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Simultaneous Electrochemical–Electron Spin Resonance Measurements. III. Determination of Rate Constants for Second-Order Radical Anion Dimerization

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In-situ electron spin resonance–electrochemical measurements have been used to measure the rate constants for the dimerization of diethylfumarate, dimethylfumarate, cinnamonitrile, and fumaronitrile radical anions in dimethylformamide solution. The mechanism was found to be second order in radical anion with rate constants for these reactions at 23° of 33, 160, 2100, and $>10^5$ M^{-1} $\sec^{-1}$, respectively. Both the mechanism and the rate constants agree with values from electrochemical studies. The applicability of controlled current pulse with simultaneous esr detection for elucidation of reaction mechanism is demonstrated.

Introduction

Electron spin resonance (esr) has been used extensively in electrochemical studies to detect and identify paramagnetic intermediates.[1] Although several techniques have been developed which permit the determination of rate constants of electrochemically generated intermediates, these techniques have used flowing solutions[2] or mixed flow systems in which a solution of a stable intermediate was mixed with a second solution to initiate a chemical reaction.[3] The development of an *in-situ* electrochemical technique in which the solution is not flowing and which could be used to determine rate constants has been difficult. This difficulty is caused by potential gradients parallel to the electrode surface resulting from the high resistance of the thin layer of solution which must be used in these types of experiments. In the conventional esr electrochemical cell, the current density is not uniform over the entire electrode surface.[4] In any reaction in which the reaction order is greater than first order in the electroactive species, such as radical anion dimerization where the reaction rate is proportional to $[R^-]^2$, or radical anion–parent dimerization in which the rate is proportional to $[R][R^-]$, then the concentration profile of the reactive species must be calculable in order to determine the reaction rate constant. If the current density is nonuniform, then the concentration profile depends upon the electrode dimensions, current, and resistivity of the solution, and becomes exceedingly difficult to calculate.[4]

In the past few years a number of esr cells have been designed to reduce or minimize the potential gradients which cause nonuniform current densities.[5-7] The cell described by Goldberg and Bard[6] permitted good control of electrochemical parameters. A previous paper in this series[8] suggested that this cell could be used to determine rate constants for reactions of electrogenerated radical ions. This paper presents the results of simultaneous electrochemical esr (seesr) measurements of the rate of olefin radical anion dimerization.

Method

The following method of studying the decomposition of radical species was suggested. A current pulse of duration t_p is passed through the seesr cell, where t_p is less than the electrochemical transition time, τ (when secondary processes begin to occur at the electrode) where $\tau = \pi D/2 \cdot (nFAC/i)$.[2] The esr signal is recorded from the start of the current pulse ($t = 0$) to a time t_m equal to $2t_p$. The ratio of the esr signal at t_m, $S(t_m)$ to the esr signal at t_p, $S(t_p)$ can then be used to determine the rate constants of a reaction, provided that the current i, the electrode area A, the bulk concentration C_b, and the diffusion coefficients of the species involved in the reaction are known. Here the diffusion coefficients of all reacting species are assumed to be equal. Tables presented in ref 8 relate $S(t_m)/S(t_p)$ to parameters which contain the rate constant and other known quantities for various mechanisms of radical decomposition.

Mechanisms and rates for the initial step of the dimerization reactions of electrochemically generated radical anions of activated olefins have been the subject of several detailed investigations[9-12] as well as a recent review.[13] The mechanisms for the cathodic dimerization of olefins that have been postulated are shown in eq 1–3. In the first two mechanisms the initial step is the generation of the anion radical.

$$R + e \longrightarrow R^- \tag{1}$$

The anion radical can then undergo a dimerization process which is second order in radical anion

$$R^- + R^- \xrightarrow{k_{11}} R_2^{2-} \tag{2}$$
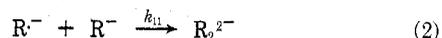
The intermediate R_2^{2-} then protonates to form the hydrodimer. A second alternative is that the radical anion reacts with a neutral species as shown in eq 3. This reaction is first order in both anion and parent species. The

$$R^- + R \xrightarrow{k_{10}} R_2^- \tag{3}$$
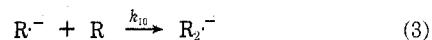
tion is first order in both anion and parent species. The

intermediate $R_2 \cdot ^-$ quickly reacts with $R \cdot ^-$ to form the intermediate $R_2{}^{2-}$ and regenerate R. A third possible mechanism is that R^{2-} is generated electrochemically as in

$$R + 2e^- \longrightarrow R^{2-} \qquad (4)$$
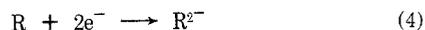
The dianion then reacts with neutral R to form the intermediate $R_2{}^{2-}$

$$R + R_2 \cdot ^- \xrightarrow{k_2} R_2{}^{2-} \qquad (5)$$
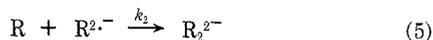
Because esr signals are obtained upon electrolysis of these species, the latter mechanism can be eliminated. The esr signal–time behavior of each of the two mechanisms involving anion radicals has been described for current-pulse experiments.[8] For the mechanism of eq 2, values of $S(t_m)/S(t_p)$ are given as a function of Y_{11} which is defined in

$$Y_{11} = k_{11}it_p{}^{3/2}/nFAD^{1/2} \qquad (6)$$

Similarly for the mechanism shown in eq 3 $S(t_m)/S(t_p)$ is given as a function of Y_{10} which is defined in

$$Y_{10} = k_{10}t_p\left(C_b - P\frac{it_p{}^{1/2}}{nFAD^{1/2}}\right) \qquad (7)$$

where P is determined by the value of t_m/t_p. For $t_m = 2t_p$, $P = 0.45$.

Experimental Section

Reagents. Tetrabutylammonium iodide obtained from Southwestern Analytical Chemicals was dried under vacuum at 110° for at least 5 hr and stored in a desiccator. Baker Analyzed dimethylformamide was purified according to the method of Faulkner and Bard[14] and stored under helium. Cinnamonitrile (Aldrich) and diethylfumarate (Aldrich) was used as received. Fumaronitrile (Aldrich) and dimethylfumarate (K and K) were sublimed three times. Nuclear magnetic resonance spectra of neat diethylfumarate and saturated dimethylfumarate in CCl_4 showed strong absorptions at 6.83 and 6.88 ppm *vs.* TMS respectively. No absorptions at 6.28 or 6.32 ppm were observed even at very high instrument gains which indicates that these reagents were virtually free of the maleate isomer. Furthermore there was no indication of absorptions of any of the half-esters or free acids.

The esr spectrometer used in these experiments was either of two modified V-4502-type esr spectrometers.[6,15] The signal was detected at 100-kHz modulation frequency using a TE 104 dual cavity. Modulation and power broadening permitted the maximum intensity to be obtained and also minimized the effects of drift in the magnetic field. Previous experiments[6] showed that this broadening did not affect the linearity of the signal–time behavior during constant current generation of stable radical anions over a wide range of concentrations. Constant current generation was carried out using essentially the cell and apparatus described and shown in ref 6. The current was monitored by passing the current through a 100-Ω 0.1% precision resistor which was across the input of a Tektronix 564 oscilloscope. The potential was measured against a silver wire quasireference electrode. A Varian C-1024 or an Enhancetron computer of average transients was used to monitor both the potential and the esr signal with time. The reaction of diethylfumarate however was slow enough so that the signal–time and either the current–time or potential–time behavior could be recorded directly on a dual channel strip chart recorder.
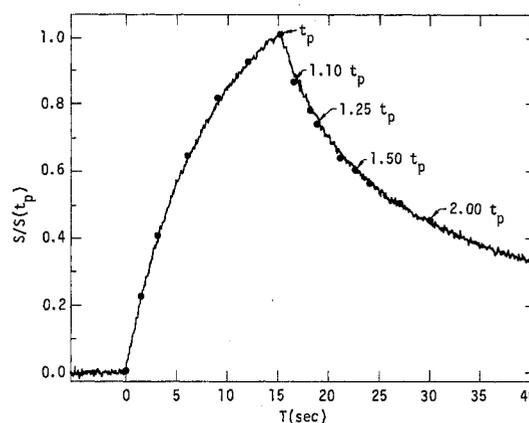
Figure 1. Esr signal time dependence for 7.5 mM diethylfumarate at $t_p = 15$ sec, $i = 0.21$ mA. Points show calculated valves for k_{11} determined at $S(2t_p)$.

The procedure proposed in ref 8 was used to determine the reaction rate constants. A constant current pulse of duration t_p which is less than the electrochemical transition time τ was passed through the cell. The esr signal was recorded from the start of the pulse over a time duration which was at least twice the pulse duration as shown in Figure 1. The ratio of the esr signal at twice the pulse time, $S(2t_p)$, to the signal at the end of the pulse time $S(t_p)$ could then be determined. Knowing the experimental parameters such as diffusion coefficients, electrode area, and concentrations, values of k_{10} and k_{11} (eq 6 and 7) for reactions 2 and 3 could be determined from the tables presented in ref 8.

Results and Discussion

Figure 1 shows a typical signal–time curve for diethylfumarate. Points on this curve represent the theoretical signal–time behavior calculated for a value of k_{11} of 38 as determined from the value of $S(2t_p)/S(t_p)$ where $2t_p$ is 30 sec. It has been pointed out that the upper limit of stability of the esr signal of stable radicals is about 20–30 sec,[6] because removal of the anion radical by convection is likely to begin about this time. This may be the reason that the calculated points fall slightly below the experimental curve at times between 15 and 20 sec. The agreement between the calculated and experimental signal time behavior is very good.

Table I shows values of k_{11} and k_{10} calculated from the esr signal–time curves for the dimerization of the diethylfumarate. The range of values of k_{11} for the radical anion dimerization varied from 26 to 40 M^{-1} sec^{-1}, with a mean value of 33 and a standard deviation of 4 M^{-1} sec^{-1}. This agrees with the value of 34 M^{-1} sec^{-1} from double potential step chronocoulometry.[10] Figure 2 compares values of the ratio of the esr signal where $t_m = 2t_p$ with a theoretical curve drawn for a value of $k = 33$ M^{-1} sec^{-1}. There is no systematic deviation of the experimental points with respect to the theoretical curve. Values of k_{10} vary from 4.5 to 19 M^{-1} sec^{-1} and exhibit a systematic increase with current. In the limiting condition of reaction 3, *i.e.,* the anion parent dimerization where the current is small, the reaction should approach pseudo-first order so that the rate would be proportional to the bulk concentration and independent of current. This pseudo-first-order behavior was not observed. As the current is increased, the effective rate parameter Y_{10} should decrease since the rate of anion decay is proportional to the remaining parent

TABLE I: Rate Constants for Radical-Anion Dimerization and Radical-Anion–Parent Addition Reaction for Dimethylfumarate, Calculated from Experimental Data[a]

i, μA	t_P, sec	$S(2t_\mathrm{p})/S(t_\mathrm{p})$[b]	Y_{11}	k_{11}, M^{-1} sec^{-1}	Y_{10}, M^{-1} sec^{-1}	k_{10}, M^{-1} sec^{-1}
			C = 2.00 mM			
25	25.0	0.683	0.780	33	0.188	4.8
50	10.0	0.764	0.465	39	0.131	9.0
100	5.0	0.827	0.285	34	0.091	14.7
			C = 4.25 mM			
80	5.0	0.845	0.245	36	0.082	4.5
100	10.0	0.722	0.610	26	0.160	5.0
100	25.0	0.480	3.10	33	0.410	6.5
200	5.0	0.757	0.485	29	0.135	9.9
250	3.5	0.790	0.38	31	0.114	12.3
500	1.0	0.912	0.122	32	0.047	18.5
			C = 7.51 mM			
210	15.0	0.460	3.688	40	0.385	5.4
580	1.60	0.902	0.137	31	0.049	6.1
660	1.0	0.814	0.312	31	0.098	18.6

[a] 0.10 M TBA in DMF, 23°, electrode area is 0.443 cm^2, diffusion coefficient 9.5 × 10^{-6} cm^2/sec (ref 10). [b] Average of two to five experiments recorded directly on chart.

TABLE II: Rate Constants for Radical Anion Dimerization and Radical-Anion–Parent Addition Reaction for Dimethylfumarate

i, μA	t_p, sec	$S(2t_\mathrm{p})/S(t_\mathrm{p})$	Y_{11}	k_{11}, M^{-1} sec^{-1}	Y_1, M^{-1} sec^{-1}	k_{10}, M^{-1} sec^{-1}
			C = 3.24 mM			
270	1.00	0.890	0.160	181	0.055	20
1000	0.32	0.840	0.250	198	0.087	122
			C = 4.30 mM			
550	0.50	0.888	0.162	171	0.053	29
			C = 5.92 mM			
1000	0.80	0.764	0.462	137	0.128	46
1250	0.63	0.782	0.405	133	0.118	45
1570	0.40	0.818	0.310	160	0.097	59
2100	0.32	0.840	0.260	140	0.074	60

Average 160; σ = 26

[a] 0.10 M TBAI in DMF at 23°. [b] Each signal time curve is averaged, ten or more repetitions by a CAT. [c] Diffusion coefficient = 1.07 × 10^5 (ref 11).

concentration. By comparison, for the anion radical dimerization, as the current increases, the rate of the reaction increases since it is proportional to the square concentration of the radical anion.

Results of experiments for dimethylfumarate are shown in Table II. Values obtained for k_{11} range from 133 to 198 M^{-1} sec^{-1}, with a mean value of 160 M^{-1} sec^{-1} and a standard deviation of 26 M^{-1} sec^{-1}. The diagnostic value of this method can be illustrated by comparing data from Tables I and II. Typical signal–time behavior of this system is shown in Figure 3.

It should be noticed that for one mechanism the esr signal–time behavior is a function of Y_{10} which contains the concentration (eq 7) whereas for the second mechanism, the signal–time behavior is a function of Y_{11} which is independent of the concentration. By using the same current and pulse duration for different concentrations, these mechanisms could be distinguished. Theoretically, for a given t_p, the ratio of $S(2t_\mathrm{p})/S(t_\mathrm{p})$ has the following behavior. For a first-order decay process the value of $S(2t_\mathrm{p})/S(t_\mathrm{p})$ should not vary with bulk concentration or current; for a radical anion dimerization $S(2t_\mathrm{p})/S(t_\mathrm{p})$ will be independent of the bulk concentration of electroactive species but will decrease with current; for a radical-anion parent dimerization, $S(2t_\mathrm{p})/S(t_\mathrm{p})$ will decrease with bulk concentration and also decrease slowly with current. Unfortu-
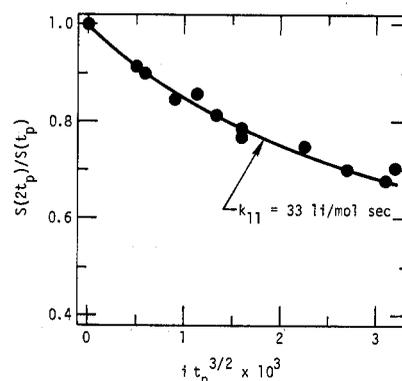
Figure 2. $S(2t_\mathrm{p}/S(t_\mathrm{p})$ vs. $it_\mathrm{p}^{3/2}$ for reduction of diethylfumarate. Solid line is drawn for k_{11} = 33 M^{-1} sec^{-1}.

nately this systematic analysis was not done for any of the systems studied. For a given concentration, however, the mechanisms could be distinguished by varying the current and pulse time at a constant concentration, as shown for diethylfumarate where C is 4.25 mM. Values for k_{11} are relatively uniform whereas k_{10} varies by more than a factor of 4. One must be aware of the possible condition where $it_\mathrm{p}^{1/2}$ is nearly constant such as in the series of experiments on dimethylfumarate, with C = 5.92 mM

TABLE III: Comparison of Rate Constants (M^{-1} sec^{-1}) for Dimerization of Anion Radicals of Several Activated Olefins Determined by Various Methods[g]

	Seesr	Rrde[a,f]	Dps[b]	Cv[c]
Diethylfumarate	30 ± 5		34 ± 3[e]	
Dimethylfumarate	160 ± 26	110 ± 20	117 ± 6[d]	160 ± 40[f]
				120 [d]
Cinnamonitrile	2100 ± 500	880 ± 40	877 ± 21[d]	790 ± [f]
Fumaronitrile	>10[5]	3 ± 1.5 × 10^{5}		Too fast

[a] Rotating ring–disk electrode. [b] Double potential step chronocoulometry and chronopotentiometry. [c] Cyclic voltammetry. [d] Reference 16. [e] Reference 10. [f] Reference 11. [g] Dimethylfumarate solutions containing 0.1–0.2 M TBAI at the Pt electrode.

TABLE IV: Rate Constants for Radical-Anion Dimerization and Radical-Anion–Parent Addition Reaction for Cinnamonitrile

i, μA	t_p, sec	$S(2t_p)/S(t_p)$	Y_{11}	$k_{11} \times 10^{-8}$, M^{-1} sec^{-1}	Y_{10}, M^{-1} sec^{-1}	k_{10}, M^{-1} sec^{-1}
$C = 1.07$ mM
120	0.402	0.81	0.33	2.88	0.100	260
120	0.804	0.81	0.33	1.02	0.100	140
120	0.804	0.60	1.34	4.14	0.255	360
290	0.402	0.72	0.62	2.24	0.160	530
290	0.402	0.70	0.70	2.53	0.175	570
700	0.100	0.85	0.24	2.92	0.080	1140
$C = 2.84$ mM
650	0.402	0.62	1.18	1.85	0.237	270
650	0.402	0.61	1.26	1.98	0.245	280
650	0.402	0.67	0.85	1.34	0.200	230
680	0.201	0.76	0.48	2.11	0.132	280
680	0.201	0.79	0.38	1.67	0.114	240
680	0.201	0.77	0.44	1.93	0.134	290
980	0.201	0.73	0.58	1.77	0.155	370
1900	0.063	0.80	0.35	3.00	0.110	270
$C = 9.22$ mM
270	0.402	0.79	0.38	1.48	0.114	32
710	0.402	0.60	1.44	2.19	0.255	75
720	0.201	0.77	0.44	1.81	0.134	77
1000	0.201	0.75	0.51	1.52	0.140	82
1950	0.201	0.58	1.51	2.30	0.262	170
1950	0.201	0.58	1.51	2.30	0.262	170
2600	0.201	0.53	2.15	2.46	0.313	215
2600	0.201	0.62	1.18	1.35	0.237	160
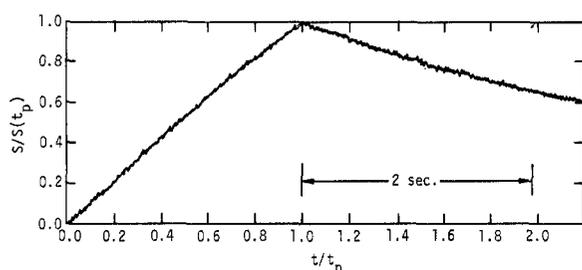
Figure 3. Esr signal time behavior for 5.9 mM dimethylfumarate at t_p = 2.00 sec, i = 1.0 mA.

(Table II) under these conditions, the value of Y_{10} calculated from eq 6 is nearly constant and therefore calculated values for k_{10} will be relatively constant.

The constants determined from seesr measurements are compared with those obtained from other electrochemical measurements in Table III.[16] Rate constants for diethylfumarate and dimethylfumarate anions obtained here agree well with those obtained by other methods. The value for cinnamonitrile differs considerably from the values obtained from cyclic voltammetry and rotating ring disk electrode measurements.

The mechanism and reaction rate constants for the dimerization of both diethyl- and dimethylfumarate an-

ions obtained by seesr agree with that determined from other electrochemical measurements[10,11] and lead to the conclusion that the predominant mechanism involves coupling of the radical anions. Saveant and coworkers[12] have reached similar conclusions using cyclic voltammetric measurements.

The values of the rate constant for cinnamonitrile determined from the equations based on reaction 2 vary from 1.02 × 10^3 to 3.00 × 10^3 M^{-1} sec^{-1} except for one experimental point. The mean value is 2.03 × 10^3 and the standard deviation is approximately 0.54 × 10^3.

Because the variation of these values is so large, we cannot conclude whether the radical anion coupling is the better mechanism, but it is clear that this mechanism fits the data slightly better than the radical-anion parent reaction, as can be seen in Table IV. Several reasons may account for the 2.3- to 2.6-fold higher rate constant obtained from seesr measurements as compared to the electrochemical measurements. First of all, an irreversible "prewave" is observed from cinnamonitrile solutions[11] which may be due to some impurity in the cinnamonitrile. In the electrochemical experiments, this prewave removed by constant potential electrolysis prior to the electrochemical measurements, but this is not easily done in the seesr cell. Although this prewave is only about 5% of the

limiting current, it could be of significance when low currents or short times are used. Constant potential experiments would probably remove this effect. No significant trend with current or time is observed. It is also possible that at high currents, the current density at the working electrode is not uniform because of small ir gradients through the solution between the center and the edge of the electrode and the center of the electrode can be as high as 0.2 V.[4,6] The result of a nonuniformity of the current in this cell would be a concentration gradient of R^- along a line normal to the edge of the electrode and parallel to the surface.

For slow reactions longer times are involved and this concentration gradient will have sufficient time to become uniform by diffusion.[4] For fast reactions, however, the apparent rate of reaction will become faster than the expected value, since the reaction rate is proportional to the square of the concentration. Finally the deviation between the rate constants determined by esr and electrochemical measurements arises from the possibility that intermediates of the form R_2^{2-} are sufficiently stable to contribute to the current in the reversal experiments. For example, it could contribute to the ring current in ring–disk experiments or to the oxidation current in cyclic voltammetry. In the analysis of electrochemical data, R_2^{2-} would be treated as if it were unreacted R^- and therefore give low values for rate constants.

The reaction of fumaronitrile anion was too fast to give good signal–time behavior. The esr signal quickly levels off at a near steady-state value which appears to be independent of the bulk concentration of fumaronitrile and depends on the current. These results indicate either a first-order decay or radical ion dimerization reaction. From the limited data available, and if a radical anion dimerization is assumed, then the rate constant can be estimated to be in the order of $3 \times 10^5 \ M^{-1} \ sec^{-1}$. This agreement is within a factor of 2 of the rate constant determined from ring–disk electrode experiments.

This work demonstrates that *in situ* esr–electrochemical experiments using a nonflowing electrolyte can be used to determine reaction mechanisms involving second-order chemical reactions and also be used to determine the rate constant of the reaction. When the current pulse method described here is used, one must be certain that impurities are not causing the current efficiency to be less than 100% and that the current is evenly distributed over the electrode surface. An alternative method using a potential step to the limiting current region of the electrochemical reaction; this technique should be considered for future work in order to avoid problems involving less than 100% current efficiency, although current pulse method appears to be satisfactory in many cases. The advantage of the current pulse method is that one concentration of the material can be used to determine the rate constant and mechanism. On the other hand, potential step experiments can only be easily used at the limiting current region. Several different concentrations must therefore be studied in order to determine the mechanism of the reaction. The potential step however offers the maximum rate of generation of radical anions, avoids problems associated with having less than 100% current efficiency, and will often lead to more uniform current densities across the electrode surface.

References and Notes

(1) I. B. Goldberg and A. J. Bard in "Magnetic Resonance in Chemistry and Biology," J. Herak, Ed., Marcel Dekker, New York, N. Y., in press; B. Kastening, *Chem. Ing. Tech.*, **42**, 190 (1970).
(2) R. Koopman and H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, **70**, 118 (1966); R. Koopmann, *ibid.*, **70**, 121 (1966); R. Koopmann and H. Gerischer, *ibid.*, **70**, 127 (1966).
(3) B. Kastening and S. Vavricka, *Ber. Bunsenges. Phys. Chem.*, **72**, 27 (1968); K. Umemoto, *Bull. Chem. Soc. Jap.*, **40**, 1058 (1967).
(4) I. B. Goldberg, A. J. Bard, and S. W. Feldberg, *J. Phys. Chem.*, **76**, 2550 (1972).
(5) R. Hirasawa, T. Mukaibo, H. Hasegawa, N. Odan, and T. Maruyama, *J. Phys. Chem.*, **72**, 2541 (1968).
(6) I. B. Goldberg and A. J. Bard, *J. Phys. Chem.*, **75**, 3281 (1971).
(7) B. Kastening, 23rd ISE Meeting, Stockholm, Sweden, Aug 1972, Extended Abstracts, p 290.
(8) I. B. Goldberg and A. J. Bard, *J. Phys. Chem.*, **78**, 290 (1974).
(9) J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, **116**, 743, 749 (1969).
(10) W. V. Childs, J. T. Maloy, C. P. Keszthelyi, and A. J. Bard, *J. Electrochem. Soc.*, **118**, 874 (1971).
(11) V. J. Puglisi and A. J. Bard, *J. Electrochem. Soc.*, **119**, 829 (1972).
(12) E. Lamy, L. Nadjo, and J. M. Saveant, *J. Electroanal. Chem.*, **42**, 189 (1973).
(13) F. Beck, *Angew. Chem., Int. Ed. Engl.*, **11**, 760 (1972).
(14) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 6284 (1968).
(15) I. B. Goldberg and W. F. Goeppinger, *Inorg. Chem.*, **11**, 3129 (1973).
(16) M. Hazelrigg and A. J. Bard, manuscript in preparation; M. Hazelrigg, Ph.D. Dissertation, University of Texas, 1973.