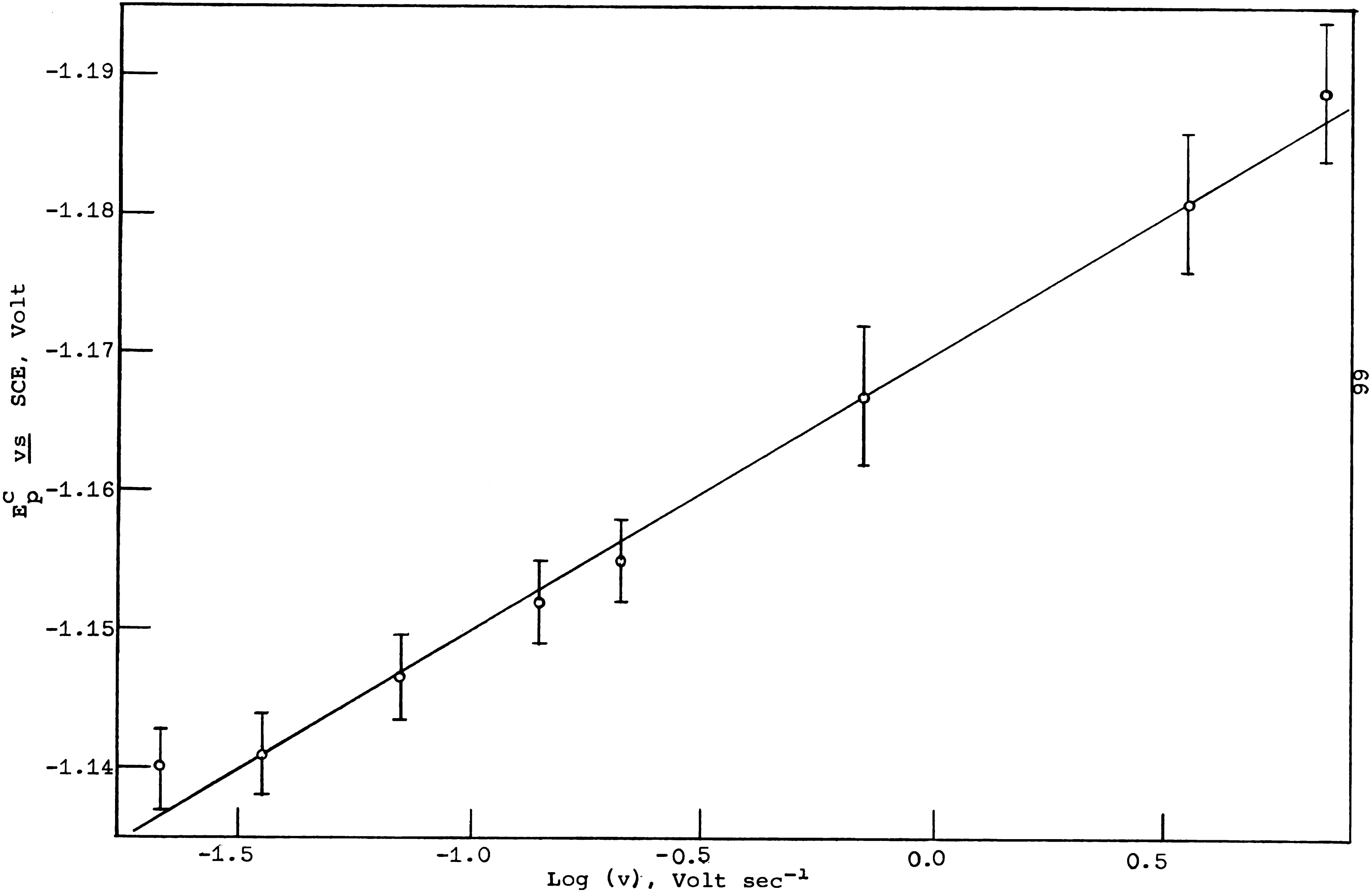

E_p^c vs SCE, Volt
-1.19
-1.18
-1.17
-1.16
-1.15
-1.14
-1.5
-1.0
-0.5
0.0
0.5
Log (v), Volt sec^{-1}

Figure 16. Variation of peak potential with scan rate for benzaldehyde in water.

$C_O^* = 1.19 \times 10^{-4}$ *M*.

0.1 *M* acetic acid.

0.01 *M* potassium acetate.

pH = 3.63

0.1 *M* tetraethylammonium perchlorate as supporting electrolyte.

slope = 20 mV/unit log (v).

Figure 16

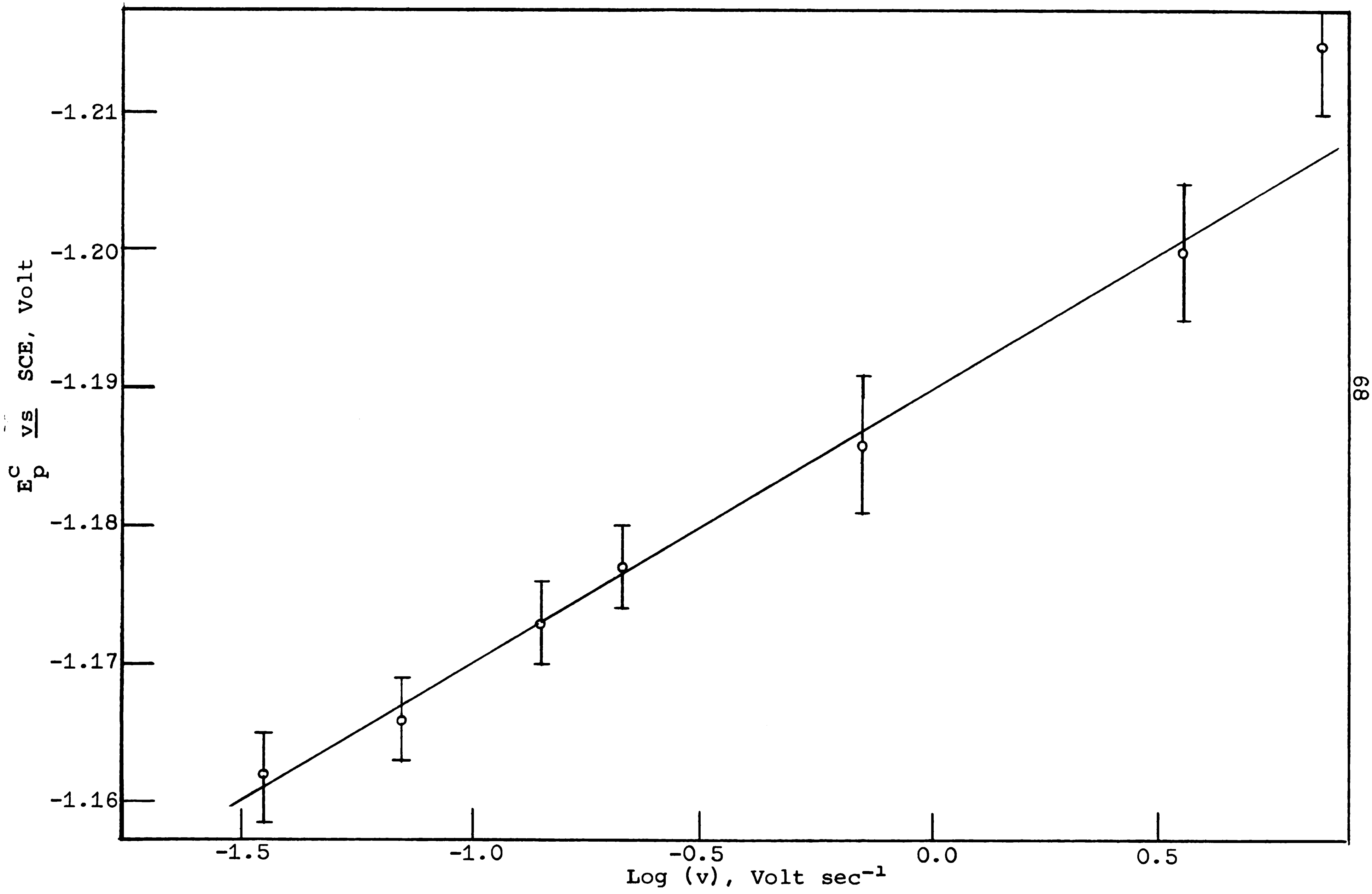

E_p^c vs SCE, Volt
-1.21
-1.20
-1.19
-1.18
-1.17
-1.16
-1.5
-1.0
-0.5
0.0
0.5
Log (v), Volt sec^{-1}

Figure 17. Variation of peak potential with scan rate for acetophenone in water.

$C_O^* = 1.02 \times 10^{-3}$ M.

0.1 M acetic acid.

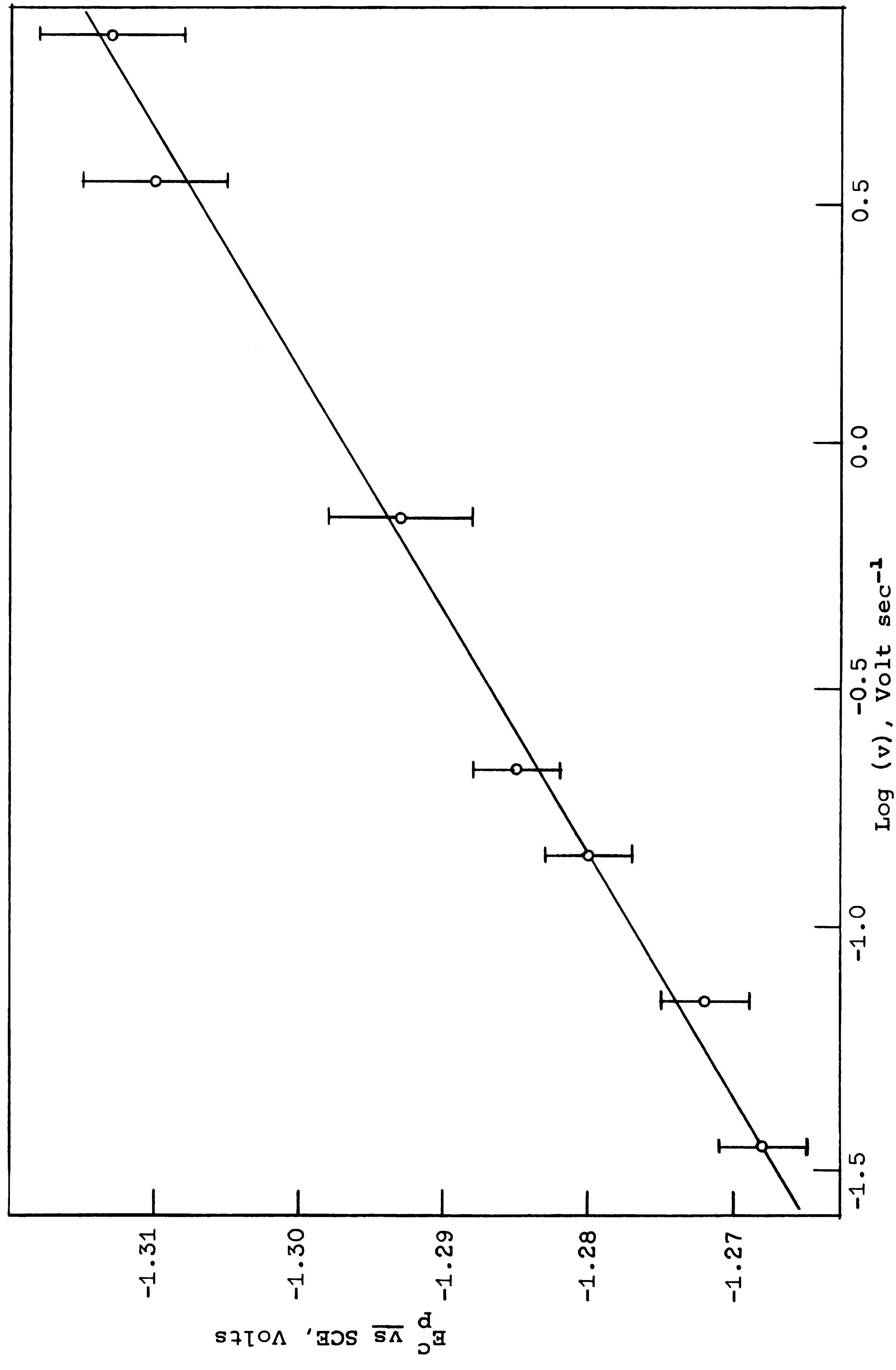
0.01 M potassium acetate.

pH = 3.63

1% ethanol.

0.1 M tetraethylammonium perchlorate as supporting electrolyte.

slope=20 mV/unit log (v).



E_p^c vs SCE, Volts
-1.27
-1.28
-1.29
-1.30
-1.31
Log (v), Volt sec^{-1}
-1.5
-1.0
-0.5
0.0
0.5

Figure 17

Figure 18. Variation of peak potential with scan rate for acetophenone in water.

$C_O^* = 1.02 \times 10^{-4}$ $\underline{M}$.

0.1 $\underline{M}$ acetic acid.

0.01 $\underline{M}$ potassium acetate.

pH = 3.63

1% ethanol.

0.1 $\underline{M}$ tetraethylammonium perchlorate as supporting electrolyte.

slope = 20 mV/unit log (v).

Figure 18

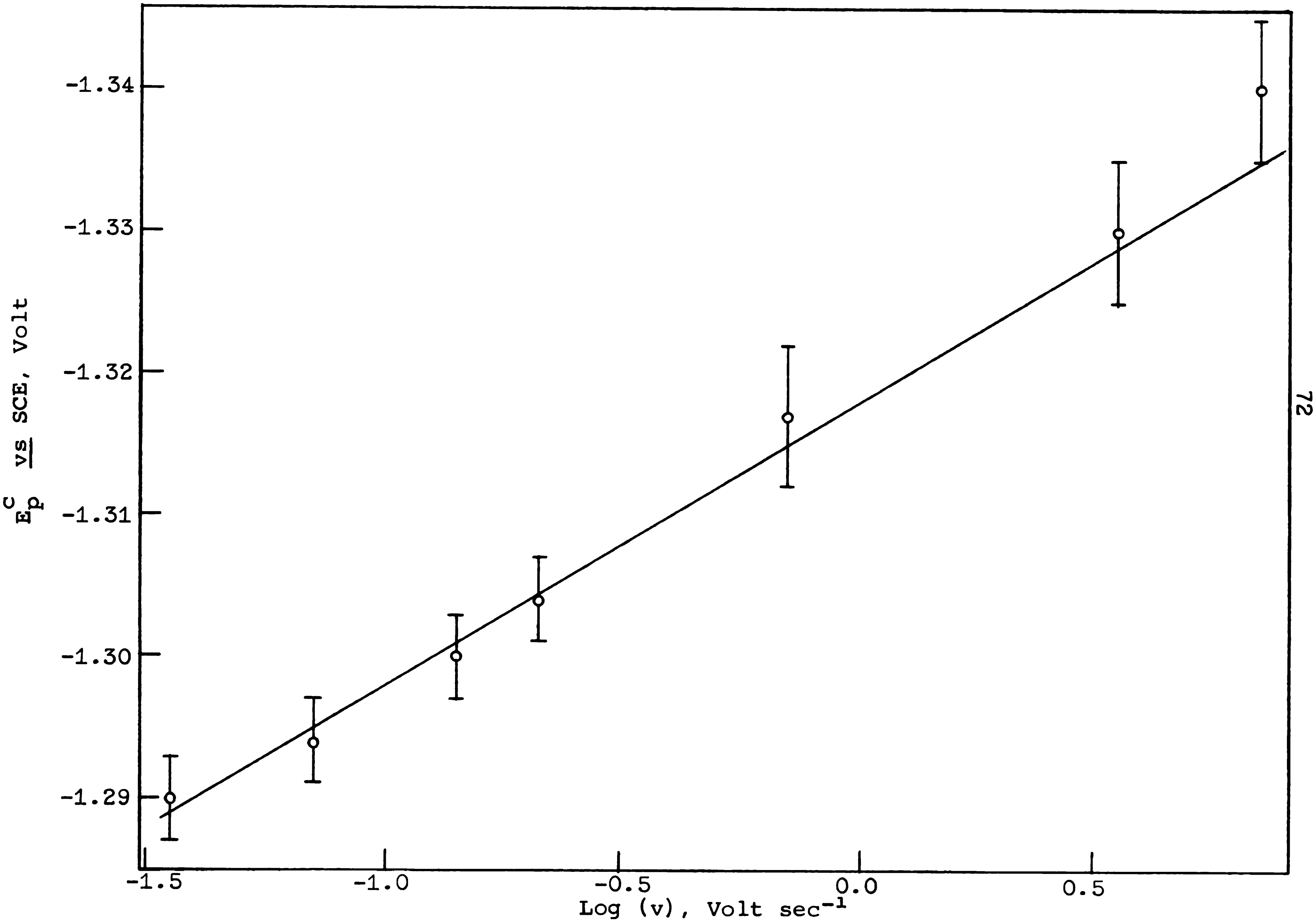

-1.34
-1.33
-1.32
-1.31
-1.30
-1.29
E_p^c vs SCE, Volt
-1.5
-1.0
-0.5
0.0
0.5
Log (v), Volt sec^{-1}

Figure 19. Variation of peak potential with scan rate for benzophenone in water.

$C_O^* = 1.20 \times 10^{-3}\ \underline{M}$.

0.1 $\underline{M}$ acetic acid.

0.01 $\underline{M}$ potassium acetate.

pH = 3.76

9.5% ethanol.

0.1 $\underline{M}$ tetraethylammonium perchlorate as supporting electrolyte.

slope = 20 mV/unit log (v).

Figure 19

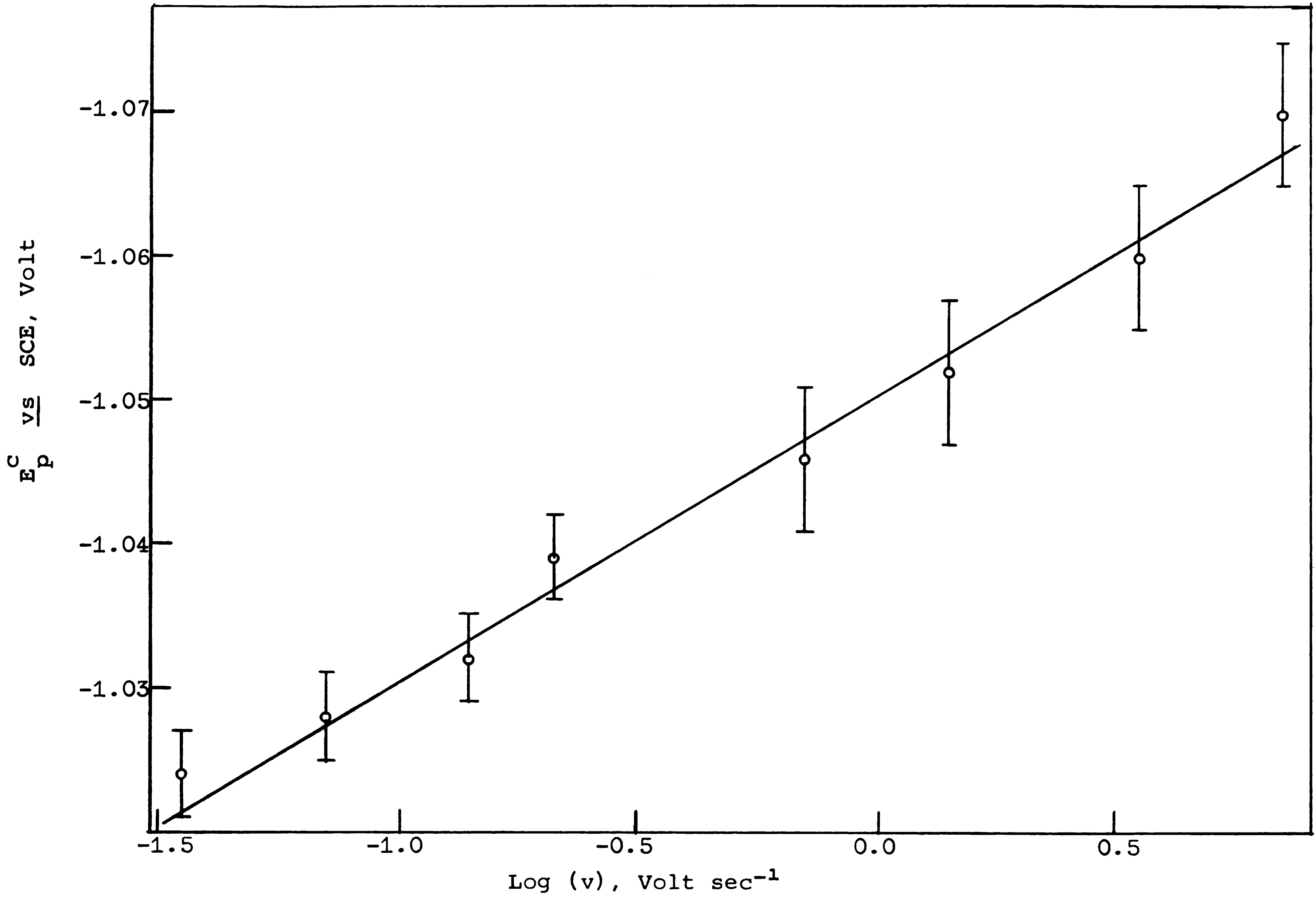


Figure 20. Variation of peak potential with scan rate for benzophenone in water.

$C_O^* = 1.20 \times 10^{-4}$ $\underline{M}$.

0.1 $\underline{M}$ acetic acid.

0.01 $\underline{M}$ potassium acetate.

pH = 3.76

9.5% ethanol.

0.1 $\underline{M}$ tetraethylammonium perchlorate as supporting electrolyte.

slope = 20 mV/unit log (v).

Figure 20

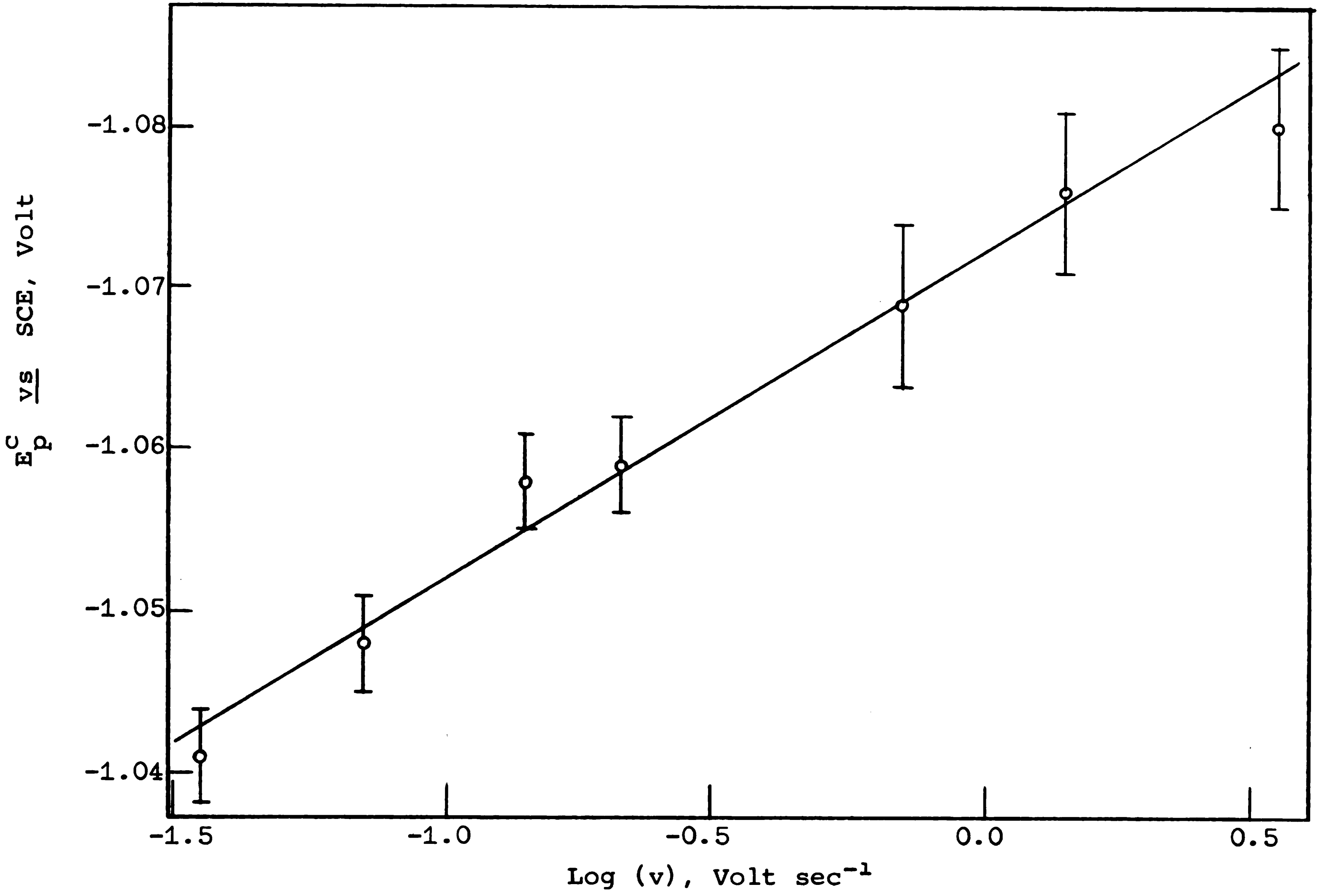


Table IX. Estimated E^{o} Values for Benzaldehyde and Benzophenone in Water

Compound	E^{o}, V *vs* SCE	$(E^{o})_{acetonitrile} - (E^{o})_{water}$
Benzaldehyde	-1.614	-501 mV
Benzophenone	-1.393	-662 mV

The estimated $\underline{E}^{o}$ values listed in Table IX are probably more accurate than those in Table V, because they were determined using reported values of $\underline{k}_{dim}$. Therefore an $\underline{E}^{o}$ value for acetophenone was calculated on the basis of the $\underline{E}^{o}$ value changes between water and acetonitrile for benzaldehyde and benzophenone listed in Table IX. The $\underline{E}^{o}$ change of acetophenone was taken as the average of the $\underline{E}^{o}$ changes of benzophenone and benzaldehyde, namely 0.582 mV. Thus, $\underline{E}^{o}$ of acetophenone was estimated to be

$$(-2.055) - (+0.250) + (+0.582) = -1.723 \text{ V } \underline{\text{vs}} \text{ SCE}$$

This $\underline{E}^{o}$ value for acetophenone, in conjunction with Equation 3 and the experimental data listed in Figure 17, gives a value of $\underline{k}_{dim} = 1.0 \times 10^{7}\ \underline{M}\ \text{sec}^{-1}$. On the basis of the data listed in Table I, this value of $\underline{k}_{dim}$ for acetophenone appears to be about one order of magnitude too low because $\underline{k}_{dim}$ for acetophenone protonated radical should lie somewhere between the values for benzaldehyde and benzophenone protonated radical. If the $\underline{E}^{o}$ change for acetophenone was considered to be closer to the $\underline{E}^{o}$ change for benzaldehyde (i.e., 562 instead of 582 mV) than to the $\underline{E}^{o}$ change for benzophenone, the calculated value of $\underline{k}_{dim}$ would be higher (i.e., $1.0 \times 10^{8}\ \underline{M}\ \text{sec}^{-1}$).

CONCLUSION

Based on the experiments reported in this thesis it can be concluded that the steady state theory of cyclic voltammetry provides a useful means of characterizing quantitatively the effect of dimerization reactions initiated electrolytically. Nevertheless, because of approximations made in the theory, in many cases its application is severely restricted. The perturbation method developed in this thesis overcame many of these limitations. Nevertheless, it can be concluded that there is a definite need for a completely general and rigorous mathematical treatment of cyclic voltammetry for the case of dimerization reactions.

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