Voltammetric Reductions of Ring-Substituted Acetophenones. 2. A Senior-Level Experiment Requiring Classification of an Electrochemical Mechanism as Stepwise or Concerted

Grant N. Holder*, Laurel L. McClure, and David G. Farrar

Department of Chemistry, Appalachian State University, Boone, NC 28608, holdergn@appstate.edu

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Abstract: An experiment suitable for upper-level undergraduates in which they determine the characteristics of a chemically coupled electron transfer (EC) mechanism is described. Students examine the free-energy barrier between an unstable radical anion and the products of its decomposition for ring-substituted and alpha-substituted acetophenones, acetanilides, and alkyl halides. Digital simulation is used to estimate the value of the standard potential, E^{o}. Calculation of the electrochemical transfer coefficient, α, allows a determination of whether the electron transfer occurs in a single step (concerted) or follows the generation of the intermediate radical anion (stepwise).

Introduction

Reaction mechanisms are important in any undergraduate chemistry course where kinetics is discussed. The topic is broached in the introductory course, and in the sophomore year students learn to move electrons around rings to justify common reactions. In physical chemistry courses, we explain mechanisms in terms of free energy curves and driving forces. Synthetic laboratories provide practical, hands-on experience as students measure product distributions obtained from any number of oxidations, reductions, condensations, alkylations, halogenations, eliminations, and similar reactions that have been thoroughly studied in class. Determining an unknown mechanism is not a common subject for undergraduate laboratories. Real-time monitoring of products or intermediates can take place using IR or NMR spectroscopy, but data from such instruments generally convey information regarding reaction products without giving much transition-state information. UV–vis methods are easy, but give few specific details. Chemiluminescence, though spectacular, is not widely applicable.

Cyclic voltammetry, in contrast, is specifically designed to probe the electron-transfer (ET) event, which makes the technique applicable to a wide range of organic/inorganic/organometallic compounds. Many examples suitable for the undergraduate laboratory have appeared [1]. In a companion publication, we have outlined mechanistic analysis of ring-substituted acetophenones as a junior/senior level experiment [2]. In this experiment, suitable for upper-level students, fundamental mechanistic and thermodynamic information is sought. Data that can be obtained to allow, for some or all species examined, estimation of intrinsic barrier height ($\Delta G^{o,\neq}$), activation free energy ($\Delta G^{\neq}$), bond dissociation energy (BDE), the dissociation rate constant (k), and the electrochemical transfer coefficient (α), all useful parameters for describing an electron transfer (ET) process.

Theory

In this exercise, students will generate the radical anion of an organic compound and investigate its fate electrochemically. Our model reaction will be an EC (electron-transfer followed by a chemical reaction) process commonly observed in organic compounds. Addition of an electron to the LUMO of an organic compound is followed by loss of some moiety from the molecule. Two possible mechanisms, given below, occur as a direct result of electrochemical reduction:

Stepwise Decomposition:

$$\text{(I)}\ AB + e^- \underset{}{\overset{k_s}{\rightleftharpoons}} AB^{\cdot -} \qquad \text{(II)}\ AB^{\cdot -} \overset{k}{\rightleftharpoons} A\bullet + B^-$$

Concerted Decomposition:

$$\text{(III)}\ AB + e \overset{k_s,k}{\rightleftharpoons} A\bullet + B^-$$

The theory for this experiment is well developed [3]. The choice between concerted and stepwise pathways depends on the relative energies of the radical anion and the dissociated fragments. If the radical anion is of sufficiently low energy, it will form as a result of ET from an electrode. If the radical anion is too unstable, then it is energetically favorable for the compound to undergo concerted (or dissociative) electron transfer.

The electrochemical transfer coefficient, α, which reflects the dependence of the free energy of activation on the driving force ($\partial\Delta G^{\neq}/\partial\Delta G^{o}$), can be derived from the variation in peak potential (E_p) or peak width ($E_{p/2} - E_p$) with scan rate. For the mechanisms that we wish to study here, electron-transfer followed by an irreversible chemical reaction (EC_i), values of α greater than 0.5 indicate bond breaking as the rate-determining step, which means that α is not a true transfer coefficient (α_{app}). When α is less than 0.5, the rate-determining step is ET, and α is a true transfer coefficient. This rate-determining ET step may be the initial ET of the stepwise path

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Table 1. Diagnostic Criteria Related to Stepwise Electron-Transfers

Scenario			
A	k rate determining	$\partial E_p/\partial \log \nu \approx 29$ mV	$E_{p/2} - E_p \approx 47$ mV
B	$k \approx k_s$	$\partial E_p/\partial \log \nu \approx 29/\alpha$ mV	$E_{p/2} - E_p \approx 47/\alpha$ mV
C	k_s rate determining	$\partial E_p/\partial \log \nu >> 29$ mV	$E_{p/2} - E_p > 94$ mV

or the dissociative ET of the concerted path. Values distinctly below 0.5 throughout the range of investigated scan rates indicate a concerted mechanism where the kinetics are of a single step possessing inner-sphere character; the rate-determining step is a combination of bond breaking, solvent reorganization, and internal reorganization. An α less than 0.5 indicates that E_p lies at potentials significantly more negative than E^o, requiring a large driving force that makes the intrinsic barrier height, $\Delta G^{o,\neq}$ larger than for cases where α is less than 0.5. As the intrinsic barrier height rises, more energy must be added to the system to produce radical anion formation. Thus, we expect peak potentials to shift cathodically as a function of scan rate ν ($\alpha = \partial E_p/\partial \log \nu$) if the rate-determining step is an electron transfer. Complicating the picture is the competition between the rates of electron transfer and bond dissociation. For a complete theoretical treatment, one is referred to some useful sources [4]; however, the effect of k and k_s in stepwise or concerted ET reactions can be divided into three general categories. The relevant criteria for those categories are summarized in Table 1 for α equals 0.5.

For the student, the goal of the experiment is to (a) perform cyclic voltammetric measurements at various scan rates, in various solvents, and at various electrode surfaces; (b) use potential data to calculate α values; (c) determine if the mechanistic pathway is concerted or stepwise; (d) use digital simulation or some other method to extract reasonable estimates for E^o and k, the cleavage rate constant; (e) calculate the values of the intrinsic barrier height and activation energy for compounds displaying concerted pathways (Scheme I); as well as (f) determine bond dissociation energies; and (g) if possible, relate this information to structural criteria.

Materials

The compounds used in this experiment consist of ring-substituted (and/or alpha-substituted) acetophenones, aryl halides, and aromatic alkyl halides. Acetophenones assigned include 4′-trifluoromethyl- (4′-CF_3AcPh), 4′-fluoro- (4′-FacPh), 4′-chloro- (4′-ClAcPh), 4′-bromo- (4′-BrAcPh), 4′-iodo- (4′-IacPh), 4′-thiomethyl- (4′-SmeAcPh), 4′-methyl- (4′-MeAcPh), and 4′-methoxy- (4′-OMeAcPh) derivatives. Also assigned are 9-(chloromethyl)anthracene (9-ClMeAn), 9,10-bis(chloromethyl)anthracene (9,10-ClMeAn), 9,10-dibromoanthracene (9,10-dBrAn); 2-bromoacetophenone (2-BrAcPh), 2-fluoroacetanilide (2-FAcN), and 3′-trifluoromethylacetanilide (3′-CF_3AcN). All are commercially available at reasonable cost from a number of sources.

The main criterion for selecting compounds is a nonreversible radical anion formation. As this is very common for organic compounds, many low-cost possibilities exist.

Only the first reduction is of consequence (the EC process) for compounds that possess more than one. This makes data acquisition faster and easier than if one were performing a scan-rate dependence study for mechanistic determination. Student pairs are assigned one of each type of compound (concerted and stepwise pathway). Data can be pooled after acquisition so students can calculate α values for all the compounds.

Data acquisition consists of scanning inside a 3-V reductive window in dry DMF (N, N′-dimethylformamide)/0.1 M $TBAPF_6$ (tetra-*N*-butylammonium hexafluorophosphate) solution. *N,N*- Dimethylformamide (99+%) is stored over activated molecular sieves before use. Acetonitrile or tetrahydrofuran may be used, though significantly different α behavior may be observed. Tetra-*N*-butylammonium hexafluorophosphate was purchased from Aldrich, stored over desiccant, and used without further purification.

For good α values, the range of scan rates examined should be as wide as possible. Scanning at spaced intervals between an upper limit of 50 to 300 V s^{-1} and a lower limit of 0.100 V s^{-1} gives coverage adequate for meaningful data. For ν less than 3 to 5 V s^{-1}, a disk of Au (A = 0.0305 cm^2), glassy carbon (A = 0.109 cm^2), Pt (A = 0.0307 cm^2), or Pd (A = 0.0977 cm^2) represents the order of desirability in terms of surface effects and useful potential range. For scan rates, ν, greater than 3 to 5 V s^{-1}, microelectrodes are used to avoid unacceptably large ohmic drop. The experimental manifestations of this are severe cathodic shifts in E_p and a loss of the characteristic *i-E* waveshape. This must be minimized if changes in α values are to be due to ET kinetics and not an experimental artifact (Figure 2). In nonaqueous solvents, some uncompensated resistance (R_u) is unavoidable; in DMF or MeCN, the value will routinely lie between 0 and 50 Ω.

Our instrumentation (BioAnalyticalSystems 100 B Workstation), allows for IR drop to be measured and compensated for either manually or automatically via positive feedback circuitry. For scan rates less than 5 V s^{-1}, automatic 100% compensation is chosen with the default overshoot value of 10%. For best results, we test IR at two points in the experiment, just before the first scan for ν less than 1 V s^{-1} and again for ν greater than or equal to 1 V s^{-1}. For microelectrode usage, IR compensation is set manually at the maximum value, 65 kΩ.

A typical experiment combines 15 to 20 mg of solid or 20 μL of liquid with 5 mL of degassed DMF/$TBAPF_6$ solution (approx. 0.02 M). Auxiliary electrodes were Pt coils or Pt wire; all reported potentials were referenced to the Ag/Ag^+ electrode (+0.197 V vs. NHE). A full data set can be acquired in 30 min, with about 5 min necessary to replace the cells for the next group and degas a new solution. Data can be stored for later analysis or printed to hardcopy. Important data gleaned from *i* versus *E* curves are $E_{p,c}$ and, $E_{p,a}$ (cathodic and anodic peak potential, if present, respectively), $E_{p/2}$ (cathodic half-height potential), $i_{p,c}$ and $i_{p,a}$(cathodic and anodic peak current, respectively), $i_{p,bkg}$ (background current), and E_{sw} (switching potential).

Data Treatment

Each species is reduced at a chosen electrode and *i* and *E* data tabulated. The reduction corresponding to radical anion formation is irreversible in some compounds at all scan rates while in others some reversibility appears at the faster rates. Examples are given as supplementary material for 0.0244M 4′-MeAcPh and 0.0244 M 4'-FAcPh. The data recorded for each compound will vary according to the features observed.

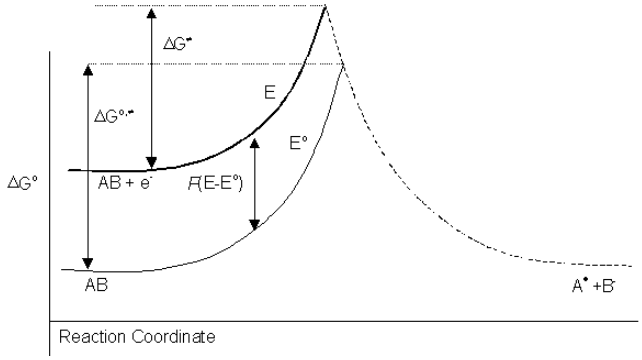

Figure 1. Simplified diagram showing a standard free-energy relationship between reactants at zero driving force (—), reactants under driving force (applied potential, *E*) (—), and products (·····).

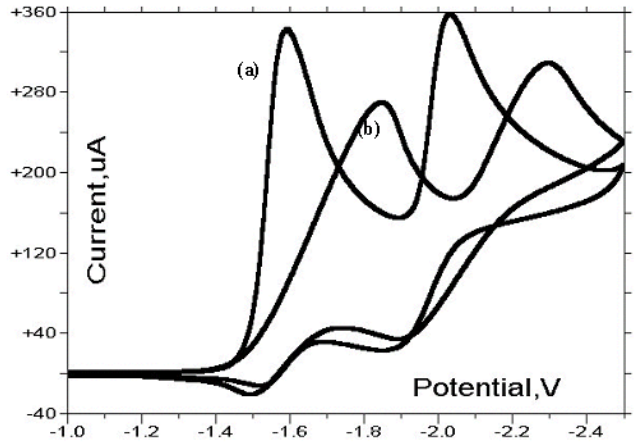

Figure 2. CV's of 4'-trifluoromethylacetophenone (dmf/0.1 M $TBAPF_6$) illustrating the impact on wave shape of IR compensated (a) versus no IR compensation (b). As results depend on accurate measure of peak width, some form of IR compensation is important.

These compounds are reduced electrochemically to form the radical anion with some heterogeneous rate constant, k_s, which is a function of E^o, the standard potential. This is followed by loss of a leaving group, an event characterized by a homogeneous rate constant, k. In order to determine which of these parameters are accessible, the students plot variations of E_p (V) and $E_{p/2} - E_p$ (mV) with log ν. Examples are shown in Figure 3.

Students then calculate values of the electrochemical transfer coefficient, α (or α_{app}), to examine its value as a function of scan rate. The transfer coefficient is sensitive to mechanism and can be used to differentiate concerted and stepwise EC pathways [5]. Calculation of α (or α_{app}) is according to eq 1 [6]. It is important to remember that the ET must be controlled by the kinetics of the electron-transfer step if α is to be true

$$\alpha\left(\text{or } \alpha_{app}\right) = \frac{1.857RT}{F\left(E_{p/2} - E_p\right)} \qquad (1)$$

and not just "apparent."

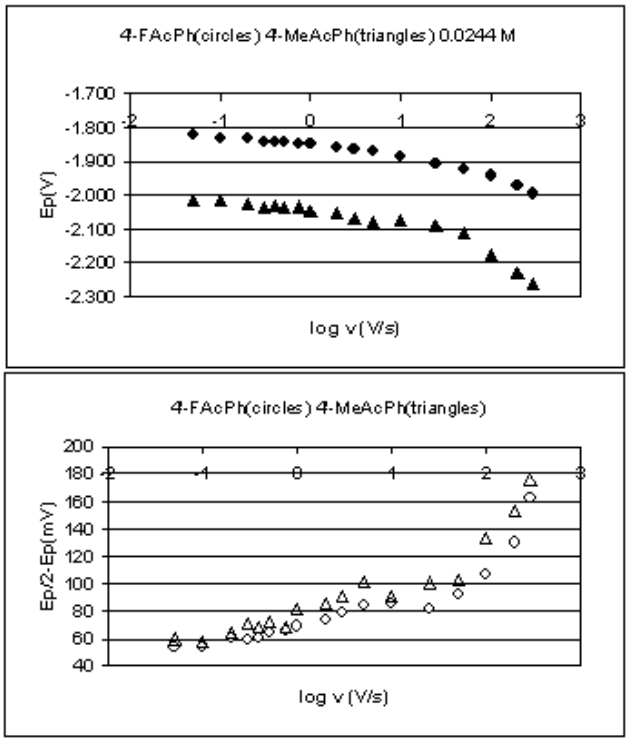

Figure 3. E_p and $E_{p/2}$-E_p vs. log ν plots for 4'-FAcPh and 4'-MeAcPh.

Plots of α (or α_{app}) versus log ν for each compound display how the transfer coefficients vary with scan rate (Figure 4). Each displays α (or α_{app}) greater than 0.5 over a significant range of scan rates. This implies a stepwise mechanism with the rate controlled by the cleavage reaction. At faster scan rates, the electrode reaction comes under mixed kinetic control with the 0.5 threshold being crossed at approximately 50 V s^{-1}.

For these compounds, $\partial E_p/\partial \log \nu$ is close to 29 mV per 10-fold increase in scan rate, the theoretical value for an EC mechanism in which k (F^- cleavage, for example) is the rate-determining step. Table 2 displays all the compounds used in the experiment, their $\partial Ep/\partial \log \nu$ slopes, peak width variations (low – high ν), and 1.00 V s^{-1} α values. Equation 1 can be used to calculate the value of α (or α_{app}), even though the students at this point do not know whether their compounds exhibit stepwise or concerted mechanisms.

For compounds classified as scenario B, increasing scan rate forces the kinetics into scenario C, where electron transfer is rate determining. This is especially true for the acetophenone, for which k_s = 0.14 cm s^{-1}, a value students use throughout the series [5a]. For that reason, the rate-determining step for these compounds is undoubtedly a mixture of k and k_s with k dominating at low scan rates and k_s dominating at high scan rates, but with each component important at all scan rates.

Compounds exhibiting α (or α_{app}) less than 0.5 over the entire scan-rate range are kinetically controlled by the electron transfer, either through a stepwise or a concerted mechanism. This is true of most of the compounds at high scan rates (> ~10 V s^{-1}), because of the relative slowness of k_s. Even in compounds characterized by relatively high k, scan rates on the order of 100 V s^{-1} can push the mechanism into the scenario B range, serving as an excellent example of the time-dependent nature of the voltammetric experiment.

Table 2. Student-Obtained Data for Compounds Useful in This Experiment. All Potentials Are in mV. Classification Is According To Table 2. (AcPh = Acetophenone; AcN = Anthracene; Can = Acetanilide)

Compound	$\partial E_p/\partial \log \nu$ (mV)	$E_{p/2} - E_p$ (mV)	α (or α_{app})	Classification
4'-FAcPh	28	53 – 93	0.68	Stepwise, A
4'-OMeAcPh	33	66 – 102	0.66	Stepwise, A
AcPh	30	50 – 55	0.65	Stepwise, A
4'-CF_3AcPh	20	62 – 87	0.65	Stepwise, A
4'-MeAcPh	33	60 – 100	0.58	Stepwise, A
4'-BrAcPh	50	66 – 91	0.55	Stepwise, B
4'-ClAcPh	48	64 – 101	0.49	Stepwise, B
9-ClMeAn	75	89 – 101	0.45	concerted
9,10-dBrAn	33	63 – 139	0.45	Stepwise, A
2-FacN	45	127 – 152	0.34	concerted
3'-CF_3AcN	107	127 – 171	0.3	concerted
2-BrAcPh	74	138 – 230	0.24	concerted

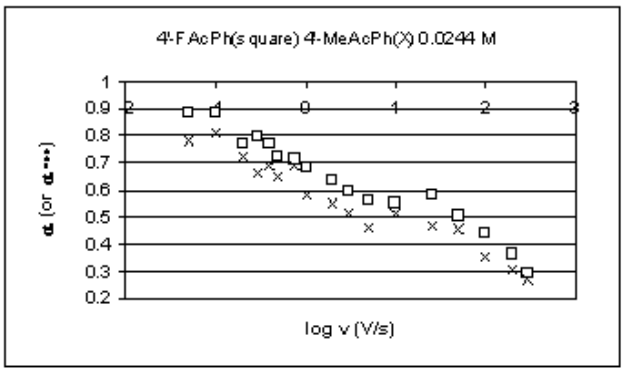

Figure 4. Variation of α with log ν for 4'-FAcPh and 4'-MeAcPh.

Digital Simulation of E^o

One of the most difficult parameters to estimate is the standard potential, E^o, related to the minimum energy necessary to cause a flow of charge across an interface. Kinetic contributions both in the formation of the transition state and in forcing charge across the interface result in an over potential (η), corresponding to the "extra" energy necessary to drive the system from a neutral species to a radical anion. This will affect wave shape and other important parameters. As E^o can be difficult to measure, its value can be estimated using digital cyclic voltammetric simulation software such as Digi-Sim 3.03 [7] or Polar 4.3 For Windows. Other parameters can be fitted as well, provided some reversibility exists at higher scan rates. Only CVs that fall in scenario A should be simulated, that is, when k is clearly the rate-determining step; if in a region of mixed kinetic control, values obtained will be less accurate. As a good value for k_s is known, it is possible to estimate both E^o and k.

Curve Fitting. If using the BAS program, a data file (translated from *.bin to *.txt format) can be imported into Digi-Sim 3.03 for fitting. Because the mechanism is known, electron transfer followed by a chemical reaction, the representation "A + e = B" <return> "B = C" should be entered under Mechanism. For 9,10-dBrAn, an ECECE mechanism is extant, requiring "A + e = B", "B = C", "C + e = D", "D = E", and "E + e = F" as the entered parameter. Now there are three E^o values, three k_s values, and two k values to fit. Students who draw this compound are often intimidated by its complex mechanism, but in reality it is one of the easiest to fit. A fit adequate for the level of this laboratory exercise appears in Figure 5.

In the CV Parameters dialog box are entered starting, switching, and ending potentials, as well as the area of the electrode, if known. If not, it can be crudely estimated from electrode diameter. Concentration should be noted by the student as well as the number of cycles, which is invariably 2.

Uncompensated resistance should, at least for scan rates less than 100 V s^{-1}, be in the 0 to 50 Ω range. After testing IR drop in the solution, 40 Ω was usually selected as a default. In the Chemical Parameters dialog box, heterogeneous reactions parameters E^o, α (known for the chosen scan rate), and k^o, as well as homogeneous reaction parameters K_{eq} and k_f must be entered. Concentration is known, and the diffusion coefficient can be assumed to be 1×10^{-5} cm^2 s^{-1} for the entire series. The value for the heterogeneous ET rate constant should be fixed at 0.14 cm s^{-1}. Values of –1 or 1 can be set for all other parameters as an initial value except α, the value of which was previously calculated for each scan rate. Runs for anthracene-based compounds have k_s values that are larger (0.5 to 3 cms^{-1}). A good hint is to fix k_s at a reasonable value and let the other values float. The difference between 0.5 and 3 is not large and guess values do not result in the larger errors that make fitting difficult. Later, once k, K, and E^o have been fit to within ca. 10%, those values can be deselected and k_s can be fit, though this usually results in only minor changes.

This having been accomplished, a selection of "Fitting" from the "Run" pull-down menu begins the process. Adequate fitting (±10 mV) usually takes four or five runs; E^o can be obtained in a few minutes. The simulation results are shown in Table 3 with values for reorganization energy, calculated as will be described later. From the literature [8], scan rates necessary to observe reversibility from systems displaying cleavage rate constants this fast were not available to us.

The maximum scan rate for our equipment, 300 V s^{-1}, allows determination of k less than 10^3 s^{-1}. Both the 4'-OMeAcPh and 4'-MeAcPh displayed reversibility at 50 V s^{-1}.

If digital simulation software is not available, it is possible to estimate k using the method of Nicholson and Shain [10]. For species showing reversible behavior at some scan rates, it can be estimated that $E^o \approx E_{1/2}$, where the half-wave potential is obtained by $(E_{p,c} + E_{p,a})/2$. The cleavage rate constant can then be extracted from eq 2 for a one-electron transfer at 25°C [9].

$$k = \left(e^{\frac{E_p - E_{1/2} + 0.0203}{0.026}} \right) \left(\frac{\upsilon F}{RT} \right) \qquad (2)$$

Using this method, values obtained agree with simulated values within 3 to 4%. For example, k for 4′-CF_3AcPh is calculated as 8.1 s^{-1} and simulated as 7.8 s^{-1}. In this experiment students were supplied with a good value of k_s, but if none is available and the CVs show some reversibility within the experimentally accessible range, a workable value of k_s can be estimated from peak separation, ΔE_p [11]. Additionally, estimation of k or E^o can be accomplished by extraction of two

Table 3. Standard Potentials, First-Order Cleavage Rate Constants, and Solvent Reorganization Energies for Compounds Exhibiting Stepwise ET

Compound	E^o (sim), 95.4% CI (V)	k (s^{-1})	λ^o (eV)
4'-SMeAcPh	–1.821 ± 0.001	4.1 ± 0.1	0.69
4'-FAcPh	–1.902 ± 0.003	6.6 ± 0.2	0.83
4'-CF_3AcPh	–1.525 ± 0.002	7.8 ± 0.8	0.81
AcPh	–1.885 ± 0.002	5.8 ± 0.4	0.86
4'-OMeAcPh	–2.082 ± 0.003	50 ± 6	0.95
4'-MeAcPh	–1.958 ± 0.002	54 ± 16	0.97
9,10-diBrAn	E_1^o = –1.389 ± 0.003	$k_1 > 3 \times 10^3$	0.68
	E_2^o = –1.583 ± 0.004	$k_2 > 3 \times 10^3$	
	E_3^o = –1.877 ± 0.003		
4'-ClAcPh	E_1^o = –1.781 ± 0.005	‡3×10^3	0.74
	E_2^o = –1.906 ± 0.004		
4'-BrAcPh	E_1^o = –1.761 ± 0.004	‡3.2×10^7	0.74
	E_2^o = –2.144 ± 0.011		
4'-IAcPh	E_1^o = –1.567 ± 0.010	‡1.9×10^8	0.68
	E_2^o = –1.912 ± 0.004		

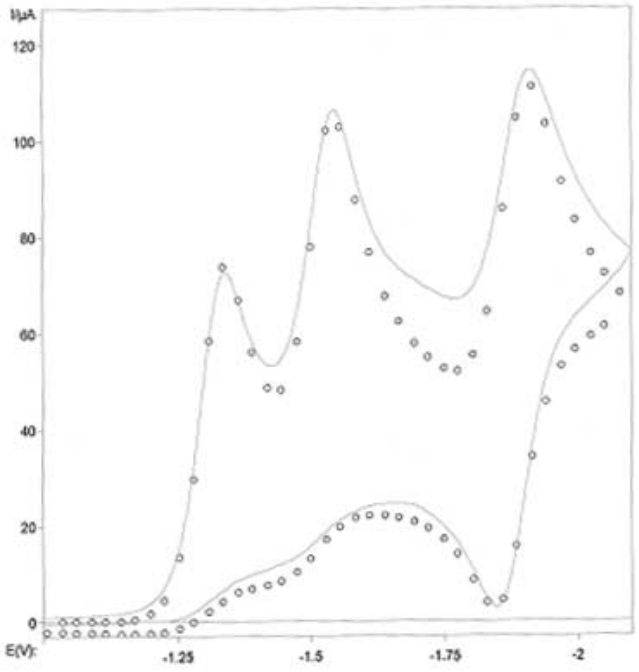

Figure 5. Full reduction of 9,10-dibromoanthracene (solid line) and simulated data (circles). Fitting was accomplished with electrode area = 0.0305.

kinetic parameters, C_1 and C_2, according to the method of Saveant, although the procedure is complex and explaining it is not enjoyable [5]. From these estimated E^o values, an estimate for the activation free energy for bond cleavage from the radical anion (in eV) may be obtained according to eq 3 [5].

$$\Delta G_c^o = BDE - E^o_{B\bullet/B^-} + E^o_{AB/AB\bullet^-} - T\Delta S \qquad (3)$$

Note that the bond dissociation energy (BDE) is for the unreduced species, which we approximate with tabulated bond dissociation energies for Ph-X or benzyl-X. The value of ΔS is estimated to be between 0.6 and 1 meV K^{-1} for one small molecule dissociating into two parts [12]. Using these values, ΔG^o_c for 4'-FAcPh equals 0.60 eV. Further work will be necessary to enhance this calculation.

Estimation of the BDE

For compounds decomposing in a concerted fashion, the difference between E_p and E^o is much greater than in the stepwise case, as in this case the transition state involves bond breaking (in our example, a C–F dissociation), and bond dissociation energy is the dominant contributor to the intrinsic barrier height, $\Delta G^{o\neq}$.

It is difficult to calculate E^o values for concerted mechanisms, some of which may be quite different than E_p values. For this reason, no attempt was made for these species although some values are available from the literature; for example 9-ClMeAn (E^o = –0.160 V vs. SCE [7]) and 2-BrAcPh (E^o = –1.19 V vs. SCE [5a]). We do not as a rule, however, require calculations based on these values.

For compounds exhibiting a concerted mechanism, bond-breaking is an intergral part of the transition state, and the bond dissociation energy is estimated through eqs 4 and 5 [13].

$$BDE = \frac{2}{3}\left(E^o_{B\bullet/B-} - E_p\right) + C \qquad (4)$$

where

$$C = 2\left(\frac{RT}{F}\ln\left[A\sqrt{\frac{RT}{\alpha F \upsilon D}}\right] - 0.78\frac{RT}{F}\right) - \frac{\lambda^o}{2} - T\Delta S \qquad (5)$$

which is not nearly as imposing as it appears (A is the pre-exponential factor, λ^o is the solvent reorganization energy, $E^o_{B\bullet/B-}$ is the standard reduction potential of the leaving group). As we assume little or no inner-sphere reorganization, an estimate of the solvent-reorganization energy is made from the size of the molecule according to $\lambda^o = 2.08/a$ (Å) with a, the hard-sphere equivalent radius, calculated from the radii of the various species present before and after dissociation (eq 6) [12].

$$a = \frac{a_X\left(2a_{RX} - a_X\right)}{a_{RX}} \qquad (6)$$

This gives good agreement with known values. For example, for 9-ClMeAn, λ_o = 0.734 eV (calc.) and 0.714 eV (lit. [14]. If the values of the static and optical dielectric constants are known, the reorganization energy may be calculated from eq 7 [15].

$$\lambda = e_o^2\left(\frac{1}{2a_{A\bullet,B-}} + \frac{1}{2a_{AB\bullet-}} - \frac{1}{d}\right)\left(\frac{1}{D_{op}}\frac{1}{D_s}\right) \qquad (7)$$

For DMF, D_{op} = 2.04 and D_s = 36.7; d is the distance between the centers of the two equivalent spheres. Use of eq 7 over eq 6 will give λ_o values that can be adapted for different solvents, and is thus probably somewhat more useful. Values of a are easily obtained from molecular volumes calculated in a few minutes on a PC via semiempirical (AM1) methods

Table 4. Estimated Parameters for Compounds Undergoing a Concerted Mechanism

Compound	a (Å)	Z (cm s^{-1})	λ^o (eV)	BDE (eV)	$\Delta G^{o,\neq}$(eV)	$\Delta G^{\neq}$ (eV)
2-FAcN	2.54	5074	0.82	3.72	1.14	0.40
2-BrAcPh	2.94	4451	0.71	2.28	0.75	0.43
9-ClMeAn	2.84	4227	0.73	2.66	0.85	0.40
9,10-ClMeAn	3.11	3785	0.67	2.34	0.77	0.39
3'-CF_3AcN	2.59	4406	0.80	3.50	1.08	0.42

using a computational chemistry program like PC Spartan Pro (Wavefunction, Inc.). These values were left over from energy calculations performed on these compounds for the companion publication [2]. The value of ΔS is as discussed previously [11]. The calculated value of C for 9'-chloromethylanthracene (298K) is 0.39 V. Using this value in eq 4, it remains for the student to lookup the oxidation potential for chloride, which is 1.79 V (F = 2.62 V; Br = 1.44 V; I = 0.99 V). Inserting experimental E_p values gives rise to a bond dissociation energy of 2.11 ± 0.03 eV (2.33 eV lit. [11]). This is somewhat less than one would expect for a benzyl-Cl bond (~2.94 eV), but BDE should be significantly lower in a radical anion.

At this point, it is possible to estimate the intrinsic barrier height, $\Delta G^{o,\neq}$ using eq 8 [5].

$$\Delta G^{o,\neq} = \frac{BDE + \lambda^o}{4} \qquad (8)$$

For 9-chloromethylanthracene, the value estimated at 0.82 eV (0.77 eV, lit. [11]).

Free energy of activation for the electrode reaction can be estimated from eq 9 [15].

$$\Delta G^{\neq} = \frac{RT}{F}\ln\left[Z\sqrt{\frac{RT}{\alpha F \upsilon D}}\right] - 0.78\frac{RT}{F} \qquad (9)$$

Z is the collision number at the electrode, which is calculated from $Z = (kT/2\pi m)^{1/2}$, where m is the mass of the reacting molecule and k is Boltzmann's constant in eV K^{-1} [16]. Z values typically fall between 3500 and 6000 cm s^{-1} for this series. The value of $\Delta G^{\neq}$ for 9-ClMeAn is estimated to be 0.40 ± 0.06 eV (0.33 eV, lit. [11]). Data obtained for compounds with concerted mechanisms is given in Table 4.

Conclusions

We have used this experiment several times with good results; students seem surprised that so much information is available from data obtained so quickly. That is indeed one of the main strengths of this exercise; for the investment of 20 to 30 minutes per student (or pair of students), hours of practical experience determining the nature of an electron transfer and its associated kinetic and thermodynamic parameters is obtained. It is best if each student is given two sets of data to analyze, one from each category. We typically use this experiment as part of a multiweek exercise that includes determination of the mechanism through computer modeling [2]. Data for that exercise is useful here as well. Another strength of the experiment is the fact that not all compounds are treatable by the same theory. For example, bond dissociation energies are available only for the concerted species, while standard potentials and cleavage rate constants are available only for stepwise compounds. It is useful because the technique itself is relatively simple, whereas the postlaboratory work-up, where there is sufficient time for reflection and computation, is somewhat involved. The compounds are inexpensive, of low toxicity, and are readily available, though there are literally hundreds of organic compounds that could be used because the EC mechanism is one of the most common. We find it to be an excellent upper-level laboratory in physical chemistry, an electrochemistry course, or instrumental analysis, though for the latter some of the rigor in follow-up calculations is relaxed. The equipment used does not have to be expensive; all that is necessary is an appropriate attention to IR compensation. Students are encouraged to relate their findings to physical organic or structural concepts. For example, one might ask students to postulate (a) why the ring-bound halides tend to decompose via stepwise mechanisms while the α-halides are more often concerted, (b) why cleavage rate constants rise going from 4'-FAcPh to 4'-IAcPh, (c) why the k_s value for acetophenone(s) is so slow, (d) why values of λ^o seem to decline as the molecule gets larger, (e) why calculated BDE values are lower than those found in neutral molecules, and (f) what is the effect of standard potential on mechanism. Correlations can be found between standard potentials, k, and free energies. Certainly the instructor can make the exercise as detailed as he or she wishes to the limit of the expertise of the student audience. Variations can include comparisons within a mechanism type, that is, to compare LUMO energies, bond strengths, and standard potential influence within compounds exhibiting a concerted mechanism or one can examine the transition between concerted to stepwise mechanism as a function of the driving force that has been observed for some similar species [17].

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Suporting Materials. One supporting file is available. Sample student-derived data tables (http://dx.doi.org/10.1007/s00897020544b).

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