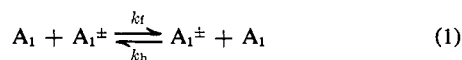# Physical and Inorganic Chemistry

Homogeneous Electron-Transfer Reactions Studied by Internal Reflection Spectroelectrochemistry
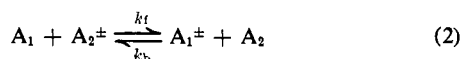
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Received November 23, 1970

Abstract: Using the technique of internal reflection spectroelectrochemistry with subsequent signal averaging, two types of fast homogeneous electron-transfer reactions have been studied. In the reproportionation type where the reacting pairs differ by two electrons ($A_1 + A_1^{2\pm} \rightleftharpoons 2A_1^{\pm}$) an electrochemical potential perturbation was applied to transform through heterogeneous transfer, A_1 to $A_1^{2\pm}$, at a diffusion-controlled rate at the electrode surface. The $A_1^{\pm}$ species was usually optically monitored during this perturbation to relate concentration in the reaction layer to the kinetics. Values of K_{eq} for the reactions were conveniently evaluated from the differences in the peak potentials obtained by cyclic voltammetry. In the other cross-electron-transfer reaction ($A_1 + A_2^{\pm} \rightleftharpoons A_1^{\pm} + A_2$), two molecular pairs (1 and 2) and their one-electron ions are involved. Particular attention was given to a series of ferrocene molecules reacting with a single redox couple, tri-p-anisylamine and its radical cation in the solvent of acetonitrile. The general magnitudes for the rate constants were correctly predicted by the Marcus theory and, for the ferrocene series, the correct relative rates were found. The rates were predominantly dependent on the standard free energy for the reacting redox pairs. Rates varying over a range of six orders of magnitude are reported. Thin platinum films deposited on glass or quartz were used as optically transparent electrodes in this work.

The kinetic rates of fast homogeneous electron-transfer reactions (HETR) between aromatic radical ions and aromatic hydrocarbons have been extensively examined in recent years. These electron-transfer reactions have involved mainly two types

$$A_1 + A_1^{\pm} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A_1^{\pm} + A_1 \tag{1}$$

and

$$A_1 + A_2^{\pm} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A_1^{\pm} + A_2 \tag{2}$$

where the species A_1, $A_1^{\pm}$ and A_2, $A_2^{\pm}$ are related through the redox reactions

$$A_1 = A_1^{\pm} \pm e^- \qquad E_1^0 \tag{3}$$

$$A_2 = A_2^{\pm} \pm e^- \qquad E_2^0 \tag{4}$$
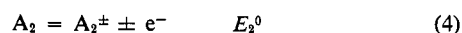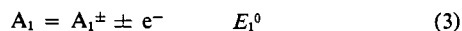
For reaction 1, the reactants and products are identical and the total standard free energy change, ΔF°, is zero. Transfer rates have been successfully measured

using electron spin resonance[1] and, of course, inorganic metal ions and metal ion complexes have been studied through the years by isotopic exchange methods.[2]

In the case of the cross homogeneous electron-transfer reaction 2 the ΔF° is not zero. Here, the equilibrium constant, K_{eq}, for the reaction can be calculated from the values of E_1° and E_2°. In those cases where the kinetic parameters for reaction 2 are not directly measurable by some experimental technique, rate estimates have been based on relationships which rely on knowledge of the equilibrium constant of this reaction and the rate constants of the exchange reaction 1 for each species A_1 and A_2.

(1) G. L. Malinoski, Jr., W. H. Bruming, and R. G. Griffin, J. Amer. Chem. Soc., 92, 2665 (1970), and references therein.

(2) For reviews and discussions see (a) W. L. Reynolds and R. W. Lumry, "Mechanism of Electron Transfer," Ronald Press, New York, N. Y., 1966; (b) N. Sutin, Annu. Rev. Nucl. Sci., 12, 285 (1962); (c) J. Halpern and L. E. Orgel, Discuss. Faraday Soc., No. 29, 7 (1960); (d) ibid., No. 29, 32 (1960).

The use of pulse radiolysis techniques by Dorfman and coworkers[3-5] has greatly extended the available rate data on cross HETR, particularly between series of aromatic hydrocarbons and several anion radicals. More importantly, the accumulation of data has now allowed semiquantitative testing of various theoretical treatments of electron-transfer reactions, principally the one by Marcus.[6-12]

In recent papers,[13-15] we have described a spectroelectrochemical approach using optically transparent electrodes (ote) for the evaluation of a third type of HETR. This is a reproportionation reaction

$$A_1 + A_1^{2\pm} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2A_1^{\pm} \tag{5}$$
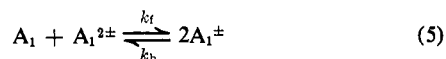
where the three species involved differ in a sequence of one-electron each and are related through redox reactions 3 and 6.

$$A_1^{\pm} = A_1^{2\pm} \pm e^- \qquad E_3^0 \tag{6}$$

The K_{eq} of the reproportionation reaction 5 is calculated from the difference in the standard electrode potentials of E_1^0 and E_3^0. This reaction, similar to the cross HETR, has a finite ΔF°. Progress in the application of the spectroelectrochemical approach has made possible the evaluation of kinetic parameters for those HETR where ΔF° is not equal to zero. Both normal transmission and internal reflection spectroscopy (irs) have been applied to evaluations for cases in which reactions 2 and 5 may be either oxidations or reductions.

The approach is one in which optical measurements are made concurrently during an electrochemical potential pulse. The electrochemical potential perturbs the concentration of either reactants or products of reactions 2 or 5, and analysis of the optical absorbance characteristics during perturbation allows calculation of the rates governing the reactants. Perhaps the most significant feature has been that irs extends the analyzable range of bimolecular rate constants to near the diffusional limit.[16] The required optical sensitivity in the range of 10^{-6} absorbance unit at a time resolution of ca. 10 μsec is made possible by a unique feature of the irs technique which allows signal averaging of the optical signal.[15,17]

A fairly wide variety of HETR of organic, inorganic, and mixed organic-inorganic molecules and ions can now be investigated; the only requirement is that one of the species be electroactive in a potential range accessible to the ote. Solvent and supporting electrolyte can be selected consistent with solubility and electrochem-

ical requirements. A much greater opportunity appears to exist now for a test of the validity of electron-transfer theories.

In this paper, irs results of evaluating rate constants for several organic molecules and ions fitting reaction types 2 and 5 are presented and are correlated with transfer rates calculated using the Marcus approach.

Theory

To describe the theoretical absorbance-time (A-t) behavior for species $A_1^{\pm}$ via irs, both the diffusional rates and the optical properties of the species must be considered in the dimensions of the irs optical cell. For a simple diffusion-controlled faradaic transformation such as given by reaction 3, the A-t behavior has been described by[16,17]

$$A(t) = N_{eff}\epsilon_{A_1}{}^{\pm}\delta C_{A_1}{}^0[1 - \exp(\lambda^2) \, \text{erfc}(\lambda)] \tag{7}$$

where N_{eff} is a sensitivity factor dependent on the film and optical parameters of the experiment, $\epsilon_{A_1}{}^{\pm}$ is the molar extinction coefficient of $A_1^{\pm}$, δ is the penetration depth, $C_{A_1}{}^0$ is the bulk concentration of A_1, and λ is equal to $(D_{A_1}t)^{1/2}/\delta$. The diffusion coefficient, D, can be evaluated either from the current-time behavior during a potential-step (chronoamperometric) experiment or from the irs behavior. It is important that $D^{1/2}/\delta$ be accurately evaluated for the kinetic analysis and that the optical conditions which maximize N_{eff} be known. Both parameters have been thoroughly studied at tin oxide and thin platinum film ote's for a number of compounds.[17]

With a quantitative description of A-t for the simple diffusional case, it is now possible to examine deviations in A-t due to coupled homogeneous chemical reactions involving the monitored, electrogenerated species. Since the optical cell is limited in the solution phase by the penetration depth, δ, the reaction must occur sufficiently fast to alter the concentration of the species before it diffuses through this distance. The diffusion kinetic equations are not, however, amenable to exact solution owing to the second-order nature of the coupled chemical reactions. The approach to the problem has been to computer calculate the concentrations of all the species in the reaction by the technique of digital simulation. The A-t behavior can be obtained by integration of the concentration profile for a given species, correcting for the decreasing energy of the incident light of penetration depth δ. In practice, working curves are constructed which relate the normalized absorbance to the rate constant of the homogeneous chemical reaction being examined. This absorbance is normalized to the value of absorbance for a "filled" optical cell, that is

$$A(t \rightarrow \infty) = N_{eff}\epsilon_{A_1}{}^{\pm}\delta C_{A_1}{}^0 \tag{8}$$

This normalization conveniently cancels the variables N_{eff}, $\epsilon_{A_1}{}^{\pm}$, and $C_{A_1}{}^0$ so that they are not needed to evaluate the kinetics.

The reproportionation case, reaction 5, has been investigated previously by both transmission spectroscopy[13,14] and irs.[15] Here, the concentration profiles of all three species as a function of time have been computer simulated by the method of finite differences for given values of k_f and K_{eq}. Examples of these profiles are shown in Figure 1. The electrode potential is being stepped to a value where the concentration of the parent,

(3) L. M. Dorfman, N. E. Shank, and S. Arai, Advan. Chem. Ser., No. 82, 58 (1968).

(4) S. Arai and L. M. Dorfman, ibid., No. 82, 378 (1968).

(5) J. R. Brandon and L. M. Dorfman, private communication.

(6) R. A. Marcus, J. Chem. Phys., 24, 966 (1956).

(7) R. A. Marcus, Discuss. Faraday Soc., No. 29, 32 (1960).

(8) R. A. Marcus, J. Phys. Chem., 67, 853 (1963).

(9) R. A. Marcus, Annu. Rev. Phys. Chem., 15, 155 (1964).

(10) R. A. Marcus, J. Chem. Phys., 43, 679 (1965).

(11) R. A. Marcus, ibid., 43, 2654 (1965).

(12) R. A. Marcus, ibid., 43, 3477 (1965).

(13) J. W. Strojek, T. Kuwana, and S. W. Feldberg, J. Amer. Chem. Soc., 90, 1353 (1968).

(14) T. Kuwana and J. W. Strojek, Discuss. Faraday Soc., No. 45, 134 (1968).

(15) N. Winograd and T. Kuwana, J. Amer. Chem. Soc., 92, 224 (1970).

(16) N. Winograd and T. Kuwana, J. Electroanal. Chem. Interfacial Electrochem., 23, 333 (1969).

(17) N. Winograd and T. Kuwana, Anal. Chem., 43, 252 (1971).

A_1, is zero at the surface. The electrode reaction is then the transformation of A_1 to $A_1^{2\pm}$ at a diffusion-controlled rate; as $A_1^{2\pm}$ moves to the bulk of the solution by diffusion, it encounters A_1 diffusing toward the electrode and reaction occurs to attain equilibrium. The consequence of this equilibrium and reaction is that the concentration profile of species $A_1^{\pm}$ has a maximum at some distance x from the electrode surface at a time t. This maximum then increases in intensity as t and x increase. For smaller k_f values, however, this process occurs at increased times and, subsequently, at increased distances from the electrode surface. Thus, for irs to be sensitive to the kinetics, assuming $A_1^{\pm}$ is being monitored, the reaction must be sufficiently rapid to occur within the boundaries of the irs optical cell. For typical values of diffusion coefficients (*ca.* 10^{-5} cm^2/sec) encountered in solutions, the lower limit of k_f is about 10^5 M^{-1} sec^{-1}. At values smaller than this, the absorbance due to $A_1^{\pm}$ becomes vanishingly small.

The present extension of the irs technique to include the cross HETR (reaction 2) is significant since it should allow the possibility of studying homogeneous electron transfer between species of any two redox reactions. Theoretical analysis is performed identically with the reproportionation case and the results are similar. For example, the concentration profiles of A_1 and $A_1^{\pm}$ correspond exactly to those of A_1 and $A_1^{2\pm}$ when the potential is stepped for reaction 3 to proceed under diffusion-controlled conditions in the presence of A_2. Working curves are again constructed relating normalized absorbance to the rate constant of the reaction (*e.g.*, see Figure 3).

A value of the rate constant, k_f, equal to about 10^5 M^{-1} sec^{-1} is a convenient dividing line between application of transmission and irs techniques. For lower values, transmission can be conveniently used, the only limitation being that the parent, A_1, should not be highly light absorbing. Irs, on the other hand, is *only* applicable to larger values of k_f. It has an advantage that any of the species in the equilibrium can be monitored if the other species do not substantially interfere at the monitoring wavelength.

The value of λ, which must be known in order to calculate the concentration profiles, can be determined by (a) calculating D from electrochemical experiments and δ from knowing the optical constants or (b) more conveniently, using a reference compound with a known D value and calculating δ from the $A-t$ behavior. This latter procedure will be demonstrated using the reference compound 9,10-dimethylphenazine.

Experimental Section

A. Instrumentation. Optical and electrochemical equipment has been previously discussed.[16,17] The overall time response of the potentiostat was on the order of 10 μsec (90% double layer charging), while the photomultiplier and associated preamplifiers had a response of 3 μsec. Under normal operating conditions, *i.e.*, for several thousand scans into the signal averager, absorbance changes as low as 1 part in 10^6 could be detected with this time resolution. Thin-film Pt ote's with resistances of 10 to15 ohms sq^{-1} were prepared using the procedure outlined by Von Benken.[16] Digital simulation calculations were performed using a Univac 1108 computer.

B. Chemicals and Special Procedures. Methyl viologen was recrystallized twice from water. All kinetic runs with methyl viologen were performed by first thoroughly degassing the cell

(18) W. Von Benken and T. Kuwana, *Anal. Chem.*, **42**, 1114 (1970).
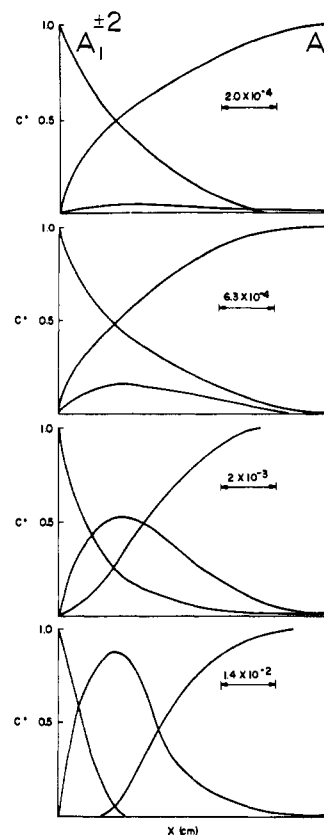

Figure 1. Concentration profiles for the mechanism given in eq 5. The different graphs are drawn for t = 1, 10, 100, and 500 msec, from top to bottom, with k_fC = 10^2 sec^{-1}. At $t > 0$, the concentration of A_1 at x = 0 is zero and the concentration of $A_1^{2\pm}$ at x = 0 is equal to the bulk concentration of A_1 (normalized to unity); the profile for $A_1^{\pm}$ is seen to rise (from top to bottom).

with argon and the cell compartment with nitrogen because of the extreme sensitivity of the second electron reduction product to oxygen. The *o*-dianisidine was recrystallized twice from ethanol. Tri-*p*-anisylamine was prepared using a previously described procedure[19] and was recrystallized twice from hexane. All ferrocene derivatives were synthesized using published procedures and were purified either by recrystalization from hexane or by sublimation.

Baker Analyzed reagent grade acetonitrile was used directly for all systems except methyl viologen, where the solvent was passed through an alumina column. The tetraethylammonium perchlorate was recrystallized twice from water and dried at 60° in a vacuum oven. All solutions were degassed with nitrogen prior to use.
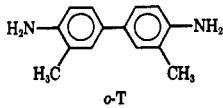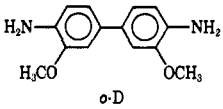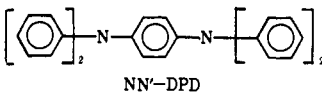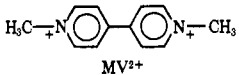
Results

A. Reproportionation Rates. A current-potential ($i-E$) curve, which is obtained by cyclic voltammetry, is shown in Figure 2a for the oxidation of *o*-dianisidine in acetonitrile at a Pt ote. This $i-E$ curve is typical of molecules or ions which undergo an electrode reaction of two consecutive one-electron transfers (EE mechanism). A value of K_{eq} can be calculated from the difference in the peak potentials of the first and second waves. Accurate evaluation of K_{eq} is crucial to the value of k_f only when $K_{eq} < 10^2$. Also, when K_{eq} is large, the potentials E_1^0 and E_3^0 are well separated and allow potential-step experiments to be conducted for the spectroelectrochemical characterization of $A_1^{\pm}$ for reaction 3. However, for small values of K_{eq} as with *o*-dianisidine, characterization is difficult and is best per-

(19) L. Papouchado, R. N. Adams, and S. W. Feldberg, *J. Electroanal. Chem. Interfacial Electrochem.*, **21**, 408 (1969).

Table I. Summary of Data for the Reproportionation Mechanism[a] $A_1 + A_1^{2\pm} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} K_{eq}$

A_1	$A_1^{2\pm}$	K_{eq}^b	Wavelength, nm	Approx time resolution	$k_f,$ M^{-1} sec^{-1}	Solution conditions	Ref
o-T structure (H₂N—⟨⟩—⟨⟩—NH₂, H₃C, CH₃) o-T	o-T^{2+}	13	438 o-T	5 msec^c	4×10^5 ^{e}	Aqueous, pH 4.0 acetate buffer	13
o-D structure (H₂N—⟨⟩—⟨⟩—NH₂, H₃CO, OCH₃) o-D	o-D^{2+}	10^3	520 o-D^{2+}	100 μsec^d	1.6×10^8 ^{f}	Acetonitrile 0.25 M TEAP	This work
NN'-DPD structure	N,N'-DPD^{2+}	>200	700 N,N'-DPD^{2+}	5 msec^c	2.3×10^6 ^{e}	Acetonitrile 0.3 M TEAP	13
MV^{2+} (H₃C—N⟨⟩—⟨⟩N—CH₃)	MV^0	10^7	620 MV$^+$	50 μsec^d	>3 $\times 10^9$ ^{e}	Acetonitrile 0.5 M TEAP	16
Ta$_6$Br$_{12}^{2+}$	Ta$_6$Br$_{12}^{4+}$	10^5	620 TaBr$_{12}^{2+}$	100 μsec^d	6.9×10^7 ^{e}	Aqueous 0.04 M HClO$_4$	15

^{a} All kinetic runs performed at 25° at concentrations varying from 0.2 to 1 mM. ^{b} $K_{eq} = k_f/k_b$, calculated from the difference in E^0 values. ^{c} Rate constant evaluated via transmission spectroelectrochemistry. ^{d} Rate constant evaluated via internal reflection spectroelectrochemistry with subsequent signal averaging. ^{e} SnO$_2$ ote. ^{f} Pt ote.

formed by using a reference compound. For oxidation in acetonitrile, 9,10-dimethylphenazine (DMP) was employed. It undergoes a reversible one-electron transfer with the generation of a stable radical cation.[19] The D

Figure 2. Representative i-E voltammetric curves for (a) 0.5 mM o-dianisidine and (b) 0.5 mM TAA and DMP oxidation. In (b), curve 1 is an equimolar mixture of TAA and DMP while curve 2 shows the TAA oxidation alone. Scan rates are 160 mV/sec; 0.25 M TEAP-acetonitrile at the Pt ote.

value for DMP is 1.68×10^{-5} cm^2 sec^{-1}, and ϵ at 662 nm for the radical is equal to 1.9×10^3 M^{-1} cm^{-1}.

For a particular cell orientation then, the value of $D^{1/2}/\delta$ for o-dianisidine can be calculated using

$$(D^{1/2}/\delta)_1 = (D^{1/2}/\delta)_2 \lambda_1 D_2^{1/2}/\lambda_2 D_1^{1/2} \qquad (9)$$

where λ is the monitoring wavelength and subscripts 1 and 2 refer to DMP and o-dianisidine, respectively.

When the first and second waves are well separated ($K_{eq} > 10^3$), $D^{1/2}/\delta$ can be evaluated directly from the A-t curve when the potential is stepped some 100–200 mV beyond the peak potential of the first wave.

Results for five different reproportionation reactions obtained by both transmission and irs are summarized in Table I. All kinetic data were determined during chronoamperometric experiments with the potential stepped 150–250 mV beyond the peak potential for the second wave. These rates vary over a wide range of values; the one-electron intermediate was optically monitored in all cases except for the tantalum bromide cluster ion, where the disappearance of the parent dication was monitored.

B. Cross-HETR Rates. Previous pulse radiolysis studies of cross HETR between a series of aromatic hydrocarbons and their radical anions by Dorfman, et al.,[3-5] have indicated a direct dependence of k_f on the magnitude of the ΔF^0 for the reaction. To further examine this dependence, a heterocyclic aromatic molecule and a series of ferrocenes were investigated with a common transfer redox couple of tri-p-anisylamine (TAA) and its radical cation (TAA·$^+$). The oxidation of TAA to TAA·$^+$ has been previously studied in detail.[20,21] The oxidation was reversible at Pt and the Pt ote, and the TAA·$^+$ formed was thoroughly characterized by both visible and electron spin resonance spectra. The electrode potential of this couple has a value which is ideal for the selection of several substituted ferrocenes, resulting in a wide range of ΔF^0
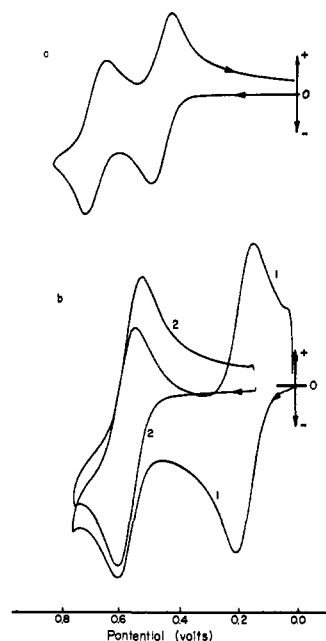
(20) R. F. Nelson, D. W. Leedy, E. T. Seo, and R. N. Adams, Z. Anal. Chem., 224, 184 (1967).

(21) H. N. Bount, N. Winograd, and T. Kuwana, J. Phys. Chem., 74, 3231 (1970).

values as estimated from the separation of the peak potentials from the cyclic i-E curves for each individual couple.

The similarity of the cross reactions to the reproportionation ones may be readily recognized by the similarity in the cyclic i-E curves. For example, Figure 2b, curve 1, is for an equimolar mixture of TAA and DMP; the cyclic i-E has a double wave characteristic of an EE mechanism such as was observed for o-dianisidine in Figure 2a. These two compounds serve as an excellent example since the electrode potentials for the one-electron oxidation of each couple are well separated (ΔE_p = 420 mV).

The cyclic i-E curve for TAA alone is shown in Figure 2b, curve 2. The irs spectroelectrochemical analysis was performed by monitoring TAA$\cdot^+$ at a wavelength of 715 nm at the Pt ote in acetonitrile containing 0.25 M TEAP. Determination of the A-t behavior at this wavelength during potential-step generation of TAA$\cdot^+$ at $+0.80$ V $vs.$ sce from various concentrations of TAA gave rise to a value of $\epsilon D^{1/2}$ of 101 ± 1. Varying amounts of DMP were then added and the experiment was repeated. As can be seen, the waves for both compounds are well developed and appear reversible. The A-t behavior deviated from the case where TAA$\cdot^+$ alone was being generated at a diffusion-controlled rate. Working curves were then constructed for the different concentration ratios of TAA:DMP, taking into account in the digital simulation process the differences in the values of the diffusion coefficients of these two molecules. Analysis of the results gave a calculated value of $k_f = (1.4 \pm 0.4) \times 10^9 \ M^{-1} \ \mathrm{sec}^{-1}$ for the reaction

$$\mathrm{DMP} + \mathrm{TAA}\cdot^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{DMP}\cdot^+ + \mathrm{TAA} \qquad (10)$$

Further details of kinetic analysis will be given in the discussion of the ferrocenes with TAA.

Ferrocene and substituted ferrocenes represent a series of compounds where $\Delta F°$ can be varied over a large range without altering significantly the structure of the basic reacting entity. The electrochemistry of

Table II. Electrochemical Data

Compound	$D^{1/2} \times$ $10^{3,a}$ cm sec$^{-1/2}$	$\Delta E_p,^b$ mV	K_{eq} ^{c}	$\Delta F°',^d$ kcal mol^{-1}
Ferrocene	4.67	−160	2.1×10^{-3}	−3.68
Vinylferrocene	4.40	−155	2.6×10^{-3}	−3.56
Acetylferrocene	3.96	60	16	+1.71
Diacetylferrocene	4.01	295	8.3×10^4	−6.79
Ferrocenyl- carboxylic acid	3.8	72	10	+1.38
DMP	4.5	−420	2×10^{-7}	−9.2
TAA	3.54			

^{a} Evaluated from chronoamperometric experiments using the Pt ote. Electrode area as calibrated using $K_3Fe(CN)_6$ oxidation in 1 M aqueous KCl = 0.35 cm². Concentration of electroactive species for i-$t^{-1/2}$ plots was 0.5 mM in 0.22 M TEAP-acetonitrile. Time range was from 4 to 16 msec. Background currents were corrected by running a blank. ^{b} $\Delta E_p = (E_p)_{\mathrm{compound}} - (E_p)_{\mathrm{TAA}}$. $(E_p)_{\mathrm{TAA}} = 590$ mV. Note that the potential is a formal potential quoted only for the given solution conditions. Error limits, ±5 mV. ^{c} Calculated for

$$\mathrm{TAA} + \mathrm{X}^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{TAA}^+ + \mathrm{X}$$
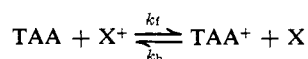
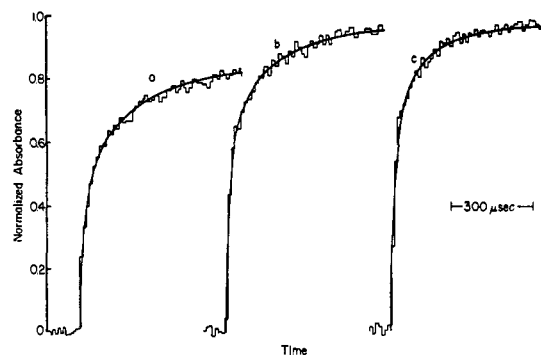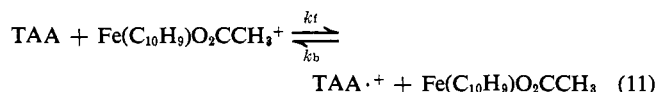For this reaction, $K_{eq} = k_f/k_b$. $^d \Delta F°' = -nF(\Delta E_p)$.

Figure 3. Experimental A-t curves for the reaction of acetylferrocinium cation with TAA. Response represents behavior for (a) 0.182 mM TAA oxidation, (b) 0.182 mM TAA oxidation in the presence of 0.182 mM AF, and (c) 0.167 mM TAA oxidation in the presence of 0.333 mM AF. An 800-μsec potential pulse from 0.40 to 0.80 V $vs.$ sce with a repetition rate of 30 Hz for a total of 2 min ($i.e.$, 3600 scans) was processed by the signal averager. The solid line represents the theoretical value for $k_f = 3.8 \times 10^6 \ M^{-1} \ \mathrm{sec}^{-1}$ and $D^{1/2}/\delta = 124 \ \mathrm{sec}^{-1/2}$. The circles correspond to the same data points enumerated in Table III and Figure 3. The total absorbance change is $\simeq 10^{-3}$ unit and the signals are all normalized to their steady-state value.

the ferrocenes has been extensively studied; those with appropriate redox potentials could be easily selected from the literature.[22,23] The heterogeneous electron-transfer rates at a Pt electrode appeared fast for these ferrocenes, and i-E curves obtained by cyclic voltammetry exhibited reversible behavior. Electrochemical data on the selected ferrocenes are tabulated in Table II. Diffusion coefficients were calculated from the i-t curve during chronoamperometric experiments. These D values were in good agreement with literature values except for those of the carboxylic acid derivative. A possible explanation is that tetraethylammonium perchlorate used in the present experiment as supporting electrolyte does not exhibit ion pairing as does lithium perchlorate which was used previously.[22]

The homogeneous electron-transfer rates for this series of compounds with TAA$\cdot^+$ were evaluated as usual by matching the experimental absorbance to the working curves which have the normalized absorbance $vs.$ log ($\beta^2 t$) plotted for various values of K_{eq}, where $\beta^2 = k_f C$. The bulk concentration, C^0, is most conveniently treated with $C_{A_1}^0 = C_{A_2}^0$.

For example, in the case of acetylferrocene and TAA, where separation of the peak potentials (ΔE_p) is 72 mV, with the acetylferricinium ion a stronger oxidant than TAA$\cdot^+$, the equilibrium in the reaction

$$\mathrm{TAA} + \mathrm{Fe}(C_{10}H_9)O_2CCH_3^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}}$$
$$\mathrm{TAA}\cdot^+ + \mathrm{Fe}(C_{10}H_9)O_2CCH_3 \qquad (11)$$

is shifted to the right. Thus, if the electrode potential is stepped to a value where both TAA and acetylferrocene are oxidized at diffusion-controlled rates, the concentration of TAA$\cdot^+$ in the reaction layer will be larger in the presence of acetylferrocene than in its absence. The signal averaged A-t curves of TAA$\cdot^+$ in the absence (curve a) and presence (curves b and c) of acetylferrocene, shown in Figure 3, clearly exhibit this increased TAA$\cdot^+$ concentration.

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Table III. Evaluation of Acetylferrocene Exchange Rate Constant

λ[a]	Time, μsec	Relative absorbance[b]	Normalized absorbance[c]	Log $\beta^2 t$[d]	$\beta^2 \times 10^{-4}$, sec^{-1}[e]
1.0	65	82.2	0.688	0.64	6.7
1.5	146	97.7	0.818	0.99	6.7
2.0	260	106.0	0.887	1.25	6.8
2.5	406	110.7	0.926	1.50	7.8
3.0	585	113.0	0.945	1.61	6.9
					Av $\overline{7.0} \pm 0.4$

[a] $\lambda = (Dt)^{1/2}/\delta$ in accord with eq 9. For a detailed description of the procedure for evaluation of λ, see ref 17. For this run $D^{1/2}/\delta = 124$ sec$^{-1/2}$. [b] Steady-state absorbance, in relative units, is 119.5 and corresponds to a total absorbance change of about 10^{-3} unit. [c] Calculated by dividing the relative absorbance by the relative steady-state absorbance. [d] $\beta^2 = k_t/C_{AF}$; for this run $C_{AF} = C_{TAA} = 0.182$ mM in 0.22 M TEAP–acetonitrile. Rate constant for reaction of TAA and AF$^+$. [e] $k_t = \beta^2/C_{AF} = 3.8 \times 10^8$ M^{-1} sec^{-1}. TAA$\cdot^+$ monitored at 7150 Å during the potential step 150 mV beyond the peak of the AF wave.

The working curves of the normalized absorbance *vs.* log ($\beta^2 t$) as a function of convenient values of λ are plotted in Figure 4. A value of k_t could then be eval-
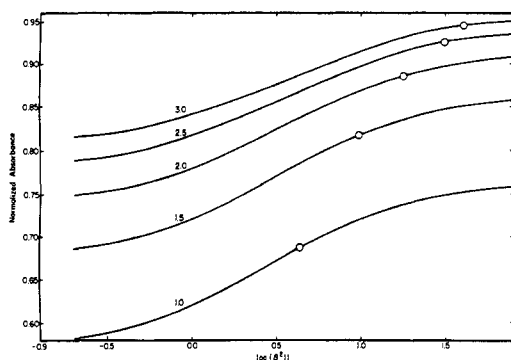

Figure 4. Internal reflection spectroelectrochemical working curve for the cross-reaction mechanism. The rate constant is calculated for the reaction of equal concentrations of TAA and acetylferrocinium cation with $D_{AF}/D_{TAA} = 1.12$, $K_{eq} = 16$, and for monitoring TAA$\cdot^+$. Each curve corresponds to a particular value of $(Dt)^{1/2}/\delta$ as indicated by the numbers shown. The circles are the experimental points shown explicitly in Table III. The normalized absorbance is calculated in accord with eq 8.

uated from this working curve by determining the normalized absorbance at any given time, t, if $D^{1/2}/\delta$ was known for that particular irs experiment. Usually, normalized absorbances are determined over a wide range of times and several penetration depths. The precision of rates expressed as β^2 is seen in Table III, where λ is varied from 1 to 3 and time is varied from 65 to 585 μsec. Results for k_t of reaction 11 for various concentration ratios of TAA to acetylferrocene are summarized for several values of $D^{1/2}/\delta$ in Table IV. The general

Table IV. Summary of Acetylferrocene Results[a]

$D^{1/2}/\delta$, sec$^{-1/2}$	C_{TAA}, mM	$C_{AF}:C_{TAA}$	$k_t \times 10^{-8}$, M^{-1} sec^{-1}
90	0.182	1:1	5.0 ± 0.8
99	0.15	1:1	2.4 ± 0.2
102	0.15	1:1	3.6 ± 0.3
90	0.167	1:1	3.9 ± 0.6
99	0.15	2:1	3.3 ± 0.4
129	0.182	1:1	3.8 ± 0.3
124	0.167	2:1	3.9 ± 0.8
			Av 3.7 ± 0.8

[a] Experimental conditions the same as in Table III.

reproducibility of k_t with these variations supports the validity of the spectroelectrochemical approach. Results for ferrocene, acetylferrocene, diacetylferrocene, and ferrocenylcarboxylic acid with TAA are included in Table VI.

Discussion of Results

Theoretical treatment of HETR has been formulated and discussed by Marcus.[6-12] His theory has been examined and compared to others in a recent monograph by Reynolds and Lumry.[2a] Arai and Dorfman[3,4] in their pulse radiolysis work have discussed the Marcus relationships as they applied to predicting electron-transfer rates between aromatic hydrocarbons and aromatic radical anions and found good correlation between the experimental and theoretical rates. These same relationships appear appropriate for the reproportionation and cross HETR studied in this paper. Only a brief discussion of Marcus' theory follows; in addition to Marcus' original papers, the excellent monograph by Reynolds and Lumry[2a] on HETR can be consulted for details. In the Marcus model, the k_t(bimolecular) is determined by the free energy of activation, ΔF^*, for the reaction through the relationship

$$k_t = Z \exp(-\Delta F^*/RT) \quad (12)$$

where Z is the gas-phase collisional frequency taken to be 10^{11} M^{-1} sec^{-1}. The ΔF^* is given by

$$\Delta F^* = W + \lambda_0/4 + \Delta F^{\circ\prime}/2 + (\Delta F^{\circ\prime})^2/4\lambda_0 \quad (13)$$

where W is the work term due to the coulombic interaction of the reactants at the configuration of the transition-state complex. When one or both reactants are uncharged, this W term will be assumed to be sufficiently small so that it can be neglected. The free energy required to reorient the solvent of the reactants from the ground-state configuration to that of the activated complex is given by the reorganizational parameter, λ_0, defined by

$$\lambda_0 = \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_{12}}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)(\Delta e)^2 \quad (14)$$

where r_1 and r_2 are the radii of reactants 1 and 2, r_{12} is the distance between the centers of reactants 1 and 2 in the activated complex, D_{op} is the optical dielectric constant, D_s is the static dielectric constant, and Δe is the change in the electric charge which is unity for all cases examined. Similar to Dorfman's calculations, an assumption is made that the inner reorganization energy is small and does not affect the value of λ_0. The $\Delta F^{\circ\prime}$ is

Table V. Correlation of Calculated Activation Parameters to Experimental Rate for Reproportionation Reaction

Parent compound	W, kcal mol^{-1}	$\Delta F^{\circ\prime}$, kcal mol^{-1}	k_{bi}, M^{-1} sec^{-1} [b]	k_{bi}(exptl), M^{-1} sec^{-1}	Ref
Methyl viologen dication, MV^{2+}	0	-9.7	$(0.7-3) \times 10^{10}$	2.3×10^{9}	15
N,N'-Diphenyl-p-phenylene-diamine, N,N'-DPD	0	-5.3	$(0.6-4) \times 10^{9}$	2.3×10^{6}	13
o-Dianisidine, o-D	0	-4.1	$(0.3-2) \times 10^{9}$	1.6×10^{8}	This work
Tantalum bromide cluster ion, Ta$_6$Br$_{12}^{2+}$	1.74[a]	-6.9	$(0.4-5) \times 10^{8}$	6.9×10^{7}	15
o-Tolidine, o-T	0.64[a]	-1.5	$(0.3-2) \times 10^{8}$	6.9×10^{7}	13, 14

[a] Aqueous solution, others in nonaqueous acetonitrile. [b] Bimolecular rate constant, k_{bi}, calculated for range 8–10 Å.

Table VI. Comparison of Experimental and Theoretical Exchange Rates for Dimethylphenazine, Ferrocene, and Substituted Ferrocenes with Tri-p-anisylamine

Reacting pair	ΔF^{*} [a] kcal mol^{-1}	k_{bi}(exptl),[b] M^{-1} sec^{-1}	k_{bi}(calcd),[c] M^{-1} sec^{-1}	$\frac{(k_{bi})_x}{(k_{bi})}$(exptl)	$\frac{(k_{bi})_x}{(k_{bi})}$(calcd)
1. DMP + TAA·$^{+}$	0.80	1.4×10^{9} (2.5×10^{10})[d]	2.6×10^{10}	1.33 (24)[d]	20
2. Diacetylferrocinium + TAA	1.53	1.5×10^{9} (2.0×10^{10})[d]	7.8×10^{9}	1.43 (19)[d]	6.0
3. Ferrocene + TAA·$^{+}$	2.61	$1.0_5 \times 10^{9}$	1.3×10^{9}	1.00	1.00
4. Vinylferrocene + TAA·$^{+}$	2.66	9.5×10^{8}	1.2×10^{9}	0.91	0.92
5. Acetylferrocinium + TAA	3.44	3.7×10^{8}	3.2×10^{8}	0.35	0.25
6. Ferrociniumcarboxylic acid + TAA	3.59	1.6×10^{8}	2.5×10^{8}	0.15	0.19
7. Ferrocene carboxylic acid + TAA·$^{+}$	4.97	1.6×10^{7}	2.5×10^{7}	1.5×10^{-2}	1.9×10^{-2}
8. Acetylferrocene + TAA·$^{+}$	5.14	2.3×10^{7}	1.9×10^{7}	2.2×10^{-2}	1.5×10^{-2}
9. Vinylferrocinium + TAA	6.22	2.5×10^{6}	3.1×10^{6}	2.4×10^{-3}	2.4×10^{-3}
10. Ferrocinium + TAA	6.29	2.3×10^{-6}	2.7×10^{6}	2.2×10^{-3}	2.1×10^{-3}
11. Diacetylferrocene + TAA·$^{+}$	8.32	1.8×10^{4}	9.4×10^{4}	1.7×10^{-5}	7.2×10^{-5}
12. DMP^{+} + TAA	10.1	3×10^{2}	5×10^{3}	2.8×10^{-7}	4×10^{-6}

[a] Calculated from eq 13; $\lambda_0 = 17$ kcal ($r_1 = r_2 = r_{12}/2 = 5.1$ Å). [b] Bimolecular rate constant, k_{bi}, for mechanism in eq 2. [c] Calculated from eq 12. [d] As pointed out by one of the reviewers, $1/k_{bi} = 1/k_{act} + 1/k_{diff}$, and when $k_{act} \ll k_{diff}$, as is the case for reacting pairs 1 and 2, $k_{bi} \cong k_{diff}$. Values of k_{diff}, assuming unit probability of reaction on each encounter, are in parentheses and are in better agreement with k_{bi}(calcd).

the standard free energy of either reaction 2 or 5 at the defined solution conditions, which can be estimated from the difference in standard electrode potentials of either reactions 3 and 4 or 3 and 6. Experimentally, it is convenient to calculate $\Delta F^{\circ\prime}$ from a difference between peak potentials for these redox reactions obtained by cyclic voltammetry. This approximation was assumed to introduce only a small error, particularly for the comparison of $\Delta F^{\circ\prime}$ values for the series of ferrocene compounds with TAA.

The activation parameters for the Marcus theory are tabulated in Table V for the reproportionation HETR. It is interesting that the reactants only differ by two electrons and the activated complex should be completely symmetric, as one would find for HETR of reaction 1. However, considerable uncertainty exists as to the best choice for the radii of each reactant and thus the distance between the centers of the reactants in the activated state. Calculated rates are therefore made for an 8–10-Å range which was chosen based on values used for the cross-HETR calculations and also from comparison with those values used by Dorfman.[3–5] Also, the assumption that $W = 0$ in three of the cases may not be valid since the products, although identical, are charged. Agreement between the calculated and experimental rates is nevertheless within an order of magnitude for all except N,N'-diphenyl-p-phenylenediamine. The lower rates encountered with the tantalum bromide cluster ion and o-tolidine reflect the coulombic repulsion between reactants and the higher

reorganizational term of ion–solvent reorientation. These terms (W and λ_0) offset the fairly large $\Delta F^{\circ\prime}$ which would have otherwise predicted a rate in the order of 10^9 M^{-1} sec^{-1}.

In the cross HETR, bimolecular rates (k_{bi}) were calculated with eq 12–14, and a value of λ_0 was selected which gave rates in close agreement with the experimental ones in the ferrocene series. In doing so, r_1 was assumed to be equal to r_2 ($r_1 = r_2 = r_{12}/2 = 5.1$ Å). A more meaningful test of the theory is then possible by comparison of the relative rate constants which are obtained by normalizing each value of k_{bi} to the rate constant for the ferrocene–TAA·$^{+}$ reaction in both the experimental and calculated cases. In the last two columns of Table VI, this comparison is made and the correlation is suprisingly good over electron-transfer rates varying over a range of six orders of magnitude. The controlling factor for this series of cross HETR is clearly governed by the magnitude of $\Delta F^{\circ\prime}$.

Less agreement is expected between the calculated and experimental ratios when the ΔF^{*} is small compared to the diffusional activation energy (ca. 2–3 kcal mol^{-1}), as is observed for the reacting pairs 1 and 2 in Table VI. Similar deviations are also then noted for rates of reacting pairs 11 and 12 since these rates are calculated from the rates and K_{eq} for reacting pairs 1 and 2.

Conclusions

There is no doubt that the Marcus theory correctly predicts the general magnitude of the kinetic rates for

homogeneous electron transfer and certainly, for a series of similar compounds, the correct relative rates. Extension of the present study to include a greater variety of compounds differing in electronic and structural features must be done to assess inductive (reflected in $\Delta F°'$) and steric effects to rates of HETR. The spectroelectrochemical approach coupled with signal averaging and computerized digital simulation methods provides an opportunity to expand the scope of HETR studies; nearly any electrochemically active molecule or ion can be spectrally probed either directly or indi-

rectly through some mediation scheme. Further, the resulting precision of the method now allows the effect of solvent, supporting electrolyte, temperature, etc., to be assessed for a wide variety of reacting pairs.

Kinetics of Proton-Transfer Reactions in Aqueous Solution. IV. The Brønsted Slope for Internally Hydrogen-Bonded Weak Acids

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Abstract: A kinetic and thermodynamic study has been carried out for the deprotonation by hydroxide ion of a series of closely related internally hydrogen-bonded weak acids. Five compounds have an ortho azo internal hydrogen bond; two have a salicylate internal hydrogen bond. Relaxation times as measured by a temperature-jump spectrometer at 15° and $I = 0.1$ were interpretable on the basis of the deprotonation reaction $OH^- + HA^r \rightleftharpoons A^{r-1} + H_2O$. Measured forward rate constants varied from 10^6 to 10^9 M^{-1} sec^{-1} for the pK range 9–12. On a plot of log k_f vs. pK_a, rate and equilibrium data were linearly related with a Brønsted coefficient $\alpha = 1.2$. This value was interpreted on the basis of Marcus' theory of Brønsted slopes as consisting of a "within-series" contribution to α of about 0.45, and a contribution of 0.75 due to changes in intrinsic properties of the compounds due to changes in structure.

Rate constants for proton-transfer reactions in aqueous solution have now been determined for many systems.[3–5] It is well established that the rates of all "normal" acid–base reactions (where the proton is attached to a singly bonded oxygen or nitrogen atom) are diffusion controlled, *i.e.*, reaction occurs as soon as the two reactants approach to within a critical distance. A diffusion-controlled reaction in water presupposes access of the solvent to the proton in order for transfer to occur *via* a skipping mechanism.[6] This is not the case where the proton participates in an internal hydrogen bond or is bonded to a carbon acid. In such instances the proton-transfer reaction may no longer be diffusion controlled and the rate constant becomes dependent on the ionization constant of the weak acid.[7,8] Such a functional dependence is represented by the Brønsted relationship $\alpha = $ d log $k/$d log $K = -$d log $k/$dp$K$.

While the Brønsted equation can be "derived"[9] by re-

lating $\Delta G^{\ddagger}$ and $\Delta G°$, it is only recently that an attempt has been made to explore theoretical relations from which it can be derived. Marcus has modified the equations developed for his theory of weak-overlap electron-transfer reactions and applied them to elementary steps of proton-transfer reactions.[10] The fundamental equation relates the free energy activation barrier, ΔG^*, to an intrinsic barrier λ (a reorganizational term) and to an extrinsic barrier $\Delta G°'$, the free energy of reaction under the prevailing experimental conditions. The Brønsted coefficient is calculated from the relation $\alpha = $ d$\Delta G^*/$d$\Delta G°'$. The results of an extensive literature search[11] showed that the values of α so calculated agreed with the experimental values. The Brønsted coefficient for proton-transfer reactions was $\sim$0.5, well within the limits of $0 < \alpha < 1$. In a later paper[12] Marcus pointed out that by using a more complete equation for α, his theory could also be used to account for unusual free energy slopes where $0 > \alpha > 1$.

The rate constants for proton transfer in pseudoacids have been well studied by classical[8] as well as relaxation techniques.[3–5] From the resulting Brønsted plots the limits on α, the Brønsted coefficient, have been substantiated as $0 < \alpha < 1$. With the utilization of rapid kinetic techniques, Brønsted plots over a sufficiently wide log k range could be made, and the expected curvature of α from $\alpha = 0$ to $\alpha = 1$ was observed for some

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