Activation/Driving Force Relationships for Cyclopropylcarbinyl → Homoallyl-Type Rearrangements of Radical Anions

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By using direct and indirect electrochemical methods, rate constants (k_o) for cyclopropane ring opening of radical anions derived from the one-electron reduction of *trans*-1-benzoyl-2-phenylcyclopropane, *trans*-1-benzoyl-2-vinylcyclopropane, 2-methylenecyclopropyl phenyl ketone, spiro[anthracene-9,1′-cyclopropan-10-one], 3-cyclopropylcyclohex-2-en-1-one, and 3-(1-methylcyclopropyl)cyclohex-2-en-1-one were determined. Qualitatively, rate constants for ring opening of these (and other cyclopropyl- and cyclobutyl-containing radical anions) can be rationalized on the basis of the thermodynamic stability of the radical anion, the ability of substituents on the cyclopropyl group to stabilize the radical portion of the distonic radical anion, and the stability of the enolate portion of the distonic radical anion. On the basis of this notion, a thermochemical cycle for estimating $\Delta G°$ for ring opening was presented. For simple cyclopropyl-containg ketyl anions, a reasonable correlation between $\log(k_o)$ and $\Delta G°$ was found, and stepwise dissociative electron transfer theory was applied to rationalize the results. Activation energies calculated with density functional theory (UB3LYP/6-31+G*) correlate reasonably well with measured $\log(k_o)$. The derived $\log(k_o)$ and $\Delta G°$ and $\log(k_o)$ vs E_a plots provide the basis for a "calibration curve" to predict rate constants for ring opening of radical anions derived from carbonyl compounds, in general.

Introduction

Over the past thirty years, radical ions have emerged as an important class of reactive species. Recognition of their role as potential intermediates in numerous organic and bioorganic reactions and the development of several new synthetic methods based upon their chemistry have led to an increased interest in these species and the general issue of single electron transfer (SET). Our work is concerned with the chemistry of radical ions, specifically unimolecular rearrangements, which may prove useful from a mechanistic perspective (i.e., as mechanistic "probes" or as radical ion clock reactions) or may be exploited in organic synthesis.

The mechanistic probe approach is essentially an *intramolecular* trapping experiment. A structural feature (e.g., a cyclopropyl group) is incorporated into the substrate, which will lead to a rearrangement uniquely ascribed to a radical or radical ion intermediate. Historically, the use of a cyclopropyl group is predicated on the expectation that the rearrangement reaction will be driven by the relief of ring strain. The prototypical example of such a process, the cyclopropylcarbinyl → homoallyl radical rearrangement (eq 1, R = R′ = X = H) is fast ($k \approx 10^8$ s^{-1}) and essentially irreversible.[1−8]

(1)

The probe approach is founded on two critical assumptions: (1) structurally rearranged products arise exclusively from the SET pathway and (2) the rearrangement is rapid and (preferably) irreversible. The kinetics (and mechanism) of numerous unimolecular rearrangements of *neutral* free radicals have been extensively studied, although, until recently, very little was actually known regarding the analogous rearrangements of radical ions. Frequently, researchers assume that the structural features leading to facile rearrangement of neutral free radicals will do the same for radical ions.

The goal of our work has been to examine the kinetics associated with the ring opening of radical anions derived from cyclopropyl and cyclobutyl ketones. In direct analogy to the cyclopropyl- and cyclobutylcarbinyl neutral free radicals,[1−19] these radical ions undergo unimolecular rearrangement as depicted in eq 1 (X = O^-).[20−26] We have learned that in terms of substituent effects, both systems behave similarly: (1) radical-stabilizing groups at the α-carbon (R) decelerate the ring opening process and (2) radical stabilizing substituents (e.g., alkyl, phenyl, vinyl) on the cyclopropyl group (R′) accelerate the reaction. For both types of processes, relief of cyclopropyl ring strain is not the sole mitigating factor associated with the rates of these rearrangements. Resonance energy (spin delocalization) in the ring-closed vs ring-opened form must also be considered. Also, unlike neutral free radicals, charge delocalization is at least as important and perhaps more important than spin delocalization; charge stabilization is the major reason for the low reactivity and thermodynamic stability of the aromatic ketyls.[20]

While our understanding of radical anion rearrangements has increased, there is still a lack of fundamental kinetic data to establish the nature of activation/driving force relationships in these systems. All of the data which are available have been obtained electrochemically, wherein the radical anion is generated from the corresponding ketone. In this paper, we report

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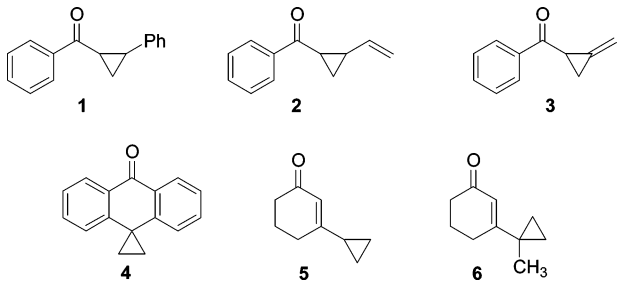
the results for the electrochemical reduction of cyclopropyl-containing ketones **1** → **6**.



Using classical electrochemical methods such as cyclic and linear sweep voltammetry (CV, LSV), and also the technique of homogeneous redox catalysis, reduction potentials for the ketones and rate constants for ring opening of the radical anions were obtained. Because some of these systems could be studied with complementary electrochemical techniques, it was possible to provide an unbiased assessment of the methods and assumptions used to obtain the pertinent kinetic and thermodynamic data.

These results, combined with previously published data from our laboratory, lead to a greater qualitative understanding of the factors which mitigate reactivity in these systems. More importantly, when analyzed in the context of an appropriate thermochemical cycle or coupled to results obtained from molecular orbital calculations, these results provide a general means of *predicting* rate constants for ring opening of cyclopropane- and cyclobutane-containing radical anions.

Experimental Section

Materials. *N*,*N*-Dimethylformamide (DMF, EM Science, 98%) was stirred over copper(II) sulfate (Aldrich, 98%) and activated alumina (Aldrich, neutral, Brockman activity 1) for >3 days and vacuum distilled immediately before use. Alumina was flame dried under vacuum (until evolution of water vapor ceased) prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was prepared by the method of House,[27] recrystallized 4× from ethyl acetate/hexane, and vacuum oven dried before use. *trans*-1-Benzoyl-2-phenylcyclopropane (**1**),[28] *trans*-1-benzoyl-2-vinylcyclopropane (**2**),[29] spiro[anthracene-9,1′-cyclopropan-10-one] (**4**),[30] 3-cyclopropylcyclohex-2-en-1-one (**5**),[31] and 3-(1-methylcyclopropyl)cyclohex-2-en-1-one (**8**) were prepared according to published procedures. 2-Methylenecyclopropyl phenyl ketone (**3**)[32] was obtained from Dr. Edward W. Thomas. All mediators used in this study except fluoranthene (Agros Organics, >98%) and anthracene (Matheson, Coleman & Bell, >98%) were obtained from Aldrich and used as received.

General. GC/MS was performed on a Hewlett-Packard HP 5890 gas chromatograph interfaced to a HP 5970 low-resolution mass spectrometer and a HP series computer. High-resolution mass spectral data were obtained from a VG Analytical model 7070 E-HF double-focusing magnetic sector high-resolution spectrometer, using electron impact (70 eV) ionization. GC analysis was performed on a Hewlett-Packard 5890A gas chromatograph equipped with an FID detector and an HP 3393A reporting integrator. Nuclear magnetic resonance spectra (^{1}H, ^{13}C) were obtained on either a Bruker WP 270 MHz, Bruker AM 360 MHz, or a Varian Unity 400 MHz FT NMR spectrometer. All chemical shifts are reported in δ units relative to TMS (δ = 0.00 ppm) in $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer model 1600 FT-IR spectrometer.

Electrochemistry. Electrochemical measurements were performed on an EG&G Princeton Applied Research (EG&G/PAR) model 273 potentiostat/galvanostat interfaced to an MS-DOS computer. The details of this system were described earlier.[23] Digital simulations of cyclic voltammograms were performed using Digisim 2.1 (Bioanalytical Systems Inc., 2701 Kent Ave. W. Lafayette, IN 47906). Products of bulk electrolysis are all known compounds; characterization was confirmed as needed and the spectroscopic data are available in the Supporting Information.

Molecular Orbital Calculations. MO calculations were performed with use of density functional theory as implemented through Spartan ′04 (Wavefunction Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612).

Description of Electrochemical Methods. The mechanism and kinetics of decay of radical anions generated from **1** → **6** were studied by using direct and indirect electrochemical techniques. Thorough descriptions of these techniques were provided in our earlier papers[21,26] and summarized in several related reviews.[33−38] Preparative-scale electrolyses were also performed to ascertain the nature of the products formed by the one-electron reduction of these substrates.

Briefly, with direct electrochemical techniques such as cyclic, derivative cyclic, and linear sweep voltammetry (CV, DCV, and LSV, respectively), the substrate (**A**, Scheme 1) is reduced at an electrode surface generating radical anion $\mathbf{A}^{\bullet-}$; k_S represents the heterogeneous rate constant for this step. This radical anion undergoes subsequent ring opening yielding $\mathbf{B}^{\bullet-}$ with rate constant k_o. Either of these steps may be rate-limiting, depending on the structure of the substrate. The mechanism depicted in Scheme 1 is the classic "EC" mechanism, where the E and C refer to the nature of the steps (electrochemical and chemical, respectively). For most of the systems studied, the radical portion of distonic radical anion produced is more easily reduced than the starting ketone, and there is a second electron transfer: $\mathbf{B}^{\bullet-} + e^- \rightarrow \mathbf{B}^{2-}$ (i.e., an ECE mechanism).

SCHEME 1

$$A + e^- \rightleftharpoons A^{\bullet-} \qquad (k_s)$$

$$A^{\bullet-} \longrightarrow B^{\bullet-} \qquad (k_o)$$

Direct electrochemical techniques typically examine the effect of sweeprate and substrate concentration on the electrochemical response, e.g., the peak potential (E_p), or when the reduction is reversible, the ratio of the anodic and cathodic currents (i_{pa}/i_{pc}). For an ECE mechanism, E_p is related to k_o, sweeprate (ν), and the standard reduction potential of the substrate (E^o) according to eq 2.[34,39]

$$E_p = E^o - \frac{0.78RT}{F} + \frac{RT}{2F}\ln\left(\frac{k_o RT}{F\nu}\right) \qquad (2)$$

When the chemical step is rate-limiting, eq 2 is applicable, and it is possible to obtain information such as the formal reduction potential of the substrate, the rate law for the chemical step (usually first order in these systems), and the rate constant k_o. When heterogeneous electron transfer is rate-limiting, eq 2 no longer applies, though it is possible to measure k_S and the electron-transfer coefficient α.

With indirect electrochemical techniques,[33,35−38] it is an electron-transfer mediator or catalyst (**M**) rather than the substrate that is reduced at the electrode surface. For this to occur, the mediator must be more easily reduced than the substrate, and the reduction must be reversible. Reduction of

the substrate occurs in solution (homogeneous) via electron transfer from the reduced form of the mediator ($\mathbf{M}^{\bullet-}$, Scheme 2).

SCHEME 2

$$\begin{aligned} M + e^- &\rightleftharpoons M^{\bullet-} \\ M^{\bullet-} + A &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^{\bullet-} + M \\ A^{\bullet-} &\xrightarrow{k_o} B^{\bullet-} \end{aligned}$$

Effects of substrate addition on the reversible electron transfer of the mediator are manifested experimentally by an increase in peak current and a loss of reversibility (if catalysis is occurring). Kinetic control may be governed by either the homogeneous electron-transfer step (k_1) or the chemical step (k_o, Scheme 2.) If the rate of the chemical step is faster than back electron transfer ($k_o > k_{-1}[\mathbf{M}]$,) then the electron-transfer step is rate-limiting, and k_1 can be determined. By measuring k_1 with several electron-transfer mediators, E^o for the substrate can be estimated either by assuming back electron transfer (k_{-1}) is diffusion controlled and using eq 3 or by using Marcus theory (vide infra).

$$K_1 = \frac{k_1}{k_{-1}} = \exp\left[\frac{F}{RT}(E^o_{A/A^{\bullet-}} - E^o_{M/M^{\bullet-}})\right] \qquad (3)$$

If the chemical step is slow relative to back electron transfer ($k_o < k_{-1}[\mathbf{M}]$), the chemical step is rate-limiting with the electron-transfer step as a rapid preequilibrium. Under these conditions the composite rate constant $k_o k_1/k_{-1}$ can be determined. Because $\log(K_1) = -F(E^o_{M/M^{\bullet-}} - E^o_{A/A^{\bullet-}})/(2.303RT)$, k_o can be extracted if the reduction potential of the substrate ($E^o_{A/A^{\bullet-}}$) is known. This technique is especially useful for systems where the kinetics are too rapid to study by direct electrochemical techniques or when the reduction potentials of the substrates fall outside the accessible potential window afforded by most solvent/electrolyte combinations.[33,35−38]

Estimates of Reduction Potentials with Marcus Theory. In accordance with Marcus theory, the relationship between k_1 (rate constant for homogeneous electron transfer between $\mathbf{M}^{\bullet-}$ and substrate **A** as depicted in Scheme 3) and the free energy of electron transfer ($\Delta G^o = F(E^o_{M/M^{\bullet-}} - E^o_{A/A^{\bullet-}})$) is described by eq 4.[40] For this analysis, k_d is the diffusion-controlled rate constant in DMF, $K_d = 0.16$ M^{-1}, and the frequency factor Z is taken to be 6×10^{11} s^{-1}. The parameters $E^o_{A/A^{\bullet-}}$ and the reorganization energy λ are obtained by fitting the observed rate constants for electron transfer (k_1) and reduction potential of the mediators ($E^o_{M/M^{\bullet-}}$) to eq 4 via nonlinear regression.[20,21]

SCHEME 3

$$M^{\bullet-} + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (M^{\bullet-}/A) \underset{k_{-el}}{\overset{k_{el}}{\rightleftharpoons}} (M/A^{\bullet-}) \xrightarrow{k_{-d}} A^{\bullet-} + M$$

$$\frac{1}{k_1} = \frac{1}{k_d} + \frac{1}{K_d Z \exp\left[\frac{-\lambda}{4RT}(1 + \Delta G^o/\lambda)^2\right]} + \frac{1}{k_d \exp(-\Delta G^o/RT)} \qquad (4)$$

Results

***trans*-1-Benzoyl-2-phenylcyclopropane (1).** Results for the direct electrochemical reduction of this compound have been reported previously.[24] The CV of this compound is characterized by an irreversible reduction wave at −2.300 V (100 mV/s sweeprate). The observed variation of peak potential (E_p) with sweeprate (ν) and substrate concentration (C) are consistent with an EC or ECE mechanism (i.e., decay of $\mathbf{1}^{\bullet-}$ was first order); product analysis reveals that this decay involves cyclopropane ring opening. Because the reduction was chemically irreversible, only rough estimates of the reduction potential of **1** and rate constant for ring opening of $\mathbf{1}^{\bullet-}$ are reported in this earlier study.[24]

In the present study, the reduction of **1** is examined by using the method of homogeneous redox catalysis with several electron-transfer mediators. The key experimental observable is the current ratio i_p/i_{pd}, where i_p and i_{pd} are the voltammetric peak currents of the mediator in the presence and absence of the substrate, respectively, at a particular value of γ (the ratio of the substrate to mediator concentrations, C^o_A/C^o_M). Specifically, the effect of sweeprate and substrate concentration on the current ratio i_p/i_{pd} are reported at constant $\gamma = 1$. The first step is to diagnose whether the rate-limiting step is homogeneous electron transfer (k_1) or the follow-up chemical step (k_o, Scheme 2). This is easily achieved because the current ratio is independent of substrate concentration if the chemical step is rate limiting and concentration dependent if electron transfer is rate limiting. By comparing plots of [i_p/i_{pd} vs $\log(1/\nu)$] and [i_p/i_{pd} vs $\log(C^o_M/\nu)$] obtained at different concentrations of substrate (γ constant), any concentration dependence is readily apparent. Once the rate-limiting step is ascertained, the pertinent rate constants are derived from the appropriate working curves. (Working curves and a complete description of the data analysis procedure were discussed in previous papers.[20,21])

For example, with use of perylene as a mediator, a plot of i_p/i_{pd} vs $\log(1/\nu)$ at three different substrate concentrations results in three discrete curves (Figure 1a), indicating that this mediated reduction is concentration dependent and thus suggesting electron transfer is the rate-limiting step. When the concentration is accounted for, e.g., a plot of i_p/i_{pd} vs $\log(C^o_M/\nu)$, the data converge into a single curve (Figure 1b) confirming that electron transfer is rate limiting. The rate constant for electron transfer (k_1) is obtained by fitting of the data in Figure 1 to the appropriate working curve as described previously.[20,21] The reduction potential of the substrate is estimated by using the reduction potential of the perylene and assuming $k_{-1} = 5 \times 10^9$ M^{-1} s^{-1}, the diffusion-controlled rate constant in DMF solvent.

However, other mediators (e.g., fluoranthene) exhibited mixed kinetic control, meaning that both electron transfer and the chemical step were partially rate limiting; neither a plot of i_p/i_{pd} vs $\log(1/\nu)$ nor vs $\log(C^o_M/\nu)$ converge to a single line (Figure 2). Under mixed kinetic control, a procedure (developed and described by Savéant)[41,42] involved treating the data in accordance with the working curves for electron-transfer control to derive an apparent rate constant for electron transfer (k_{app}).

A plot of $1/k_{app}$ vs substrate concentration (Figure 3) in accordance with eq 5 allows resolution of k_1 and k_o.[41,42]

$$\frac{1}{k_{app}} = \frac{1}{k_o} + 0.33\left(\frac{k_{-1}}{k_1 k_o}\right)C^o_M \qquad (5)$$

The results for all the mediators studied are summarized in Table 1. It is well worth noting that despite the differences in data treatment and assumptions, each of these mediators yields nearly identical values of E^o and k_o. Also, the estimated reduction potential for this compound agrees well with that obtained by reconciling the k_1 values in Table 1 to Marcus theory (eq 4, −2.478 V with $\lambda = 9$ kcal/mol).

***trans*-1-Benzoyl-2-vinylcyclopropane (2).** This compound was also studied previously with direct electrochemical meth-

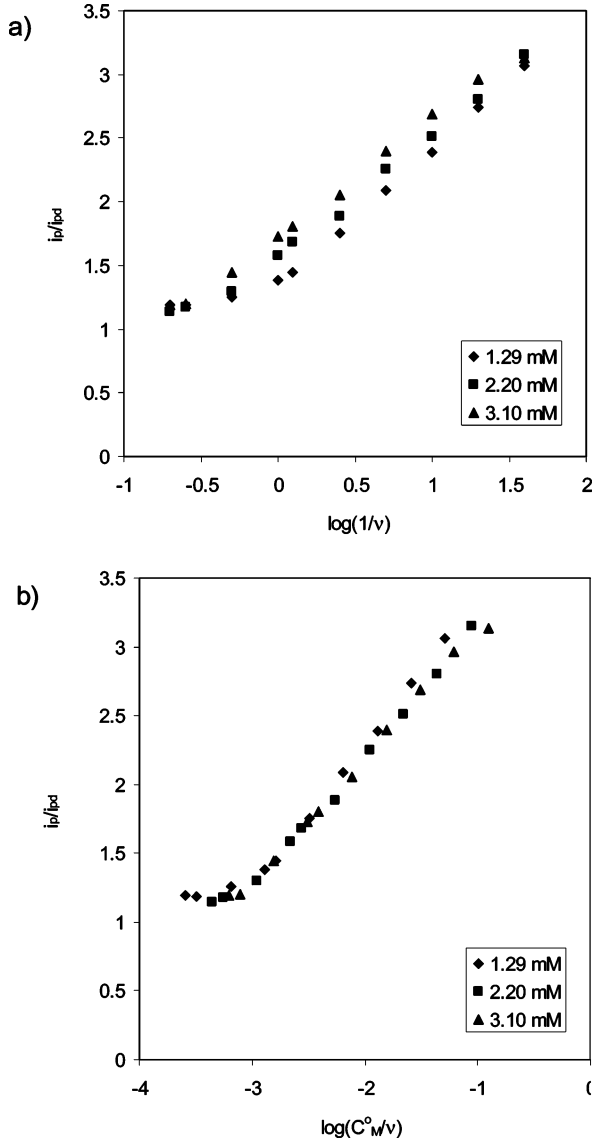


Figure 1. Mediated reduction of *trans*-1-benzoyl-2-phenylcyclopropane (**1**) by perylene (DMF, GCE, 0.5 M TBAP, $\nu = 0.025-5.0$ V s^{-1}, $\gamma = 1$).

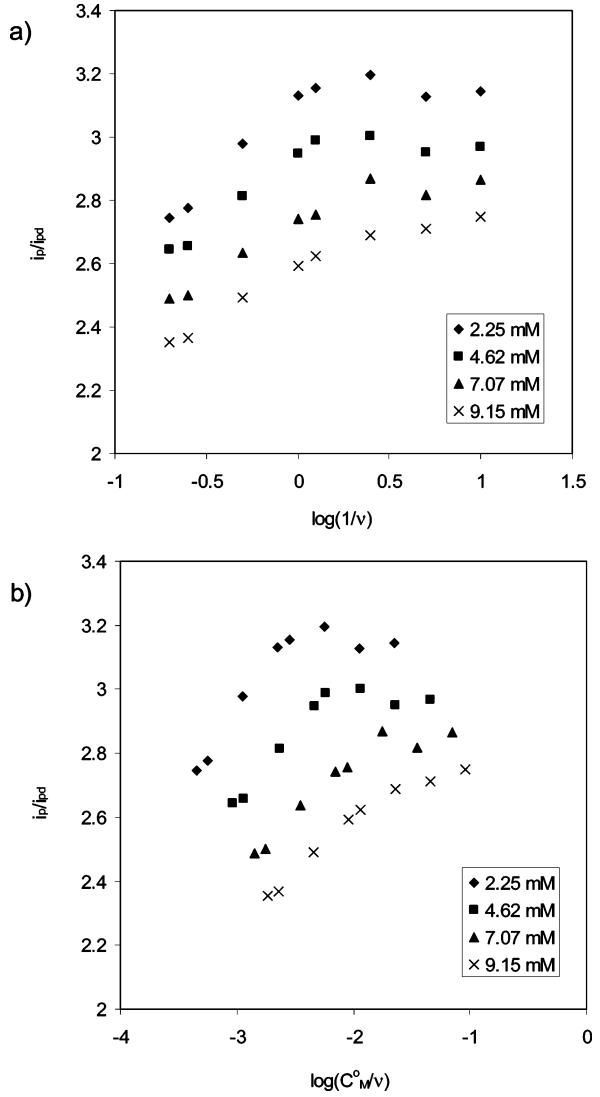


Figure 2. Mediated reduction of *trans*-1-benzoyl-2-phenylcyclopropane (**1**) by fluoranthene (DMF, GCE, 0.5 M TBAP, $\nu = 0.025-5.0$ V s^{-1}, $\gamma = 1$).

ods.[24] Its CV was characterized by an irreversible reduction wave at −2.200 V, with no reversibility observed at sweeprates up to 50 V/s. And like **1**, the observed variation of peak potential (Ep) with sweeprate (ν) and substrate concentration (C) were consistent with an EC or ECE mechanism. Product analyses indicated that the radical anion decays via cyclopropane ring opening. Again, only crude estimates of E^o and k_o were obtained previously.[24]

The mediated reduction of **2** is possible with phthalonitrile. Plots of i_p/i_{pd} vs $\log(1/\nu)$ and i_p/i_{pd} vs $\log(C^o_M/\nu)$ clearly indicate electron-transfer control for this system; fitting yields the rate constant for electron transfer $k_1 = 2.1 \times 10^3$ M^{-1} s^{-1} (a value nearly identical with that obtained for **1**, suggesting these two compounds likely have identical reduction potentials). Assuming back electron transfer to be diffusion-controlled ($k_{-1} = 5 \times 10^9$ M^{-1}s^{-1}), application of eq 3 yields E° = −2.400 V; application of eq 2 yields $k_o = 2.4 \times 10^5$ s^{-1}.

2-Methylenecyclopropyl Phenyl Ketone (3). The cyclic voltammogram of **3** was characterized by a peak at −2.24 V (100 mV/s); no oxidation wave was observed. A linear sweep voltammetry study of the effect of concentration and sweeprate on peak potential revealed $\partial Ep/\partial \log(\nu) = -34.9(\pm 1.6)$ mV/decade and $\partial Ep/\partial \log(C) = -0.4(\pm 1.5)$ mV/decade, consistent with either an EC or ECE mechanism for which the theoretical

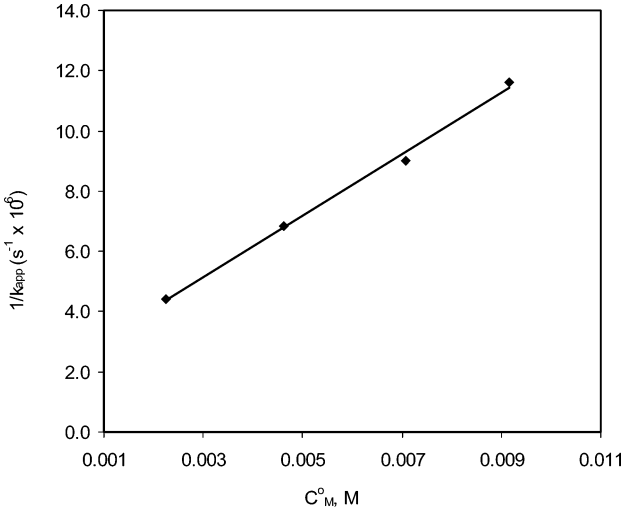


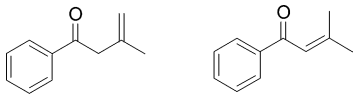
Figure 3. Plot of $1/k_{app}$ vs C^o_M for the mediated reduction of *trans*-1-benzoyl-2-phenylcyclopropane (**1**) by fluoranthene; k_{app} is the apparent rate constant obtained assuming electron transfer is the rate-limiting step.

TABLE 1. Results Obtained from the Mediated Reduction of *trans*-1-Benzoyl-2-phenylcyclopropane (1)

mediator	$E^o_{M/My\bullet-}$ [a]	kinetic ontrol[b]	k_1 (M^{-1} s^{-1})	$E^o_{A/A\bullet-}$ [a,c]	k_o (s^{-1})
phthalonitrile	−2.027	E	1.9×10^3	−2.405	2.3×10^6 [d]
perylene	−2.040	E	5.3×10^3	−2.390	1.1×10^6 [d]
fluoranthene	−2.150	M	3.3×10^5	−2.400	5.0×10^6 [e]
4-cyanopyridine	−2.168	M	5.0×10^5	−2.380	3.3×10^6
average				−2.400	3.0×10^6 [e]

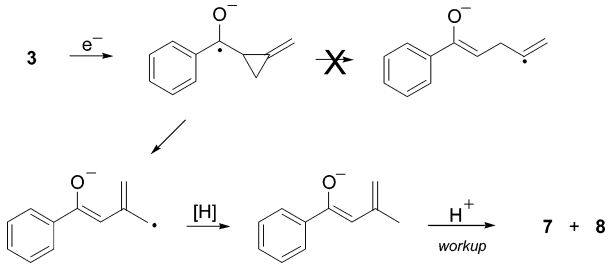
[a] Volts vs 0.1 M $AgNO_3$ (CH_3CN)/Ag. [b] E = electron transfer, C = chemical, M = mixed. [c] Equation 3, assuming k_{-1} is diffusion controlled. [d] Equation 2. [e] Equation 5.

response is $\partial Ep/\partial \log(\nu) = -30$ and $\partial Ep/\partial \log(C) = 0$ mV/decade, respectively. Constant current electrolysis of **3** resulted in the formation of two ring-opened products, **7** and **8**, formed in isolated yields of 49% and 18%, respectively, with a plausible mechanism presented in Scheme 4.



7 **8**

SCHEME 4



Only a limited quantity of **3** was available, consequently a mediated reduction was not attempted. However, because substituents on the cyclopropyl group do not appear to affect the reduction potential of phenylcyclopropyl ketones and making the reasonable assumption that E_o for **3** is around −2.42 V (the reduction potential of phenyl cyclopropyl ketone) yields, based upon eq 2, an estimated rate constant for ring opening of $\mathbf{3}^{\bullet-}$, $k_o = 1.7 \times 10^7$ s^{-1}.

Spiro[anthracene-9,1′-cyclopropane-10-one] (4). The cyclic voltammogram of **4** was characterized by a wave at −2.12 V (1 V/s), which became partly reversible at higher sweeprates (>10 V/s, Figure 4). A linear sweep voltammetry study of the effect of concentration and sweeprate on peak potential revealed $\partial Ep/\partial \log(\nu) = -30.5(\pm 3.5)$ mV/decade and $\partial Ep/\partial \log(C) = -0.3(\pm 0.5)$ mV/decade, consistent with either an EC or ECE mechanism. Constant current electrolysis, followed by quenching with CH_3I gave rise to cyclopropane ring-opened products **9** and **10** in 50% and 10% yield, respectively, with a plausible mechanism presented in Scheme 5.

Because the CV of **4** becomes partially reversible at higher sweeprates, it is possible to directly measure the rate constant for ring-opening of $\mathbf{4}^{\bullet-}$ by reconciling the ratio of the anodic/cathodic currents to working curves for an EC/ECE mechanism (which were generated via digital simulation). At room temperature, $k_o = 1.4 \times 10^2$ s^{-1}. When reconciled to eq 2, this rate constant and the LSV data yield $E^o = -2.094$ V for **4**.

The mediated reduction of **4** was studied with terephthalonitrile ($\gamma = 1.00$). Plots of i_p/i_{pd} vs $\log(1/\nu)$ and i_p/i_{pd} vs $\log(C^o_M/\nu)$ (Figure 5) indicated that the response is not concentration dependent and that the chemical step is rate limiting. Fitting of the results in Figure 5a to working curves yielded the rate constant ratio $k_{obs} = (k_1/k_{-1})k_o = 8.1 \times 10^3$ s^{-1}. Using the value of k_o obtained from direct CV measurements to determine k_1/k_{-1}, coupled with eq 3 provided another estimate of E^o for **4** of −2.052 V, consistent with the results obtained by LSV.

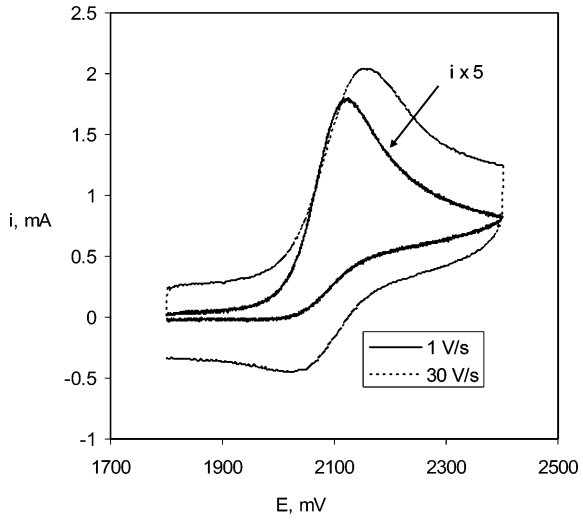
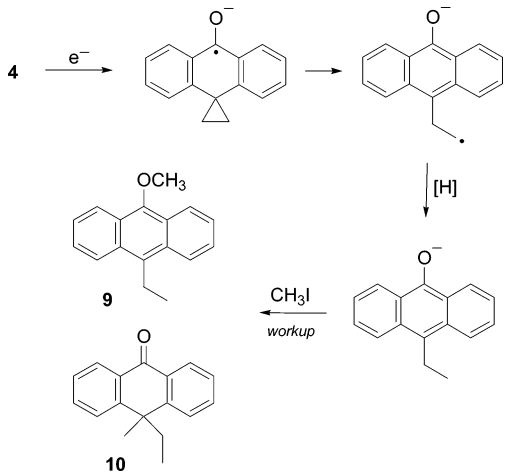


Figure 4. Cyclic voltammogram of spiro[anthracene-9,1′-cyclopropan-10-one] (**4**) at 1 and 30 V/s.

SCHEME 5



3-Cyclopropylcyclohex-2-en-1-one (5). The CV of **5** is characterized by an irreversible reduction wave at approximately −2.600 V (vs 0.1 M $AgNO_3$ (CH_3CN)/Ag at 100 mV/s). Preparative scale electrolysis of **5** gave exclusively ring-opened product (3-propylcyclohex-2-ene-1-one (**11**) in 44% yield and 57% unreacted starting material) after the transfer of 0.8 equiv of electrons; a plausible mechanism is depicted in Scheme 6.

A linear sweep voltammetry study of the effect of concentration and sweeprate on peak potential revealed $\partial Ep/\partial \log(\nu) = -31.5(\pm 4.8)$ mV/decade and $\partial Ep/\partial \log(C) = -1.9(\pm 4.3)$ mV/decade, consistent with either an EC or ECE mechanism. The mediated reduction of **5** was studied with several mediators including anthracene, 9-methylanthracene, dimethyl phthalate, dibutyl phthalate, pyrene, and ethyl 3-fluorobenzoate ($\gamma = 1.00$). For all these mediators, plots of i_p/i_{pd} vs $\log(1/\nu)$ and i_p/i_{pd} vs $\log(C^o_M/\nu)$ indicated the response to be concentration dependent indicating rate limiting electron transfer. Fitting of the results as described above yielded the results summarized in Table 2. For other mediators (methyl benzoate, ethyl benzoate**)** mixed

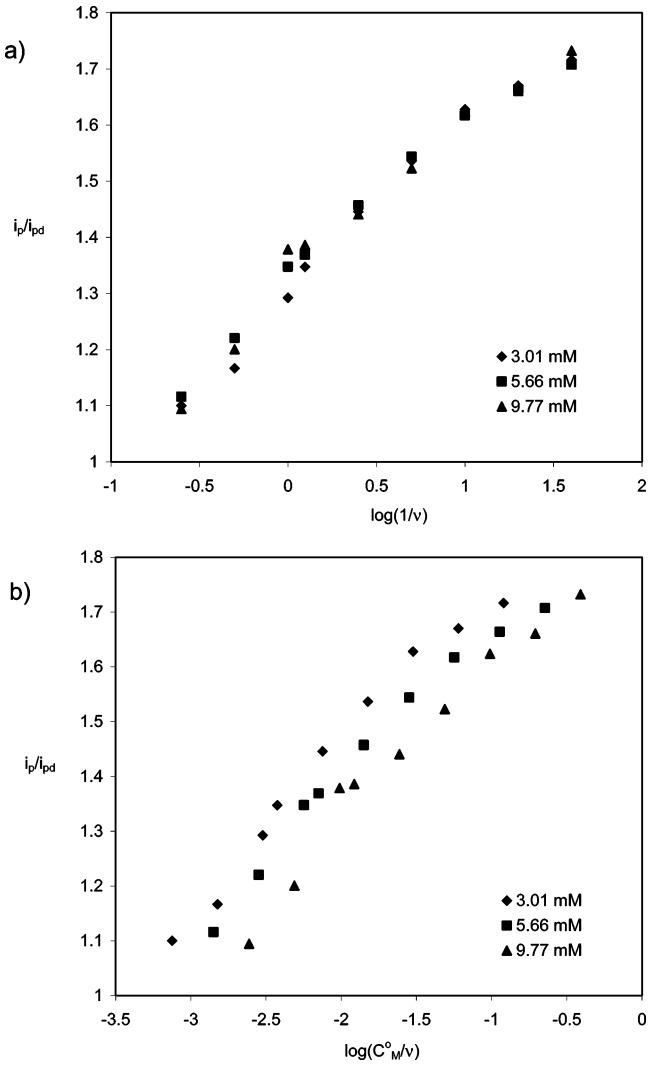
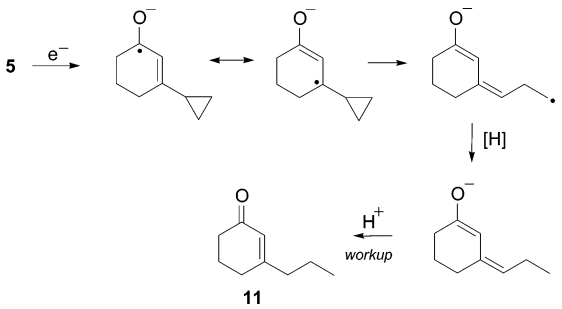


Figure 5. Mediated reduction of spiro[anthracene-9,1′-cyclopropan-10-one] (**4**) by terephthalonitrile (DMF, GCE, 0.5 M TBAP, ν = 0.025−5.0 V s^{-1}, γ = 1).

SCHEME 6



kinetic control was observed, and analysis in accord with eq 5 provided k_1 and k_o (Table 2). Finally, reconciling the k_1 values in Table 2 to Marcus theory (eq 4) yielded E^o, −2.867 V with λ = 10 kcal/mol.

3-(1-Methylcyclopropyl)cyclohex-2-en-1-one (6). The CV of **6** was characterized by a peak at −2.640 V (100 mV/s); no oxidation wave was observed. An LSV revealed $\partial Ep/\partial \log(\nu)$ = −32.8 mV/decade and $\partial Ep/\partial \log(C)$ = −1.9 mV/decade, which clearly supports a first-order (EC or ECE) mechanism. The mediated reduction of **6** was studied, and the results

TABLE 2. Results Obtained from the Mediated Reduction of 3-Cyclopropylcyclohex-2-ene-1-one

mediator	$E^o_{M/M-\bullet}$ [a]	kinetic control[b]	k_1 ($M^{-1}s^{-1}$)	$E^o_{A/A-\bullet}$ [a,c]	k_0 (s^{-1})[c]
anthracene	−2.337	E	680	−2.743	
9-methylanthracene	−2.359	E	1100	−2.753	
dimethyl phthalate	−2.342	E	66.7	−2.808	
dibutyl phthalate	−2.377	E	95.5	−2.833	
pyrene	−2.459	E	6048	−2.809	
ethyl 3-fluorobenzoate	−2.466	E	9844	−2.803	
methyl benzoate	−2.633	M	9.9×10^6	−2.793	1.67×10^6
ethyl benzoate	−2.644	M	3.9×10^6	−2.828	1.43×10^6
average				−2.796	1.55×10^6

[a] Volts vs 0.1 M $AgNO_3$ (CH_3CN)/Ag. [b] E = electron transfer, C = chemical, M = mixed. [c] Fitting of results to eq 5.

TABLE 3. Results Obtained from the Mediated Reduction of 3-(1-Methylcyclopropyl)cyclohex-2-ene-1-one (6)

mediator	$E^o_{M/M-\bullet}$ [a]	kinetic control[b]	k_1 ($M^{-1}s^{-1}$)	$E^o_{A/A-\bullet}$ [a,c]	k_0 (s^{-1})[c]
pyrene	−2.459	E	1.1×10^3	−2.853	
ethyl 3-fluorobenzoate	−2.466	E	1.4×10^3	−2.853	
isoquinoline	−2.580	E	2.8×10^5	−2.832	
methyl benzoate	−2.633	E	2.8×10^5	−2.885	
ethyl benzoate	−2.644	E	3.8×10^5	−2.887	
benzonitrile	−2.688	M	7.3×10^5	−2.915	2.5×10^6
average				−2.872	

[a] Volts vs 0.1 M $AgNO_3$ (CH_3CN)/Ag. [b] E = electron transfer, C = chemical, M = mixed. [c] Fitting of results to eq 5.

summarized in Table 3. Reconciling the k_1 values in Table 3 to Marcus theory (eq 4) yielded E^o, −2.915 V with λ = 12 kcal/mol.

Discussion

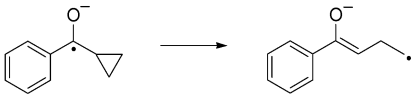
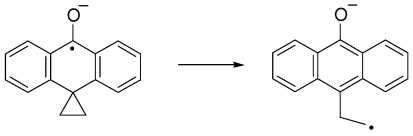
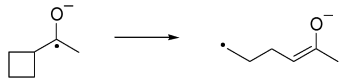
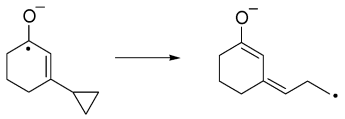
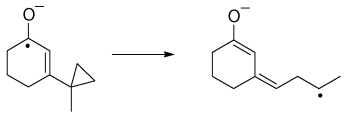
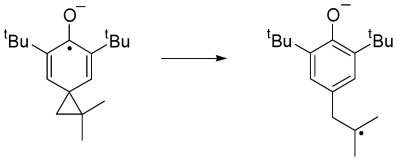
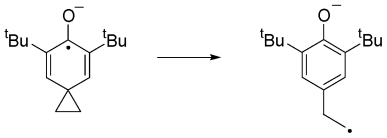
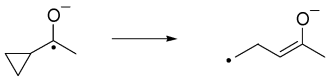
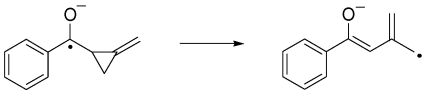
Rate constants for ring opening of cyclopropyl- and cyclobutyl-containing radical anions derived from several classes of carbonyl compounds are summarized in Table 4. Based upon these and other published results from our laboratory, several generalizations can now be made regarding the interplay between structure and reactivity in these systems.

Rate constants for ring opening of radical anions generated from various classes of carbonyl compounds increase in the order depicted in Figure 6; radical stabilizing substituents on the cyclopropyl group (R) also affect the rate: Ph ≥ vinyl > aliphatic > H. This reactivity order is likely the result of the interplay between charge and spin delocalization in the ring-closed and ring-opened (distonic) radical anions.

A thermodynamic cycle can be constructed which, qualitatively at least, identifies three mitigating factors for this reactivity order (Scheme 7): (1) the thermodynamic stability of the radical anion (as reflected by the reduction potential of the carbonyl compound), (2) the strength of the C−C bond of the cyclopropane (which is a measure of the ability of R to stabilize the radical portion of the distonic radical anion), and (3) the stability of the enolate portion of the distonic radical anion, reflected by the oxidation potential of the corresponding enolate. Unfortunately this thermochemical analysis cannot be made quantitative because key thermodynamic values are not available: All of the C−C bond strengths are unknown, and true (thermodynamic) oxidation potentials of most enolates are not available because the oxidations are not electrochemically reversible.

Instead a related thermochemical cycle is presented in Scheme 8. Based upon this thermochemical cycle, the estimates of ΔG^o

TABLE 4. Kinetic and Thermodynamic Data for Rearrangement of Cyclopropyl- and Cyclobutyl-Containing Radical Anions Derived from Carbonyl Compounds in DMF

entry	system	E^{o} [a]	k_o (s^{-1})	ΔG^{o} [b]	E_a [c]
1		-2.42[d,f]	< 10^{d}	6.0	17
2		-2.12[e,f,g]	1.4 x 10^{2} [e]	3.0	12
3		-3.22[i,h]	2.5 x 10^{4} [i]	-5.8	7.5
4		-2.40[e,g]	2.4 x 10^{5} [e]	-4.7	5.4
5		-2.80[e,g,h]	1.6 x 10^{6} [e]	-7.6	8.1
6		-2.87[e,g,h]	2.5 x 10^{6} [e]	-8.8	8.5
7		-2.44[e,g,h]	3.0 x 10^{6} [e]	-3.4	4.7
8		-2.60[i,h]	>10^{7} [j]	-18	1.6
9		-2.56[i,h]	>10^{7} [j]	-15	2.8
10		-3.22[i,h]	>10^{7} [i]	-4.9	3.4
11		-2.42[k]	1.7 x 10^{7} [e]	-21	8.1

[a] Volts vs 0.1 M $AgNO_3$ (CH_3CN)/Ag. [b] kcal/mol. [c] UB3LYP/6-31+G* calculated in kcal/mol. [d] References 22 and 23. [e] This work. [f] Directly measured from reversible CV. [g] Obtained from eq 3 assuming k_{-1} is diffusion controlled. [h] Obtained via Marcus theory (fitting of eq 4). [i] References 20 and 26. [j] References 21 and 25. [k] Assumed.

in Table 4 are derived from eq 6, where $E^{o}_{A/A\bullet-}$ represents the reduction potential of the ketone, ΔG^{o}_{H} is the energy of hydrogenation of the cyclopropane, BDE(C−H) is the strength of the C−H bond, and the pK_a is that of the corresponding ketone. The value of −36.2 kcal/mol accounts for the reactions needed to complete the thermochemical cycle, i.e., the redox

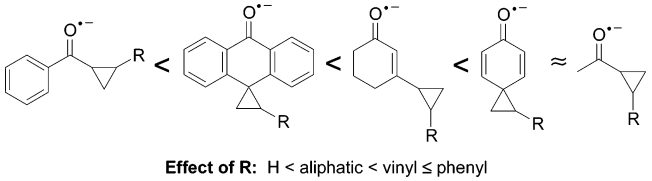
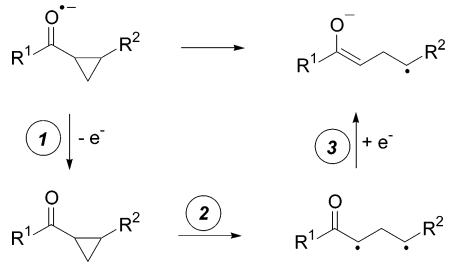
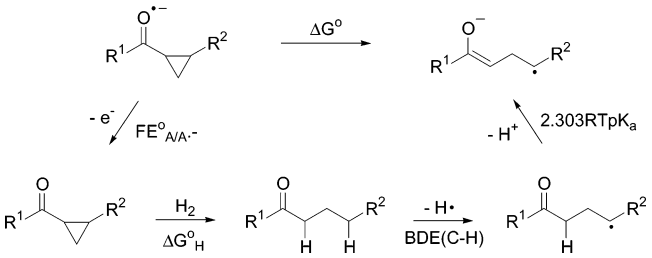


Figure 6. Effect of structure on the rate of ring opening of cyclopropyl-containing radical anions derived from carbonyl compounds.

SCHEME 7



SCHEME 8



potential of the $H^+/H^\bullet$ couple in DMSO ($H^+ + e^- \rightarrow H^\bullet$),[43] which is assumed to be the same in DMF, and the strength of the H_2 bond ($H_2 \rightarrow 2\ H^\bullet$).

$$\Delta G^{o} = FE^{o}_{A/A^{\bullet -}} + \Delta G^{o}_{H} + \mathrm{BDE(C{-}H)} + 2.303RT\mathrm{p}K_a - 36.2\ \mathrm{kcal/mol} \quad (6)$$

The key thermodynamic values needed for application of eq 6 are experimentally available ($E^{o}_{A/A^{\bullet -}}$, Table 4), or they can either be estimated with a reasonable degree of certainty (pK_a, BDE(C−H)) or calculated with density functional theory (ΔG^{o}_{H}). The advantage of this approach to ΔG^{o} is that solution-phase measurements are used for the charged species, and it avoids the need to use MO theory to calculate thermodynamic quantities for either charged or odd-electron species. (The Supporting Information provides values of pK_a and BDE(C−H) for the model compounds which were used in this analysis.) It should be noted that this treatment assumes that the radical and enolate portions of the distonic radical anion do not interact, that entropy contributions to ΔG^{o} are small and/or cancel out in this thermochemical cycle, and that bond strengths are the same in the gas phase and in solution.

With these caveats, a plot of log(k_o) vs ΔG^{o} for ring opening of these radical anions (excluding data for the radicals anions of cyclobutyl methyl ketone and 2-methylenecyclopropyl phenyl ketone (**3**) for reasons discussed below) is presented in Figure 7. Although much of the kinetic and thermodynamic data are approximate, a reasonable correlation is observed, suggesting that this analysis (a) has successfully identified the factors which influence the rate constants for ring opening of these radical anions and (b) may be a predictive tool for estimating rate constants for new systems. (The line drawn in Figure 7 is based on the application of theory pertaining to stepwise dissociative electron transfer, vide infra.)

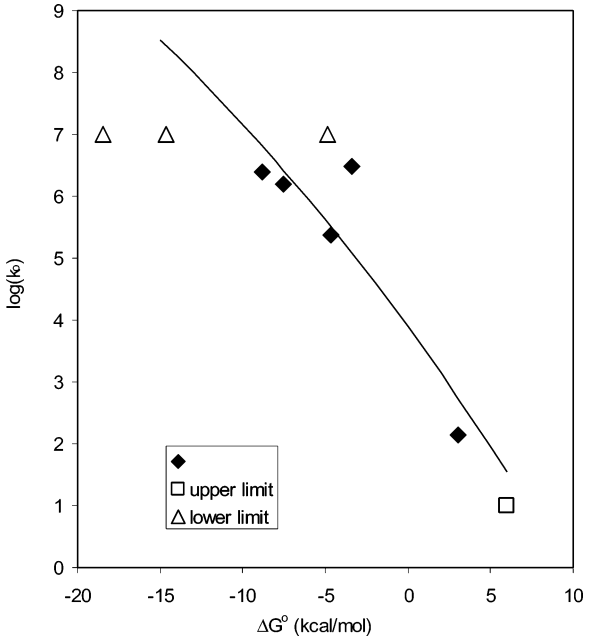


Figure 7. Plot of log(k_o) for ring opening of simple cyclopropyl-containing radical anions as a function of driving force.

Maslak has classified radical ion fragmentations as either homolytic or heterolytic.[44,45] In a heterolytic cleavage, charge is transferred to a different region of the molecule (e.g., $^{\bullet -}A{-}B \rightarrow A^{\bullet} + B^{-}$), while for a homolytic cleavage the negative charge remains on the fragment on which it is first introduced (e.g., $^{\bullet -}A{-}B \rightarrow A^{-} + B^{\bullet}$). The thermochemical cycle used to estimate ΔG° for ring opening of these radical anions as derived assumes homolytic cleavage, and the correlation between log(k_o) and ΔG^{o} in Figure 7 seems to confirm that this assumption is correct.

An understanding of the relationship between the activation energy (kinetics) and driving force (thermodynamics) pertinent to radical ion rearrangements is necessary for predicting the behavior of unknown systems. On the basis of a Marcus-type approach, Savéant has developed theory pertaining to radical anion fragmentations which occur in a stepwise manner (e.g., $R{-}X + e^- \rightarrow RX^{\bullet -} \rightarrow R^{\bullet} + X^{-}$).[46,47]

The relationship between $\Delta G^{\ddagger}$ and ΔG^{o} is described according to eq 7: $\Delta G_o^{\ddagger}$ refers to the intrinsic barrier (activation energy at zero driving force) and accounts for the reorganization of solvent and/or counterion (external reorganization) or changes in the molecule itself (internal reorganization), which may be required in order to reach the transition state.

$$\Delta G^{\ddagger} = \Delta G_o^{\ddagger}\left(1 + \frac{\Delta G^{o}}{4\Delta G_o^{\ddagger}}\right)^2 \quad (7)$$

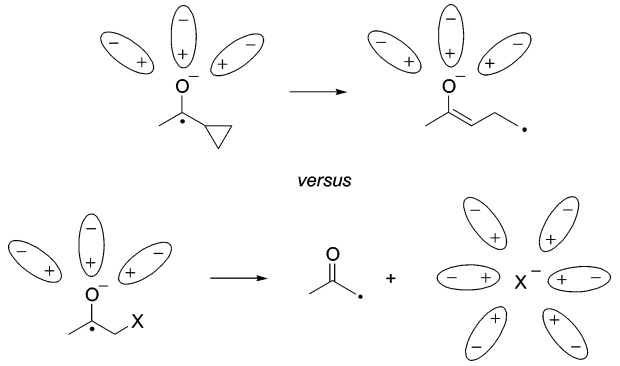
Combined with the Eyring equation, the relationship between log(k_o) and ΔG^{o} can be expressed according to eq 8.

$$\log(k_o) = \log\left(\frac{k_B T}{h}\right) - \frac{\Delta G_o^{\ddagger}}{2.303RT}\left(1 + \frac{\Delta G^{o}}{4\Delta G_o^{\ddagger}}\right)^2 \quad (8)$$

The curved line depicted in Figure 7 is derived from a nonlinear least-squares fitting of the experimental data (using only the well-established rate constants) to eq 8, resulting in a reorganization energy ($\Delta G_o^{\ddagger}$) of 12 kcal/mol. This reorganization energy is lower than that associated with fragmentations of other, structurally related ketyl anions. For the cleavage of

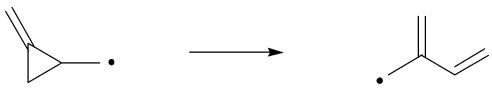
α-substiuted acetophenone radical anions, $Ph(C{=}O^{\bullet-})CH_2X \rightarrow Ph(C{=}O)CH_2^{\bullet} + X^-$, the reorganization energy is on the order of 16 kcal/mol with solvent reorganization being the major contributing factor to the intrinsic barrier.[48] For the ring openings described herein, a lower reorganization energy is reasonable because the negative charge and the solvent molecules do not move appreciably when ring opening occurs (Scheme 9). To the extent that the calculated gas phase activation energies can be trusted, it appears that both structural and solvent reorganization contribute significantly to the reorganization energy associated with ring opening.

SCHEME 9



As noted, the results for the cyclobutyl methyl ketone are excluded from Figure 7. Although the thermodynamic driving force is nearly the same, rate constants for rearrangement of cyclobutylcarbinyl-type neutral free radicals and radical anions are several orders of magnitude lower than rate constants for cyclopropylcarbinyl-type systems. This difference can be related to the unique properties of the cyclopropyl group as a π-electron donor to electron deficient centers.[20,49,50] Similarly, the radial anion derived from 2-methylenecyclopropyl phenyl ketone (**3**) is excluded because this radical anion appears to undergo ring opening via a unique mechanism.

Liu, Newcomb, et al. have reported that the (methylenecyclopropyl)methyl radical undergoes ring opening to the 2-vinylallyl radical (eq 9) at a rate only about 10× greater than the



(9)

cyclopropylcarbinyl radical,[51] despite the increased driving force for rearrangement associated with formation of an allylic radical. The same holds true for the (methylenecyclobutyl)methyl radical, which ring opens slightly faster than the cyclobutylcarbinyl radical.[52]

Although both systems undergo ring opening to a resonance-stabilized allylic radical, this resonance stabilization is not realized in the transition state because the rupturing C−C bond is orthogonal to the π-system of the C=C as illustrated for the (methylenecyclobutyl)methyl radical in eq 10. Walton has discussed this in the context of the principle of nonperfect synchronization (i.e., bond breakage occurs before the rotation needed to achieve resonance stabilization in the transition state).[52]

(10)

Because of this precedent, it was surprising to find that the radical anion derived from 2-methylenecyclopropyl phenyl ketone (**3**) underwent ring opening at a rate at least *6 orders of magnitude faster* than that derived from phenyl cyclopropyl ketone (Table 4, entries 11 and 1, respectively), suggesting that C−C bond cleavage and rotation were synchronized.

To probe this further, density functional theory calculations were performed at the UB3LYP/6-31+G* level on model radical anion **12** to elucidate the mechanism and potential energy diagram for ring opening. Starting with the ring-closed radical anion, fixing only the C−C bond length and allowing it to vary in 0.1 Å increments (from 1.50 to 2.50 Å), the energy profile depicted in Figure 8 emerged. The corresponding structures suggested that ring opening is occurring via a disrotatory-type process. A transition state calculation on the high energy point led to a structure with a single imaginary frequency whose motion (bond stretching and torsion) confirmed this hypothesis.

Given the apparent success of density functional theory to rationalize the unusually high rate constant for ring opening of $\mathbf{3}^{\bullet-}$, it seemed reasonable to suspect that transition state calculations might provide a general, predictive tool for estimating rate constants for ring opening of these radical anions. Accordingly, calculations were performed at the UB3LYP/6-31+G* level on the ring-closed radical anions and corresponding transition states for ring opening. The resulting energy differences, expressed as an activation energy, are summarized in Table 4. In all cases, the transition states were characterized by a single imaginary frequency, corresponding to the reaction coordinate (i.e., C−C bond stretching); in the case of $\mathbf{3}^{\bullet-}$, this bond stretch was coupled with a torsion corresponding to rotation of the exocyclic methylene as was observed for **12**. Because no experimental activation energies are available for comparison and also because of the obvious difference between these reactions conducted in solution (experiment) and the gas phase (theory), the energies were not corrected for zero-point energy. Rather, the objective was to ascertain whether theory would be able to reproduce the observed reactivity trends.

A plot of $\log(k_o)$ vs the DFT-calculated activation energy is depicted in Figure 9 for all the systems listed in Table 4; the straight line depicted in this figure is based upon systems for which good experimental values for k_o are available. These results demonstrate that DFT calculations are able to reproduce the observed reactivity trends for a diverse variety of substrates to a reasonable extent, and suggest that by using a plot such as this as a "calibration curve", it may be possible to estimate rate constants for radical anion ring openings in general.

Summary and Conclusions

1. Rate constants for ring opening of cyclopropyl- and cyclobutyl-containing radical anions derived from several classes of carbonyl compounds are reported. The resulting reactivity order is the result of the interplay between charge and spin delocalization in the ring-closed and ring-opened (distonic) radical anions, which can be qualitatively accounted for on the basis of the thermodynamic stability of the radical anion, the ability of substituents on the cyclopropyl group to stabilize the radical portion of the distonic radical anion, and the stability of the enolate portion of the distonic radical anion.

2. A thermochemical cycle for estimating ΔG^o for ring opening is presented, and for simple cyclopropyl-containg ketyl anions, there is a reasonable correlation between $\log(k_o)$ and ΔG^o (Figure 7). Theory pertaining to stepwise dissociative electron transfer seems to be applicable to these systems.

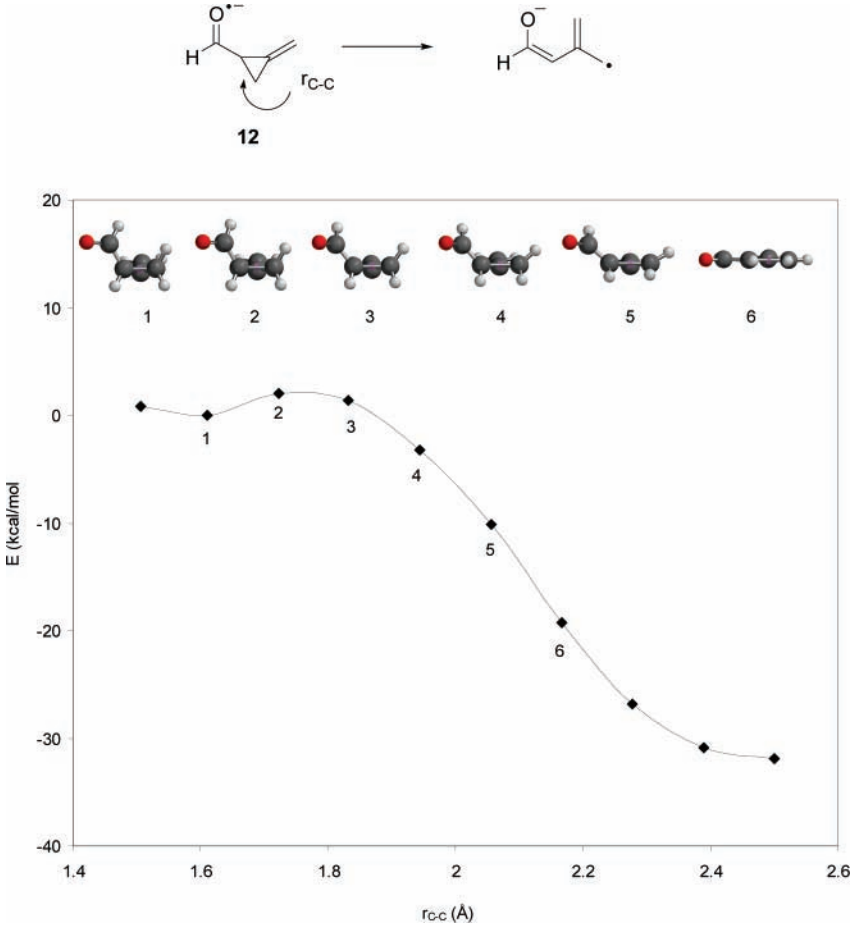


Figure 8. Energy profile for ring opening of radical anion **12** calculated by using UB3LYP/6-31+G*.

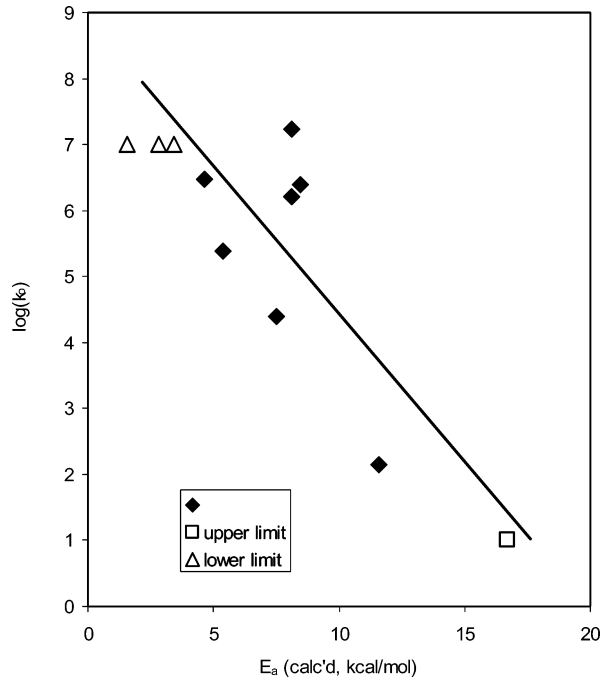


Figure 9. Plot of log(k_o) for ring opening of radical anions derived from various carbonyl compounds vs calculated (UB3LYP/6-31+G*) activation energy.

3. Calculated (UB3LYP/6-31+G*) gas-phase activation energies correlate reasonably well with measured log(k_o) values (solution) for a more diverse set of substrates (Figure 9).

4. Figures 7 and 9 may provide the basis for a "calibration curve" to predict rate constants for ring opening of radical anions derived from carbonyl compounds, in general. It should be noted, however, that these curves are based upon kinetic data obtained in DMF solvent and *n*-Bu_4N^+ counterion. Whether and to what extent these rates vary as a function of counterion, ion-pairing, and solvent is unknown at this time.

Acknowledgment. Financial support from the National Science Foundation (CHE-0108907) is acknowledged and appreciated. We also thank Prof. T. Daniel Crawford for stimulating conversations and Dr. Edward W. Thomas for providing us with the sample of **3** that was used in these experiments.

Supporting Information Available: Model compounds and thermodynamic values used to calculate $\Delta G°$ for ring opening of radical anions in Table 4 and spectroscopic data for bulk electrolysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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