

Electron-Transfer Reactions with Significant Inner Reorganization Energies. Reduction of Some Fully α -Methylated Cycloalkane-1,2-diones

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Abstract: Electron-transfer reactions of 3,3, ω -tetramethyl-1,2-cycloalkanediones with 5-, 6-, 7-, and 8-membered rings (1-4, respectively) have been investigated. The standard heterogeneous electron-transfer rate constants, measured with mercury electrodes in acetonitrile solvent, decrease by 3 orders of magnitude along the series 1-3 and then increase a factor of 2 on going from 3 to 4. The self-exchange rate constant for the 3,3- was found to be 70 L mol⁻¹ s⁻¹. The cause of these changes is thought to be larger inner reorganization energies for the 7- and 8-membered ring diketones compared with those of 1 and 2. Qualitatively, the largest change in structure on going from neutral 3 and 4 to the radical anion is movement of the O=C-C=O dihedral angle from values near 80-100° toward coplanarity of the diketone function. 1 and 2 undergo smaller changes upon reduction. The radical anion of 4 exists in a transoid conformation. Semiempirical molecular orbital calculations (AM1) give inner shell contributions to the enthalpic barrier for electron transfer in agreement with the order found by experiment, 3 > 4 > 2 > 1. Linear correlation of calculated electron affinities and reversible reduction potentials was observed, and deviation of the result for 4 was explained by weaker solvation of the less polar transoid anion as compared to 1-3, whose anions have a polar *cis* structure. A linear log-log correlation of heterogeneous and self-exchange electron-transfer rate constants was found for 3 and three acyclic 1,2-diketones. The electron-transfer reactions of 1-4 appear to be one-step reactions without formation of a discrete high energy intermediate anion. The factors that favor two-step electron transfer reactions are discussed in terms of the energetics of reduction of bianthrone.

Introduction

It is now well accepted that there are three principal factors governing the magnitude of the rate constant of both heterogeneous and homogeneous (self-exchange) electron-transfer reactions. These are the inner shell and outer shell reorganization energies and a combination of factors (adiabaticity, solvent dynamic effects) that influence the preexponential factor.

For the vast majority of electron-transfer reactions of organic compounds, the inner shell (vibrational) reorganization is overshadowed by the outer shell contribution, the latter arising from the necessary solvent reorganization that accompanies the change in charge on going from reactant to product. This generalization holds for most instances of simple electron transfer reactions, for example, those in which a neutral reactant is either reduced to form the radical anion or oxidized to the radical cation. The underlying cause of the small inner reorganization energy is the fact that usually only very minor changes in structure accompany the electron-transfer reaction.

The classical definition of the inner reorganization energy is the energy difference between the reactant in its equilibrium nuclear configuration and the reactant in the configuration of the product.³ In most instances, this energy is almost identical to the energy difference between the product in its equilibrium configuration and the product in the configuration of the reactant. In any case, these reorganization energies can be computed from knowledge of the changes in bond lengths, bond angles, and torsional angles and the corresponding force constants. When the changes in these structural parameters are small, the inner reorganization energy will also be small, often much smaller than the outer reorganization energy.

Certain transition metal coordination complexes have large inner reorganization energies due to stiff bonds and substantial changes in bond length accompanying reduction.⁴ By contrast, the contribution of structural change to the electron-transfer barrier in metallocenes is insignificant.⁵ In other inorganic systems,⁶ sluggish electron-transfer kinetics has been observed and attributed to such structural changes as out-of-plane movement of the metal in metalloporphyrins and changes in ligand hapticity in organometallic compounds. Nevertheless, there are other systems that are known to undergo substantial structural change yet show surprisingly facile electron-transfer kinetics.⁷

There are very few examples of organic reactions with large inner reorganization energies. An early example is the reduction of the tub-shaped cyclooctatetraene to the more planar radical anion.⁸ However, as stated above, typically the effects are much smaller. The contribution of inner shell reorganization was calculated by Grampp and Jaenicke⁹ for a series of *p*-phenylenediamine derivatives and found to be only about 1-2 kcal/mol.

The electron-transfer reactions of tetraalkylhydrazines are unique in their sensitivity to structural changes. These species are easily oxidized to persistent cation radicals, and significant

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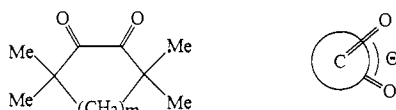
Table I. Summary of Data for Electron-Transfer Reactions of 1,2-Diketones^a

compd	$E_{1/2}/V^b$	α_0^c	$(d\alpha/dE)/V^{-1}$	$k_s/cm\ s^{-1}$	$\Delta G^*_{ex}^d$	$\Delta H^*_{ex}^e$	ref
1	-0.26	<i>f</i>	<i>f</i>	0.5 ± 0.2	5.8	1.5	<i>g</i>
2	-0.45	0.40		0.09 ± 0.01	6.9	2.5 ₅	<i>g</i>
3	-0.80	0.30	0.08	$0.000\ 60 \pm 0.000\ 03$	9.8 ₅	3.3	<i>g</i>
		0.35	0.13	0.000 39			<i>h</i>
		0.35	0.0	0.0034			<i>i</i>
4	-1.03	0.39	0.20	0.0012 ^j	9.4 ₅	2.7	<i>g</i>
biacetyl	-0.43	0.42	0.32	0.14	6.6	1.6	14
3,4-hexanedione	-0.45	0.42	0.32	0.050	7.2	1.6	14
bipivaloyl	-0.69	0.42	0.40	0.0055	8.5	3.0	14

^a Unless otherwise specified, all data were obtained at 25 °C in 0.10 M TBAP in acetonitrile at a mercury electrode. ^b Reversible half-wave potential with respect to cobaltocenium/cobaltocene couple. Error, ± 5 mV. The half-wave potential is very close to the reversible formal potential, E° , the relationship being $E_{1/2} = E^{\circ} + (RT/2F) \ln(D_R/D_O)$ where D_R and D_O are the diffusion coefficients of the reduced and oxidized forms, respectively.¹¹ ^c Transfer coefficient at $E_{1/2}$. ^d Free energy of activation (kcal/mol) for heterogeneous electron transfer. Calculated from k_s using 10^4 cm/s as preexponential factor. ^e Calculated contribution of inner shell reorganization to enthalpic barrier (kcal/mol) for heterogeneous electron transfer. ^f Cannot be determined for cases with large k_s . ^g This work. ^h This work. Single determination by normal pulse voltammetry with pulse durations of 50 and 200 ms. ⁱ This work. 0.10 M TEAP. Single determination by cyclic voltammetry. ^j Two separate determinations gave identical values for k_s .

structural changes accompany the electron transfer, including movement of the lone pair-lone pair dihedral angle toward 0° or 180° and, most importantly, significant flattening in the geometry at the nitrogen atoms. Within this class of compounds, certain sesquibicyclic hydrazines have abnormally small self-exchange rate constants for the neutral/cation radical pairs. Semiempirical quantum mechanical calculations (AM1) have shown that the contribution of inner reorganization to the enthalpic reaction barrier is quite significant, as much as 10 kcal/mol for the self-exchange process.¹⁰

In the search for other organic systems that might have large inner shell reorganization energies, our attention was drawn to $\alpha,\alpha,\omega,\omega$ -tetramethylated cycloalkane-1,2-diones 1-4 ($m = 1-4$, respectively). In the neutral diketone, the dihedral angle between



the two carbonyl groups varies from 0° to over 100° on going from 1 to 4. However, for the radical anions, the double-bond character in the intercarbonyl carbon-carbon bond is quite strong, causing a marked preference for coplanarity (0° or 180°) of the diketone function. Thus, a substantial change in structure is expected upon reduction of the larger ring members of the series.

In this paper we report the results of studies of the rates of the electron-transfer reactions of diketones 1-4 and demonstrate that this series comprises a new example of organic systems in which the contributions of structural change to the reaction barrier are substantial.

Results

Electrochemistry. Cyclic voltammetry reveals large differences in the apparent standard heterogeneous electron-transfer rate constants, k_s , for diketones 1-4. At one extreme, the five-membered ring compound 1 gives close to reversible voltammograms even at 100 V/s. The results are summarized in Table I, where it may be seen that k_s for 1 is near 0.5 cm/s, close to the upper limit for measurement by cyclic voltammetry with electrodes of conventional size.¹²

The rate constant for reduction of cyclohexanedione 2 is considerably smaller, while the seven- and eight-membered ring compounds 3 and 4 produce highly irreversible cyclic voltammograms due to their sluggish electron-transfer reactions. In

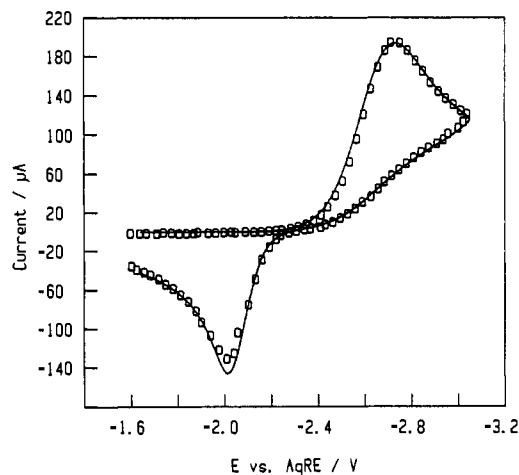


Figure 1. Cyclic voltammogram of 1.7 mM 3,3,8,8-tetramethyl-1,2-cyclooctanedione (4) at a scan rate of 100 V/s. Tetrabutylammonium perchlorate (0.10 M) in acetonitrile at 298 K. Mercury working electrode. Simulation, \circ ; background-corrected experimental voltammogram, —. Simulation parameters listed in Table I.

Figure 1 is shown the voltammogram for cyclooctanedione 4 at 100 V/s. The peak separation is approximately 700 mV, compared to a value near 60 mV expected for reversible (large k_s) behavior. The precision of the cyclic voltammetric method is very good for rate constants in the range encountered for 3 and 4. For each compound, the results given in Table I are averages of data obtained for several scan rates between 5 and 400 V/s using 2-5 independently prepared solutions. The error estimates for k_s are smallest for 3 and 4, larger for 2, and quite substantial for 1. As noted above, k_s for 1 is near the upper limit for measurement by our technique. When k_s is large, the kinetic effect displaces the voltammetric curve only a few millivolts from the reversible response. Under these circumstances, the residual uncertainty in the correction for solution resistance results in large random and systematic errors. As has been noted before,¹²⁻¹⁵ the introduction of a potential dependence of the transfer coefficient brings about small but significant improvements in the fit of simulation to experiment.

To confirm that the results are independent of the experimental method, compound 3 was studied using normal pulse voltammetry (NPV). The value of k_s so obtained was about 35% lower than the result from cyclic voltammetry, possibly due to less efficient removal of residual water in the NPV experiment. Small amounts of water are known to suppress k_s .¹⁴

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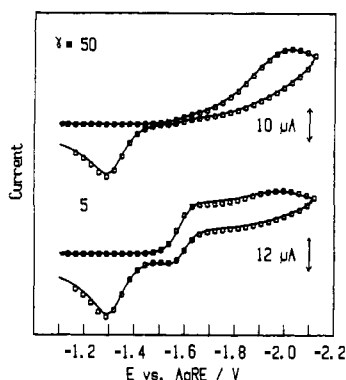


Figure 2. Comparison of digital simulation (O) with homogeneous redox catalysis data (—) for 1.1 mM 3,3,7,7-tetramethyl-1,2-cycloheptanedione (**3**) catalyzed by 4-cyanopyridine. Tetrabutylammonium perchlorate (0.10 M) in acetonitrile at 298 K. Scan rate: 20 V/s. γ is the ratio of the concentration of **3** to that of the catalyst. Simulation parameters: for the catalyst couple, $E^{o'}$ = -1.60 V, reversible; for the **3,3**-couple, $E^{o'}$ = -1.54 V, k_s = 4.8×10^{-4} cm/s, α = 0.33, $d\alpha/dE$ = 0.13 V^{-1} . Rate constant for electron transfer from radical anion of catalyst to **3** was $7.0 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$.

As has been noted for reduction of nitroalkanes,^{14,15} acyclic 1,2-diketones,¹⁴ nitromesitylene, and benzophenone,¹⁶ the value of k_s obtained is a function of the size of the cation of the supporting electrolyte, with larger cations leading to smaller rate constants. This has been interpreted as a blocking effect caused by a layer of cations on the negatively charged electrode surface. The electron tunneling distance is larger when larger cations are present, causing the observed k_s to be smaller. This effect is also present with the cyclic diketones studied here. The k_s for **3** obtained with the smaller tetraethylammonium cation was about 6 times larger than that observed with tetrabutylammonium perchlorate (Table I).

Thus, comparison of rate constants for a series of compounds will be meaningful when the constants are obtained for each compound in the series with the same solvent and electrolyte, in the present case acetonitrile with 0.10 M TBAP. Results for three acyclic 1,2-diketones obtained under these same conditions¹⁴ are also included in Table I.

The heterogeneous electron-transfer reaction of diketone **3** is particularly slow, and we thought it of interest to determine if the rates of homogeneous electron transfers to **3** are likewise suppressed. A convenient means of determining such rates is the method of homogeneous redox catalysis^{13,14} in which the measurements can be performed under precisely the same conditions as used for heterogeneous electron-transfer kinetics. In this technique, a catalyst couple, which has a large k_s and hence exhibits reversible behavior, is used to reduce indirectly the diketone **3**. Mixtures of the catalyst (4-cyanopyridine in the present case) and **3** were studied by cyclic voltammetry. The catalyst is reduced to its radical anion at a potential where direct reduction of **3** is negligible. The radical anion encounters **3** near the electrode and may transfer its electron to **3** and thus regenerate neutral 4-cyanopyridine, which can return to the electrode and be again reduced, producing additional current. It is the magnitude of this additional ("catalytic") current that is related to the rate constant for electron transfer from 4-cyanopyridine radical anion to diketone **3**.

A series of experiments was performed for scan rates from 1 to 50 V/s and ratios of the concentration of catalyst to that of **3** falling in the range of 0.5 to 0.02. Examples of voltammograms and fits of simulation to the data are shown in Figure 2. The rate constant that provided the best fit with all of the data was $7.0 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$. The formal potential for the catalyst couple was found to be 60 mV negative of that of **3**.

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Table II. Self-Exchange Rate Constants for Diketones^a

compd	$k_{ex}/\text{L mol}^{-1} \text{ s}^{-1}$
3	70
biacetyl	1.4×10^6
3,4-hexanedione	8.0×10^5
dipivaloyl	1.6×10^4

^a 0.10 M electrolyte in acetonitrile. Electrolyte: TBAP for **3** and dipivaloyl; tetraethylammonium perchlorate for biacetyl and 3,4-hexanedione. 25 °C. Results for acyclic diketones from ref 14.

Table III. O=C—C=O Torsional Angle in Diketones and Their Radical Anions

compd	$\theta/^\circ$		anion calc
	neutral calc	exp ^a	
1	0	0	0
2 ^b	60	42	5
3 ^c	85	82	30
4 ^d	105	98	145
biacetyl	180	158	180
3,4-hexanedione	180		179
dipivaloyl	116	122	179

^a From ref 18. Determined from dipole moments measured in carbon tetrachloride. ^b Two conformations of similar energy were found, the chair and the twist-boat. Results are shown for the twist-boat. ^c Two conformations of similar energy were found, a chair conformation and a twist-boat. Results are shown for the twist-boat. ^d Four low energy conformations were found: crown, chair-boat, twist-chair-chair, and chair. Similar structures have been found to be important in studies of cyclooctane.¹⁹ Results for the neutral are for the crown conformation, and the chair-boat was used for the anion.

The above rate constant and difference in formal potentials can be combined with the known self exchange rate constant for the catalyst couple¹⁷ to obtain^{3,13,14} the self-exchange rate constant for **3** and its radical anion. The result, $70 \text{ L mol}^{-1} \text{ s}^{-1}$, has been entered in Table II along with similar results for three acyclic 1,2-diketones.¹⁴

Molecular Modeling. To gain some insight into the relative magnitudes of the inner reorganization energies for these electron-transfer reactions, calculations were carried out using the semiempirical MO method AM1. The approach used was similar to that of Nelsen *et al.*,^{10a} who used AM1 to estimate the inner reorganization energies for electron-transfer reactions of amino nitrogen compounds.

The method was first applied to the neutral diketones **1–4**. One of the principal changes expected upon addition of an electron to form the anion radical is movement of the O=C—C=O torsional angle θ toward 0 or 180°. The calculated torsional angles at minimum energy are given in Table III, and the structures of two of the lowest energy conformations of **4** are shown in Figure 3. The energy minima are rather shallow for **1–4**, variations of $\pm 10^\circ$ generally costing less than 1 kcal/mol. Close adherence of these torsional angles, calculated for the isolated gas-phase molecule, to those measured in the solution phase is not expected, as the solvent should diminish the dipole-dipole interactions in the diketo function that are prevalent near $\theta = 0^\circ$. Nevertheless, the agreement is generally good (Table III), the fact that the value of θ measured for **2** in CCl_4 (42°) is lower than that calculated (60°) being perhaps attributable to the dielectric effect mentioned above. Not surprisingly, $\theta = 0^\circ$ for **1** in the solid state,²⁰ a fact readily duplicated by the calculations.

The radical anions of 1,2-diketones (semidiones) are known to prefer a coplanar diketo functionality with either a *cis* ($\theta = 0^\circ$)

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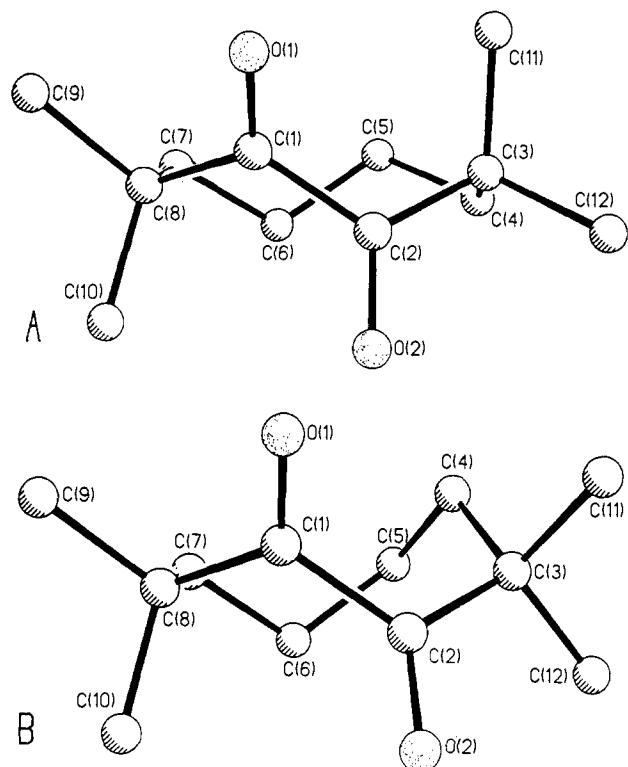


Figure 3. Conformations of 3,3,8,8-tetramethyl-1,2-cyclooctanedione with the lowest heats of formation as calculated by AM1. (A) Crown. (B) Chair-boat. ($\theta = ca. 105^\circ$ for each.)

or *trans* ($\theta = 180^\circ$) structure. The relative populations of the two isomers depend on the solvent used and ion pairing.²¹ Cyclic C_{11} – C_{15} semidiones can exist in either the *cis* or the *trans* form,^{21e} whereas C_4 – C_9 have only been detected in the *cis* form.^{21c} However, ring inversion occurs in C_9 , and cyclooctane-1,2-semidione is described as conformationally complex.^{21d} As expected, AM1 calculations for the radical anions of 1–3 (Table III) reveal a tendency to close θ toward 0° due to the increased double-bond character in the intercarbonyl carbon–carbon bond.

By contrast, with the radical anion of the eight-membered ring compound 4, we could not successfully optimize the geometry when starting with $\theta < 90^\circ$. This is consonant with the finding that the energy of neutral 4 near the *cis* structure was extremely high, about 20 kcal/mol above the minimum energy. Instead, the minimum energy conformation of the radical anion of 4 involves an increase in θ from about 105 to 145° , i.e., the anion adopts a more *transoid* structure.

AM1 calculations were used to estimate the contribution of inner reorganization to the barrier for the electron-transfer reactions of 1–4. First, the structure of minimum energy of the neutral diketone was determined. Calculations were then performed in which θ was driven in increments toward its characteristic value in the anion, with all other structural parameters being optimized at each step. In like manner, the structure of minimum energy of the radical anion was determined, and θ was then driven toward the torsional angle prevalent in the neutral diketone. In this way, changes in the energies of the neutral diketone and the radical anion as a function of θ were determined. An example of the output is shown in Figure 4, where results are given for 3.

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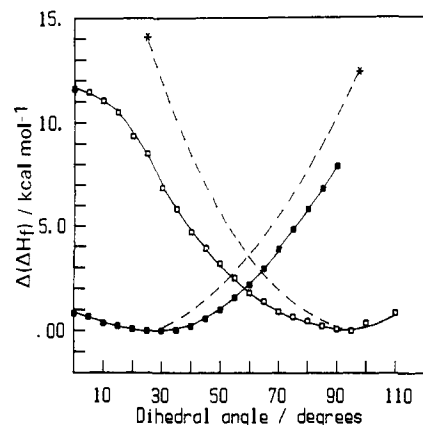


Figure 4. Relative heats of formation (as calculated by AM1) plotted vs the $O=C-C=O$ dihedral angle for 3,3,7,7-tetramethyl-1,2-cycloheptanedione (\square) and its radical anion (\blacksquare). (—) energies determined by considering only changes in dihedral angle; (*) energies calculated by starting with the minimum energy structures (neutral or radical anion) and switching the charge value; (---) parabolic sketch of energies for intermediate θ .

The energy of the anion increases as it is forced to adopt θ characteristic of the neutral diketone and vice versa. At θ of about 60° , the increase in energy of the two forms is equal. The energy at this point can be taken as an estimate of the contribution of inner reorganization to the barrier height.

In fact, this estimate is substantially too low. When, for example, the energy of neutral 3 was calculated with $\theta = 30^\circ$ (the torsional angle in the anion), all other structural parameters were optimized, and they undoubtedly differed from those of the anion in its structure of minimum energy. In fact, the Marcus inner reorganization energy corresponds to the energy of the neutral species with its nuclear coordinates identical to those of the anion in its structure of minimum energy and vice versa. However, the desired reorganization energy is easily calculated simply by taking the optimized structure of the anion as the initial structure for a single point calculation of the energy of the neutral. The result is shown as the asterisk at 14 kcal/mol in Figure 4. Similarly, the optimized structure of the neutral was taken as the starting configuration for a single point calculation of the energy of the anion, giving 12.4 kcal/mol.

If the energies are parabolic functions of the polydimensional reaction coordinate, the enthalpic inner reorganization barrier is one-fourth of the inner reorganization energy when the same value is obtained for both neutral and anion. The slight asymmetry found for 3 leads to $\Delta H_{in}^* = 3.3$ kcal/mol.²² To illustrate, approximately parabolic curves are sketched in Figure 4 (dashed curves), where, of course, the polydimensional reaction coordinate is represented only by θ . In this approximate graphical treatment, ΔH_{in}^* appears to be about 3.5 kcal/mol.

There are various ways to refine the calculations within the context of the AM1 method. For example, the structural parameters (bond lengths, bond angles, torsional angles) that undergo the greatest change between the neutral and anion could be identified. These parameters could then be varied in increments from those corresponding to one form to those of the other, calculating the energies of the neutral and anion radical at each step. This procedure was followed by Nelsen, Blackstock, and Kim.^{10a} However, it is not likely that the results would differ significantly from the single-point calculations illustrated in Figure 4.

The method of single point calculation of the inner reorganization energies of neutral diketone and anion radical was

(22) If λ_n and λ_a are the inner reorganization energies of the neutral and anion, respectively, and $\gamma = \lambda_n/\lambda_a$, then $\Delta H_{in}^* = \lambda_n[(1 - 2\gamma^{1/2} + \gamma)/(1 - 2\gamma + \gamma^2)] \approx (\lambda_n + \lambda_a)/8$ when $\gamma \approx 1$.

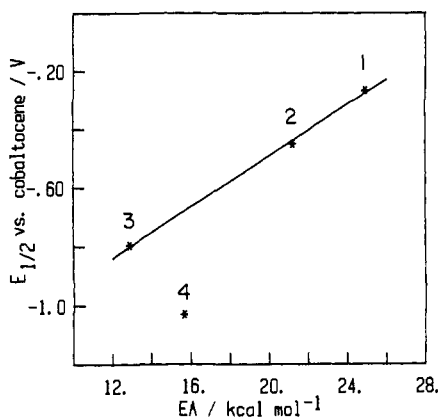


Figure 5. Reversible half-wave potentials vs electron affinities calculated by AM1.

repeated for 1, 2, 4, and three acyclic diketones, and the values of ΔH^*_{in} are included in Table I.

Discussion

A number of physical properties are affected by the structural differences that exist among diketones 1–4. For example, the $n \rightarrow \pi^*$ absorption band^{18,23} undergoes a blue shift on going from 1 to 3 and then shifts back to longer wavelengths for 4. The qualitative MO explanation of this shift focuses on the fact that the level of the lower π^* orbital associated with the two carbonyl groups is a function of the torsional angle, θ . The energy is lowest when $\theta = 0^\circ$ or 180° and is at its maximum value at 90° . For 1–3, θ was calculated to increase from 0° to 85° , consistent with the decrease in λ_{max} seen for the series. For 4, θ was calculated to be 105° , *i.e.*, greater than 90° . Hence, λ_{max} shifts back toward the red.

The lower π^* orbital is also the LUMO into which an electron is inserted on going from the neutral diketone to the radical anion. Thus, it is expected that diketones with $\theta = 0^\circ$ or 180° will be easily reduced due to the lower level of the π^* orbital, while the formal potentials for those with θ near 90° will be displaced in the negative direction. Indeed, this trend has been found by polarography²⁴ of 2–4 in 2-propanol/water and by cyclic voltammetry²⁵ of 1–4 in acetonitrile or DMF. The present determination of the reversible formal potentials, based on the fit of simulations to the voltammograms, should be of good accuracy. Inspection of the results in Tables I and III shows the same correlation between $E^{o'}$ and θ noted in the earlier work.

It would be desirable to include the effects of all structural parameters (not only θ) on the predicted $E^{o'}$ of these diketones. In principle, the reversible potentials for neutral/radical anion couples should correlate linearly with the gas-phase electron affinity if the solvation energies of the species either remain constant along a series of compounds or also correlate with electron affinity.²⁶ The electron affinities of 1–4 were calculated by AM1 as the differences between the optimized heats of formation of the anion and neutral diketone. In Figure 5 these electron affinities are plotted vs the formal potentials from Table I. Remarkably, the data for 1–3 form a line whose slope is 0.986 (when the electron affinity is expressed in electron volts) compared to the theoretical value of 1.00 expected when the difference between the free energy of solvation of neutral and anion remains constant along the series. Unfortunately, there are insufficient data to determine whether the excellent linearity and close to theoretical slope arise from

the excellence of the AM1 calculations or are merely the result of offsetting errors.

The result for cyclooctanedione 4 deviates markedly from the line. The reversible potential for 4 is actually more negative than that of 3, even though 4 is computed to have the higher electron affinity. The most obvious distinguishing characteristic of 4 compared to the other cyclic diketones is that its radical anion is the only one that is computed to adopt a transoid structure ($\theta = 145^\circ$). It is the solvation energy of the radical anion rather than that of the neutral that dominates the effect on $E^{o'}$.²⁶ The *cis* structure in the anions of 1–3 is highly polar and will be more strongly solvated than the anion of 4, whose transoid form leads to lower polarity.

If such is the case, the lower solvation energy for the anion of 4 will cause its $E^{o'}$ to be more negative than the values for 1–3, *i.e.*, 4 is correspondingly more difficult to reduce to the less stabilized anion. The 0.35-V deviation from the line in Figure 4 corresponds to 8 kcal/mol lower free energy of solvation of the anion of 4. In support of this interpretation are the molecular dipole moments computed by AM1 for the anions, *viz.*, 7.6, 7.9, and 8.1 D for 1–3 but only 4.0 D for 4. The above may be taken as indirect confirmation of the transoid form of the radical anion of 4 predicted by AM1.

The luminescence and photochemistry of 1–4 are also influenced by structural factors.^{18,27,28} Upon electronic excitation ($n \rightarrow \pi^*$), the double bond character of the intercarbonyl carbon–carbon bond will increase, causing a preference for $\theta = 0^\circ$ or 180° in the excited state for the same reason that the radical anions are driven toward these values of the dihedral angle. In fact, analysis of the fluorescence and phosphorescence spectra of 1–4 and other diketones reveals that emission occurs from states with a coplanar diketone geometry.¹⁸

Photochemistry also provides insight into the structures of the excited states of these compounds. When solutions of 1, 2, or 3 were irradiated in a poor hydrogen-atom-donating solvent (benzene), products arising from intermolecular hydrogen atom abstraction and α -cleavage were seen.²⁷ However, when 4 was irradiated, it reacted mainly by intramolecular hydrogen abstraction in which a hydrogen atom is transferred from a methyl group to the oxygen on the more distant carbonyl. Such an intramolecular reaction can occur only from an excited state in the *trans* configuration. Thus, the excited states of 1–3 are assigned a *cis* structure, whereas 4 is *trans*. This conclusion was supported by the results of photochemical reactions with alkenes.²⁸

Thus, there is a strong analogy between the structures of the radical anions and those of the excited states, with 1–3 adopting *cis* structures and 4 being *trans*. The eight-membered ring is large enough to accommodate a *trans*-like structure. After the Franck–Condon-governed excitation, the structure changes, with θ increasing from around 100° (Table III) to 180° . An analogous structural change occurs upon reduction of 4, but in this case we assume that the structural change accompanies electron transfer rather than occurring as a discrete conformational change following electron transfer. This point will be discussed below.

The present work shows that the rates of the heterogeneous and homogeneous electron-transfer reactions of 1–4 are affected by the structural differences among these diketones. Related to these observations are NMR studies of the rates of ring inversion in 2–4.^{29,30} For example, in the cyclohexanedione 2 there are two types of methyl groups, axial and equatorial. Inversion of the ring exchanges the identity of the methyl groups, allowing rate measurements by ^1H NMR. The transition states for ring

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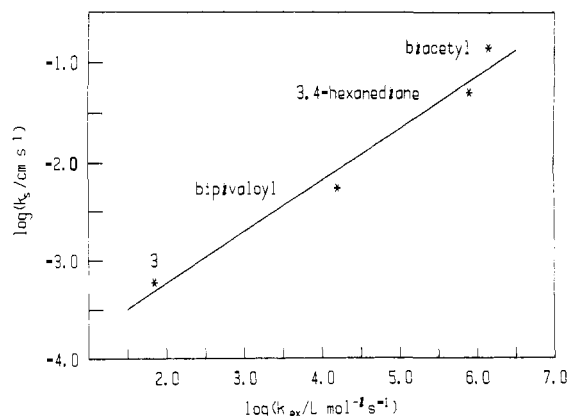


Figure 6. Comparison of heterogeneous and homogeneous (self-exchange) electron-transfer rate constants. Slope = 0.523, y -intercept = -4.28 , $r = 0.985$.

inversion should have θ near 0° so that the observed free energies of activation, ΔG^* , are measures of the energy required to reach the *cis*-like structure. The values found³⁰ were 9.0, 9.3 (8.7),²⁹ and 14.9 kcal/mol for 2–4, respectively. The significance of these results to the present work is that they demonstrate how much more difficult it is for 4 to approach $\theta = 0^\circ$ than for the other diketones.

The standard heterogeneous electron-transfer rate constant, k_s , is strikingly different for diketones 1–4, with the value for 3 being 3 orders of magnitude smaller than that of 1. We attribute these differences to substantial variations in the inner reorganization energies among these compounds. The rate of homogeneous electron transfer is also suppressed for 3, its self exchange rate constant being several orders of magnitude lower than that observed for acyclic diketones (Table II). The homogeneous and heterogeneous rate constants are correlated as shown in Figure 6 as a plot of $\log k_s$ vs $\log k_{ex}$ (slope = 0.523; $r = 0.985$). If the effect of electrode image charges on k_s is ignored, the slope is expected to be 0.5.³

Calculations of the enthalpic contribution to the barrier for electron transfer have been carried out using AM1 with the results shown in Table I. These calculations indicate that the contributions of structural change to the barrier height are significant. Furthermore, the calculated values of ΔH^*_{in} fall in the order 3 > 4 > 2 > 1, which is in the same order as that for the experimental free energies of activation, ΔG^*_{ex} , for the heterogeneous electron-transfer reaction (Table I).

Qualitatively, the most striking success achieved is the correct prediction that the rate constant for the eight-membered ring compound 4 should actually be larger than that of the seven-membered ring analog 3. This somewhat unexpected inversion in rates arises from the lower energy path available to 4, in which it moves to a transoid structure in the anion radical.

A more rigorous test of the validity of the calculations is provided by a comparison of the calculated ΔH^*_{in} with the experimental values of ΔG^*_{ex} (Table I). The latter were calculated by arbitrarily assuming an invariant preexponential factor of 10^4 cm/s. As may be seen, the change in the barrier calculated by AM1 accounts for the increase in ΔG^*_{ex} seen on going from 1 to 2 as well as the decrease found on going from 3 to 4. What is not well accounted for is the increase in ΔG^*_{ex} of 3 kcal/mol between the 1,2 and 3,4 pairs, with AM1 giving less than a 1 kcal/mol increase in the barrier.³¹

There are several obvious limitations of the calculations that discourage a more detailed analysis. First, the calculations refer to isolated, gas-phase molecules. The effect of solvent on the inner reorganization energy may be substantial because of the significant changes in polarity experienced on reaching the transition state. This is thought to be the reason that the rates of ring inversion are larger in more polar solvents.^{29,30} The

calculations only provide the enthalpic contribution to the barrier, whereas the activation free energy is needed. This may not be a significant limitation, as the activation entropy for ring inversion in 3 was found to be negligible.³⁰

Part of the change in ΔG^*_{ex} may be due to changes in the outer reorganization energy. One feature that attracted us to the 1–4 series is the fact that the structures are identical in the region of the molecule that bears most of the charge in the anion, *i.e.*, 1–4 all contain the $-\text{C}(\text{CH}_3)_2\text{C}(\text{O})\text{C}(\text{O})\text{C}(\text{CH}_3)_2-$ group. Thus, it might be expected that interactions of the anion with the solvent, the source of the outer reorganization energy term, will remain constant along the series. However, it has already been noted in the analysis of the E° data that the radical anion of 4 appears to be less strongly solvated than the other anions, a factor that would influence the outer reorganization energy for the 4,4 couple.

Finally, the k_s values may be affected by differences in the preexponential factor among the four diketones. As pointed out above, the rate of reduction of 3, in common with many other electrode reactions, is influenced by the size of the cation of the electrolyte, and this has been attributed to a blocking effect by a layer of cations covering the negatively charged cathode and inhibiting the electron-transfer reaction. If the reactant is able to approach the electrode more closely (for example, when the electrolyte contains small cations), the rate will be higher. Similarly, if the structure of the reactant features an electroactive group (the diketone function) that is blocked by other parts of the molecule, that reactant will, on the average, be unable to achieve close approach to the electrode and hence will have a smaller electron-transfer rate constant. Obviously, the diketone function of the seven-membered ring compound 3 is more shielded by the α -methyl groups than is the much more open *cis* structure in the cyclopentanedione 1.

In spite of these uncertainties in the quantitative interpretation of the heterogeneous electron-transfer rate constants of 1–4, the principal conclusion remains intact, *viz.*, these compounds comprise an unusual group of organic molecules in which there is a significant contribution of structural change to the electron-transfer barrier.

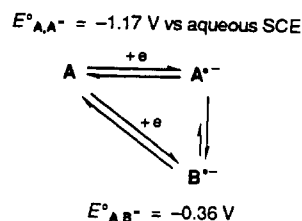
These results bear on another question of contemporary interest in electron-transfer reactions, *i.e.*, what factors lead to the structural change that accompanies electron transfer (one-step) as opposed to electron transfer to form a discrete intermediate that subsequently undergoes structural change (two-step electron transfer).³² Cycloheptanedione 3 is an obvious candidate for a two-step electron transfer reaction. The neutral diketone exists in a conformation with θ near 90° and will have a low electron affinity due to the factors discussed earlier in the paper. This conformation could be reduced at a rather negative potential to form a radical anion with substantially the same structure as the neutral diketone. Presumably, this conformation of the radical anion would be a high-energy intermediate which would rapidly convert to the preferred form with θ near 30° .

It is very difficult to distinguish this two-step mechanism from the one-step reaction by analysis of electrochemical data.³³ In the extensive AM1 calculations performed on the radical anion of 3, no hint of an energy minimum near the structure of neutral

(31) A reviewer has pointed out that perhaps the more striking result is that the self exchange rate constants, k_{ex} , are abnormally low for all of the four diketones studied (Table II). The k_{ex} for certain tetraalkylhydrazines and their radical cations¹⁰ are as small as that of dipivaloyl, but the calculated ΔH^*_{in} is 9–10 kcal/mol, compared to only 6 kcal/mol calculated for dipivaloyl (Table I; ΔH^*_{in} for self exchange is twice that for the electrode reaction). This suggests that some factor is at work causing the diketone couples to exhibit slower electron-transfer kinetics than indicated by the inner reorganization energies. This may be related to a larger outer reorganization energy caused by the localization of charge in the radical anion of the diketones^{12,14} or to the effects of ion pairing. The AM1 calculations account for the relative values of k_{ex} (and k_s) for the diketones reasonably well but do not explain the fact that the rate constants are unusually small in general.

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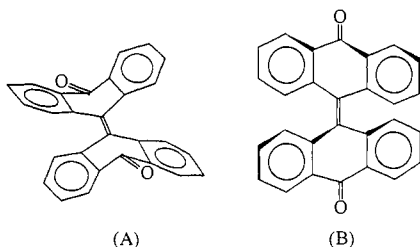
Scheme I



3 was found though several trial conformations were used and the two known to be of low energy, the twist-boat and the chair, were examined thoroughly. The only minimum found was that of the relaxed radical anion with θ near 30° . Thus it seems likely that reduction of 3 occurs by the direct one-step reaction as opposed to the two-step process with electron transfer and subsequent conformational change.

A clear requirement for a two-step electron-transfer reaction is the existence of a high energy intermediate that lies along the natural reaction pathway. Thus, for example, a high-energy intermediate form of the radical anion of the cyclooctanedione 4 may exist in a *cis*-like structure, perhaps with θ near 30° as with the radical anion of 3. Our calculations failed to locate such an intermediate, but even if it exists, it is not a likely candidate for an intermediate in the two-step reduction of 4, as the structural change to form it is in the wrong direction (decreasing θ as opposed to increasing θ) for reaching the final structure of the radical anion of 4 with θ calculated to be about 145° .

These systems may be contrasted with ones in which two-step reduction clearly occurs. An example is the molecule bianthrone^{8,34} which exists in two forms, the yellow A form and the green form designated as B. There are substantial structural



differences between the two forms, the A-form having anthrone systems folded away from each other without appreciable twisting of the connecting double bond. The B-form features two planar anthrone groups with considerable twisting about the connecting bond. The neutral molecule exists in the A-form at room temperature, and the radical anion prefers the B structure.

Extensive studies have shown that the electrochemical reduction of bianthrone involves electron transfer to A, forming an intermediate radical anion ($A^{\cdot-}$) that rapidly converts to the stable form, $B^{\cdot-}$. The free energy gap between $B^{\cdot-}$ and $A^{\cdot-}$ is 19 kcal/mol at 298 K. The reversible potentials for reduction of A to $A^{\cdot-}$ and the direct reduction of A to $B^{\cdot-}$ have been determined and are shown in Scheme I.

The reversible potentials indicate that, from a thermodynamic point of view, it is 0.81 V easier to reduce A to $B^{\cdot-}$ than to the high-energy intermediate $A^{\cdot-}$. Yet the reaction actually proceeds

by the two-step pathway of $A \rightarrow A^{\cdot-} \rightarrow B^{\cdot-}$. The reason for this must be that $\Delta G^{\ddagger}_{\text{ex}}(A \rightarrow B^{\cdot-})$ is sufficiently larger than $\Delta G^{\ddagger}_{\text{ex}}(A \rightarrow A^{\cdot-})$, to provide at least 0.81 V (18.6 kcal/mol) larger overpotential for the direct reduction, thus forcing the reaction to proceed in the two-step manner. Making the normal assumptions of equal preexponential factors and $\alpha = 0.5$, 0.81 V increased overpotential requires that $\Delta G^{\ddagger}_{\text{ex}}(A \rightarrow B^{\cdot-})$ exceed $\Delta G^{\ddagger}_{\text{ex}}(A \rightarrow A^{\cdot-})$ by at least 9.3 kcal/mol.

The origin of this increased free energy of activation is principally the much larger reorganization energy required to effect the structural change in the direct $A \rightarrow B^{\cdot-}$ reaction as opposed to electron transfer in the structurally similar $A, A^{\cdot-}$ pair. The structural change accompanying conversion of A-like to B-like structures involves twisting of the central bond and the hindered movement of benzo rings from each anthrone unit past one another. The barrier to this process is more than enough to account for the needed 9.3 kcal/mol.

The features of the bianthrone system that cause the electron-transfer reaction to proceed in two steps are the existence of a high-energy intermediate ($A^{\cdot-}$) and the substantial barrier for the direct, one-step process. The energy of the intermediate cannot be so high as to prevent its formation at potentials which would overcome the overpotential for the direct reaction. To prevent the direct reaction from occurring, it is necessary for any increase in the energy of the intermediate to be matched by half that amount as an increase in the barrier for the one-step reaction (assuming the transfer coefficient equals one-half).

It is hoped that experimental data of the type gathered and discussed here will provide insights for the design of molecules that will undergo direct (one-step) electron-transfer reactions, those that will react by a two-step path, and also those in the intriguing transition region, wherein one might be able to force a direct reaction to become two-step by a slight structural variation.

Experimental Section

Chemicals. HPLC-grade acetonitrile (Fisher) was passed through a column of alumina (80–200 mesh, Fisher) activated under nitrogen at 400°C prior to each experiment. Alumina was also added to the cell. Tetrabutylammonium perchlorate (TBAP, Southwestern Analytical Chemicals) was recrystallized twice from ethyl acetate and vacuum dried overnight at 60°C . Tetraethylammonium perchlorate (TEAP) was prepared according to the literature³⁵ and stored in a vacuum desiccator. 4-Cyanopyridine (Aldrich) was recrystallized twice from water and dried overnight in a vacuum oven at 60°C .

3,3,5,5-Tetramethylcyclopentane-1,2-dione (1),³⁶ 3,3,6,6-tetramethylcyclohexane-1,2-dione (2),^{29,37,38} 3,3,7,7-tetramethylcycloheptane-1,2-dione (3),^{29,30,39,40} and 3,3,8,8-tetramethylcyclooctane-1,2-dione (4)^{29,39,41} were prepared according to the literature.

Electrochemical Instrumentation and Procedures. The electrochemical cell was a small volume cell (3–5 mL) with four inlet ports available for electrodes and a purge tube. To control the temperature during measurements, the cell was constructed with a water jacket through which water from a Lauda Model M 20 water bath was pumped. All experiments were conducted at $25 \pm 1^\circ\text{C}$.

The working electrodes were hanging mercury drop electrodes of varying sizes. The mercury drop supports were prepared according to the method of Bersier and Bersier.⁴² The mercury drops used in the experiments were weighed on a semimicrobalance to determine their volume, which was in turn used to compute the electrode radius, a quantity needed for computing the required resistance compensation.⁴³

The counter electrode was a coil of platinum wire immersed in the test solution, and the reference electrode was composed of a silver wire in contact with 0.010 M AgNO_3 , 0.10 M tetrabutylammonium hexaflu-

(33) (a) In a recent study^{33b} of the electrochemical oxidation of 2,3-diisopropyl-2,3-diazabicyclo[2.2.2]octane, a high-energy intermediate cation radical was identified by calculation, and it was found to be formed from the prevalent conformation of the neutral hydrazine through a "gearing effect" of the isopropyl groups. The electrochemical data could be accommodated by the two-step mechanism using reasonable values of the conformational equilibrium and rate constants. However, the direct one-step oxidation of the hydrazine could not be excluded. (b) Nelsen, S. F.; Chen, L.-J.; Petillo, P. A.; Evans, D. H.; Neugebauer, F. A. *J. Am. Chem. Soc.*, in press.

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orophosphate, and acetonitrile. The reference electrode compartment made contact with the main compartment *via* a Luggin capillary. Cobaltocenium hexafluorophosphate was added to the cell at the end of a series of experiments. The cobaltocenium/cobaltocene couple served as an internal standard, and the reported potentials are referenced to its reversible potential, which in acetonitrile is -0.93 V *vs* aqueous SCE.²⁶ Solutions were purged with high-purity nitrogen or argon that had been presaturated with acetonitrile.

The data were obtained using an EG & G Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat with either a 176 or a 276 current follower. A PAR Model 175 universal programmer was used to apply the triangular waveform for cyclic voltammetry. Solution resistance was partially compensated by positive feedback. The data were recorded with either a Nicolet 4094 or a 4094C digital oscilloscope that was interfaced to an IBM PC (8 MHz, 80286 system).

All the data obtained were subjected to both background subtraction and correction for residual uncompensated solution resistance. Background signals were obtained in the absence of the electroactive species for subsequent subtraction. Correction for solution resistance was carried out as described earlier.⁴⁴ The solution resistance to be corrected for was calculated from the solution resistivity (from the literature^{12,44}), the size of the tip of the support, and the electrode radius.⁴³ The effectiveness of these resistance corrections has been confirmed in a number of studies of heterogeneous electron-transfer kinetics.¹²⁻¹⁴ As a further test of the accuracy of the corrections, the procedures were applied to voltammograms obtained at constant sweep rate but with increasing concentration (1–10 mM) of 2,3-butanedione. The separation in peak potentials in the corrected voltammograms remained constant though the current (and hence any residual *iR* error) increased by a factor of 10. Simulations of the voltammograms were performed as described previously.¹²⁻¹⁵ Diffusion coefficients needed to calculate k_s were estimated from the correlation with molecular weight reported earlier.¹²

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The procedures for homogeneous redox catalysis have been described elsewhere.¹³ It was not possible to add alumina directly to the cell (to remove traces of water) because some of the catalyst and diketone were adsorbed, thus changing their concentrations to an unknown degree. Concentrations must be accurately known in the technique of homogeneous redox catalysis.

The normal pulse voltammetry (NPV) data were obtained using a PAR Model 273 potentiostat/galvanostat interfaced with a Model 303A static mercury drop electrode operating in the static mercury drop mode. An IBM-compatible PC interfaced with the potentiostat was used to control the experiment and to collect the data. The solution resistance was measured prior to each experiment and was 85% compensated through positive feedback.

Theoretical curves for NPV⁴⁵ were generated and fit to the data by adjusting the standard heterogeneous electron-transfer rate constant (k_s), the transfer coefficient (α), and its dependence on potential. The reversible half-wave potential $E_{1/2}$ was determined by simulating cyclic voltammograms obtained during the same experiment.

Molecular Modeling. Calculations were performed using a Tektronix CAche workstation equipped with MOPAC 6.0 version 2.8.2 software that incorporates the semiempirical method AM1,⁴⁶ which calculates heats of formation. Calculations for the radical anions were performed by setting charge = -1 (Dewar's half-electron method). All calculations correspond to isolated gas-phase molecules at 298 K.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE9100281. J.C.R. was supported by a National Science Foundation Graduate Fellowship.

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