

Electron-Transfer Reactions Accompanied by Large Structural Changes. 1.

Lucigenin-10,10'-Dimethyl-9,9'-biacridylidene Redox System

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Abstract: The reduction of lucigenin, 10,10'-dimethyl-9,9'-biacridinium ion, proceeds first to the cation radical and then to the neutral molecule. The homogeneous redox equilibrium, dication + neutral molecule (k_f) \rightleftharpoons two cation radicals (k_b), is solvent dependent and is shifted to the left by polar solvents. In dichloromethane at -50°C the cyclic voltammogram for the reduction of the dication shows two reversible one-electron redox couples, which implies not only the stability of the cation radical, but also the metastable existence of the neutral molecule in a twisted configuration resembling that of lucigenin. Similar behavior was observed at -50°C in *N,N*-dimethylformamide, in which case the two electron transfers were not resolved. The kinetics of the configurational change, twisted neutral (B) (k_p) \rightarrow most stable form (A), could be studied by double potential step chronoamperometry over the temperature range $+23$ to -20°C , with apparent first-order rate constants ranging from 300 to 3 s^{-1} . The activation energy for the transformation was found to be equal to 16.4 kcal/mol.

A number of electron-transfer reactions have been reported which involve conformational changes before or after heterogeneous charge transfer at an electrode. For organic redox systems, 1,3,5,7-cyclooctatetraene (COT) is a classic example.¹⁻⁶ COT exists in the so-called tub conformation, while a more planar structure is adopted by the anion radical,⁷ and thus the conformation of COT⁻ resembles that of the planar dianion, COT²⁻. The early work of Allendoerfer and Rieger¹ showed that electron transfer to COT at electrodes is slow and that the activation energy roughly corresponds to that observed for the inversion of COT, a process which is believed to proceed via a planar transition state.⁸ Another pertinent example of an electron-transfer process accompanied by ring flattening is found in the reduction of 3,8-dimethyl-2-methoxyazocine (DMMA), which parallels that of COT.^{9,10}

In this paper, we report the details of the voltammetric behavior of lucigenin (B^{2+}) to 10,10'-dimethyl-9,9'-biacridylidene (A). The voltammetry of this redox system has previously been reported¹¹⁻¹³ to take place according to Scheme III, a proposal which we found highly unlikely and which prompted our reinvestigation. Since the most stable forms of the two oxidation states differ considerably in structure, it could be expected that the reduction process, in analogy to the observations for COT, would involve a slow electron-transfer step. Although the voltammetric behavior of B^{2+} is very similar to that observed for COT in liquid ammonia,⁶ the results that we report here can be generalized to show that the reduction of B^{2+} and related substances is best described by two reversible one-electron transfers followed by a chemical step, i.e., the configurational change, and that the term slow electron transfer for such systems is not applicable.

Results

Throughout this paper the compounds are identified by capital letters, which represent actual configurations as illustrated in Scheme II and which are discussed in detail later. The oxidation state is indicated by the formal charge. Thus, lucigenin and 10,10'-dimethyl-9,9'-biacridylidene are abbreviated B^{2+} and A, respectively.

The reduction of B^{2+} at platinum electrodes in (a) dichloromethane and (b) *N,N*-dimethylformamide (DMF) at room temperature is illustrated in Figure 1. The reference electrode used throughout this study was Ag/Ag^+ in acetonitrile separated from

the voltammetric solution by porous glass.¹⁴ The measured potentials were converted to volts vs. SCE by addition of 0.36 V. The significant features of the voltammograms are that in dichloromethane (a) the reduction peak is broad and exhibits a shoulder indicating successive one-electron transfers with an appreciable difference in the standard potentials, while in DMF (b) the reduction peak is much sharper, indicative of a smaller separation in standard potentials for the two electron transfers. In dichloromethane some oxidation current is observed on the backward scan, corresponding to the oxidation of the cation radical ($\text{B}^{\cdot+}$) back to the dication, B^{2+} , but in both cases the major product under the conditions of the experiment was the two-electron reduction product, 10,10'-dimethyl-9,9'-biacridylidene (A), the oxidation of which is seen as the major peak on the backward scans of both voltammograms. The difference in peak potentials for the reduction of B^{2+} and the oxidation of A ($\sim 790\text{ mV}$ in DMF) suggests that important changes in configuration are associated with the electron transfers.

The effect of lowering the temperature during the voltammetric reduction of B^{2+} in either (a) dichloromethane or (b) DMF is shown in Figure 2. At -50°C in both solvents the reductions appear to be reversible processes, indicating the finite lifetimes of both the cation radical and the neutral species in configurations

- (1) R. D. Allendoerfer and P. H. Rieger, *J. Am. Chem. Soc.*, **87**, 2336 (1965).
- (2) B. J. Huebert and D. E. Smith, *J. Electroanal. Chem.*, **31**, 333 (1971).
- (3) R. D. Allendoerfer, *J. Am. Chem. Soc.*, **97**, 218 (1975).
- (4) B. S. Jensen, A. Ronlán, and V. D. Parker, *Acta Chem. Scand., Ser. B*, **B29**, 394 (1975).
- (5) A. J. Fry, C. S. Hutchins, and L. L. Chung, *J. Am. Chem. Soc.*, **97**, 591 (1975).
- (6) W. H. Smith and A. J. Bard, *J. Electroanal. Chem.*, **76**, 19 (1977).
- (7) M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Am. Chem. Soc.*, **91**, 7521 (1969).
- (8) N. L. Allinger, J. T. Sprague, and C. J. Finder, *Tetrahedron*, **29**, 2519 (1973), and references cited herein.
- (9) J. L. Mills, R. Nelson, S. G. Shore, and L. B. Anderson, *Anal. Chem.*, **43**, 157 (1971).
- (10) L. B. Anderson, J. F. Hansen, T. Kakihana, and L. A. Paquette, *J. Am. Chem. Soc.*, **93**, 161 (1971).
- (11) K. D. Legg and D. M. Hercules, *J. Am. Chem. Soc.*, **91**, 1902 (1969).
- (12) K. D. Legg, D. W. Shive, and D. M. Hercules, *Anal. Chem.*, **44**, 1650 (1972).
- (13) S. Wada, K. Maeda, and K. Nakada, *Nippon Kagaku Kaishi*, 639 (1977).
- (14) N. S. Moe, *Anal. Chem.*, **46**, 968 (1974).

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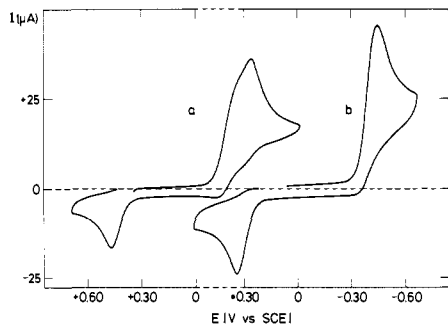


Figure 1. Cyclic voltammograms for the reduction of lucigenin (B^{2+}) at room temperature in (a) dichloromethane and (b) DMF containing Bu_4NBF_4 (0.1 M); voltage sweep rate 86 mV/s.

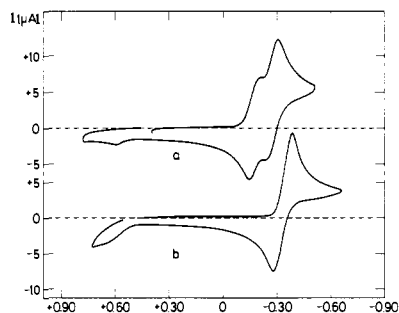


Figure 2. Cyclic voltammograms for the reduction of lucigenin (B^{2+}) at $-50\text{ }^\circ\text{C}$ in (a) dichloromethane and (b) DMF containing Bu_4NBF_4 (0.1 M); voltage sweep rate 86 mV/s.

similar to that of B^{2+} . The oxidation of the stable form of the neutral A is now observed only as a minor peak on both voltammograms. The difference in reversible potentials for reduction of the dication and the cation radical in dichloromethane is about 80 mV.

The room-temperature voltammogram of B^{2+} in dichloromethane suggests that B^+ resulting from one-electron reduction is longer lived than the initially formed two-electron reduction product (B). This is confirmed by the potential-step sweep voltammograms^{15,16} shown in Figure 3. The potential was stepped first to near the foot of the reduction wave and then scanned in the positive direction after a delay of 20 s (1 in Figure 3). A small oxidation peak due to B^+ was observed. In successive experiments the hold potential was made more negative by 50-mV increments. This resulted in first an increase in the cation radical oxidation peak current (1–3) and then a decrease (3–5) as the potential became more negative and B^+ was reduced to the unstable form, B, of the product which rapidly converts to A.

Rotating ring disk electrode (RRDE) voltammetry indicates that the reduction current can be quantitatively accounted for by the oxidation of B^+ , B, and A. In Figure 4a the disk potential was scanned over the region where reduction of B^{2+} occurs in dichloromethane with the ring potential locked at +0.7 V where all three reaction products are oxidized. The ratio of normalized ring current to the disk current was found to be equal to 1.0 and independent of the angular rotation rate (ω) of the RRDE. With the ring potential locked at +0.15 V where only B^+ and B are oxidized (Figure 4b), the ratio of the normalized ring current to the disk current was considerably less than unity and dependent upon ω . That B^+ is more stable than B is also indicated by the RRDE experiments (Figure 4b). The ring current goes through a maximum as the disk potential passes through the region where only the first charge transfer occurs to that where both processes take place.

The kinetics of the reaction $B \rightarrow A$ (Scheme II) were studied by double potential step chronoamperometry.¹⁷ Initially, data

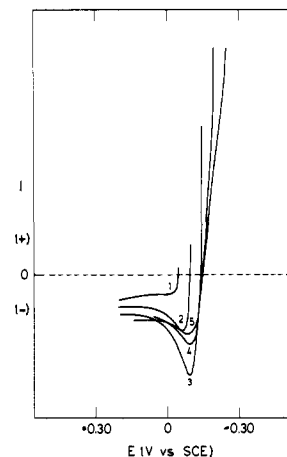


Figure 3. Potential-step sweep voltammograms of lucigenin (B^{2+}) at room temperature in dichloromethane containing Bu_4NBF_4 (0.1 M). Hold potentials: (1) -0.05 V , (2) -0.10 V , (3) -0.15 V , (4) -0.20 V , (5) -0.25 V ; voltage sweep rate 86 mV/s.

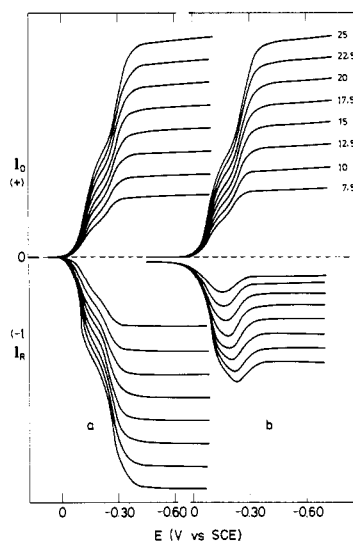
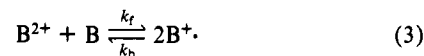


Figure 4. RRDE voltammograms for the reduction of lucigenin (B^{2+}) at room temperature in dichloromethane containing Bu_4NBF_4 (0.1 M). Ring potential locked at (a) $+0.70\text{ V}$ and (b) $+0.15\text{ V}$. The angular rotation rate ($\omega = 2\pi f$) is varied between $\omega^{1/2} = 7.5\text{ s}^{-1/2}$ and $\omega^{1/2} = 25\text{ s}^{-1/2}$.

from experiments conducted in DMF were compared with a theoretical working curve for an EEC mechanism (eq 1 and 2)



constructed in the manner described by Bard¹⁸ from data obtained by digital simulation.¹⁹ Experimental data did not fit the EEC working curve. A good fit was obtained when experimental data were compared to a working curve simulated for a mechanism taking into account the homogeneous redox equilibrium (eq 3)



where the equilibrium constant, $K_3 = k_f/k_b$, was estimated to be equal to 2.17 from analysis of the voltammetric peak,²⁰ and the

(17) W. M. Schwarz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).

(18) W. V. Childs, J. T. Maloy, C. P. Keszthelyi, and A. J. Bard, *J. Electrochem. Soc.*, **118**, 874 (1971).

(19) S. Feldberg in "Electroanalytical Chemistry", Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York 1969, p 199.

(20) R. L. Myers and I. Shain, *Anal. Chem.*, **41**, 980 (1969).

(15) L. Papouchado, J. Bacon, and R. N. Adams, *J. Electroanal. Chem.*, **24**, App 1 (1970).

(16) A. Ronlan, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **95**, 7132 (1973).

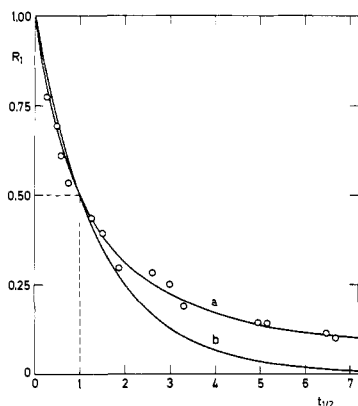


Figure 5. Double potential step chronoamperometric results at 23 °C for the reduction of lucigenin (B^{2+}) in DMF containing Bu_4NBF_4 (0.1 M). The circles are experimental values, and the lines show the results of digital simulation for the EEC mechanism (a) including and (b) without the homogeneous redox equilibrium (eq 3). Potential-step times varied between 1 and 100 ms.

Table I. Effect of Temperature on Apparent First-Order Rate Constants Determined by Double Potential Step Chronoamperometry^a

temp, °C	k_{app}, s^{-1}	
	$[B^{2+}] = 5 \times 10^{-3}$	$[B^{2+}] = 10^{-2}$
23	314	365
10	82	
9		76
0	28	31
-10	9.0	12
-20	2.8	2.9

^a Determined in DMF containing Bu_4NBF_4 (0.10 M) for the configuration change following reduction of 10,10'-dimethyl-9,9'-bianthrone ion (B^{2+}).

rate constants k_f and k_b were taken to be large in comparison to k_p , the rate constant for the configurational change. The simulation assumed reduction of B^{2+} and B^+ to B at the more negative potential step and oxidation of B and B^+ to B^{2+} at the lower potential where A is electroinactive. Experimentally, this situation was accomplished using a 500-mV potential step which was nearly symmetric about the reduction peak potential. Finite difference forms of the rate eq 4–6 were used in the simulation. Experimental

$$-d[B]/dt = k_f[B][B^{2+}] - k_b[B^+]^2 + k_p[B] \quad (4)$$

$$-d[B^{2+}]/dt = k_f[B][B^{2+}] - k_b[B^+]^2 \quad (5)$$

$$\frac{1}{2}d[B^+]/dt = k_f[B][B^{2+}] - k_b[B^+]^2 \quad (6)$$

data for a representative set of experiments along with the two working curves described above are shown in Figure 5.

Apparent first-order rate constants, k_{app} , at two different concentrations of B^{2+} (5 and 10 mM) over a temperature range of 43 °C in DMF are summarized in Table I. Values from about 300 to 3 s⁻¹ were observed. A plot of $\log k_{app}$ vs. $1/T$ (5 mM) is shown in Figure 6. Least-squares analysis of the data gave slopes equal to -3.57×10^3 (5 mM) and -3.58×10^3 (10 mM) with correlation coefficients of -0.9998 and -0.9987, respectively. From the slopes an activation energy (E_a) equal to 16.4 kcal/mol was estimated.

Discussion

The voltammetric behavior of B^{2+} in dichloromethane at -50 °C (Figure 2) indicates that the reduction proceeds by two successive, reversible, one-electron transfers leading first to the cation radical and then to the neutral molecule, both with a configuration similar to that of B^{2+} . This configuration involves an atomic arrangement in which the two tricyclic ring systems are twisted considerably around the central bond (Scheme I).²¹ In accordance

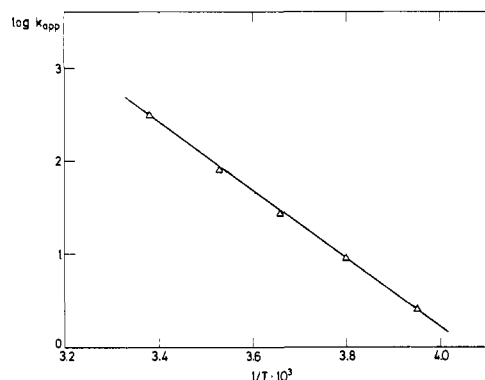
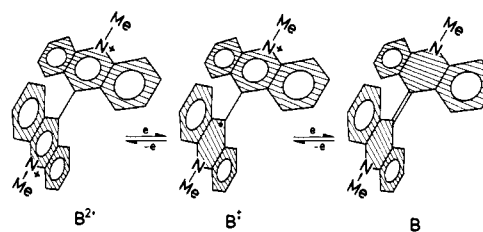
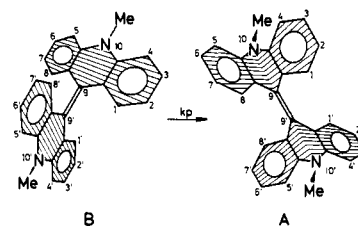


Figure 6. Arrhenius plot of apparent first-order rate constants obtained by double potential step chronoamperometry; $[B^{2+}] = 5 \times 10^{-3}$.

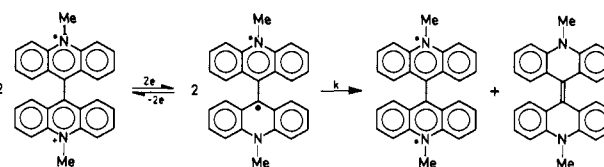
Scheme I



Scheme II



Scheme III



with previous discussion on the interconversion of the two forms of the related bianthrone system, we have been using the capital letter B for this configuration and A for the more stable folded structure (Scheme II).²²

The observation that the peak potentials measured in dichloromethane are more positive than those measured in DMF is in agreement with the common observation that positive charge is more readily neutralized and more difficultly formed in dichloromethane as compared to more polar solvents.²³ Solvation

(21) We do not attempt in this paper to answer the question of whether the B configuration of the neutral molecule is best represented as a biradical or as a species having a double bond between the two ring systems. The notation has been chosen in agreement with the results obtained for the related bianthrone.²²

(22) G. Kortüm, *Ber. Bunsenges. Phys. Chem.*, **78**, 391 (1974), and references cited herein.

(23) For the oxidation of aromatic hydrocarbons and related materials it is found that oxidation potentials measured in dichloromethane are 30–150 mV more positive than those observed in acetonitrile. Due to the variations in the potential shifts, this observation cannot be accounted for as being solely due to the difference in liquid junction potential in going from one solvent to another. Likewise, the separation between the first and second oxidation peak is greater in dichloromethane than in acetonitrile, resulting in smaller values of the equilibrium constants for disproportionation in the former solvent. Cf., e.g., O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).

of cations is particularly strong in dipolar aprotic solvents which carry a high degree of electron density on unscreened oxygen atoms as in the case of DMF and dimethyl sulfoxide (Me_2SO). Accordingly, cation solvation decreases along the series, $\text{Me}_2\text{SO} > \text{DMF} > \text{MeCN} > \text{CH}_2\text{Cl}_2$, and thus it is expected that peak potentials for reduction of positively charged ions, in the absence of other effects, will trend toward more negative values in going from CH_2Cl_2 to Me_2SO . The reduction potential of B^{2+} , a dipositive ion, is more affected than that of the cation radical, which results in a larger separation between the first and second electron transfers in dichloromethane (80 mV) than in DMF (20 mV). This finding is in analogy to the observation that ΔE° for the oxidation of tetra-*p*-anisylethylene decreases from 92 to 4.5 mV when the solvent system is changed from dichloromethane to a mixed solvent to acetonitrile²⁴ and to similar effects which have been observed in related systems.²⁵

At room temperature the change from B to the more stable structure A is too fast to allow the observation of current, at low sweep rates, for the oxidation of B to B^+ , and the only oxidation current observed is due to the process $\text{A} - 2e^- \rightarrow \text{B}^{2+}$. At the same time, the two reduction peaks observed in dichloromethane at -50°C have nearly merged, the first peak being barely visible as a shoulder on the second. This decrease in ΔE_p should be seen in light of the relative stability of B^+ and B. The preferred configuration of the cation radical is similar to B^{2+} , as already indicated by the choice of notation, and the reactivity of this species is therefore not due to a direct configurational change. However, because of the small difference in E° values of the two one-electron transfers, the formation of B^{2+} and reactive B from B^+ in a disproportionation reaction (reverse of eq 3) is a feasible reaction. The disproportionation equilibrium constant, $K_{-3} = k_b/k_f (=1/K_3)$, in dichloromethane is equal to about 0.05. The apparent first-order rate constant for the disappearance of B^+ is equal to $k_p K_{-3}$, and the disproportionation equilibrium causes the overall rate from B^+ to be considerably lower than the direct reaction of B. Thus, the kinetic shift of the peak due to the reduction of the cation radical is less pronounced than that for the reduction of the dication. The overall result is then a smaller ΔE_p value at room temperature than at -50°C where the rate of the configurational change is almost negligible. The lower reactivity of B^+ also explains the observation of the trace current for the first reduction peak in the room-temperature voltammogram in dichloromethane (Figure 1) and the potential-step voltammograms (Figure 3) as well as the unusual maximum in the ring current during the RRDE experiment (Figure 4).

Thus, the cyclic voltammetric data can be summarized as follows. The reduction of lucigenin in dichloromethane and DMF at room temperature proceeds via two closely spaced, reversible, one-electron transfers followed by the reaction of B to A. There is no indication that the electron transfers are slower than those normally observed with aromatic compounds in aprotic media. In the very narrow potential region at the foot of the first voltammetric wave, B^+ predominates over B, and a considerable portion of the reaction will proceed via disproportionation of B^+ .

Disproportionation was also proposed by Hercules and co-workers^{11,12} but not in the correct context. The importance of the configurational change was not recognized, and the disproportionation of the cation radical was assumed to be the rate-determining step in the reaction. In that the configurational change is relatively slow, the disproportionation can be considered as a fast equilibrium. The postulation of slow disproportionation led to the erroneous interpretation that any reverse current observed during cyclic voltammetry at high sweep rates in Me_2SO was due to oxidation of the cation radical. When considered in light of the comparable results obtained in this study at -50°C in DMF, it is obvious that the oxidation current in question is due to the overlapped waves involving oxidation of B and B^+ . Since cations are expected to be even better solvated in Me_2SO than

in DMF, the separation between the two electron transfers is expected to be even less than 20 mV in Me_2SO , precluding the possibility of observation of a single one-electron transfer. The peak potential separation for the cathodic and anodic processes during fast-scan cyclic voltammetry was reported to be close to 300 mV,¹² and this was discussed in relation to the reversibility of the electrochemical reaction. Since we find no evidence for slow electron transfer in this system, it is our view that the large peak separation was more likely due to an experimental artifact. A quantitative analysis of the data was attempted¹² by fitting experimental data to working curve, $\psi_p = f(\log \lambda_d)$, where ψ_p is the peak current function and λ_d is the dimensionless forward rate constant for disproportionation.²⁶ After normalization of the current-function data, a good fit was obtained. However, the analysis is not valid in view of the discussion above. It does point out the fact that working curves used in this type of analysis are often very similar for several mechanisms, and an observed fit of experimental data to a theoretical curve is a necessary but in itself insufficient criterion for the validity of a proposed mechanism.

Double potential step chronoamperometry is a reliable kinetic method for reactions proceeding at moderate rates. We have found that the analysis procedure devised by Bard¹⁸ where the normalized current ratio (R_1) is plotted vs. time in units of $t_{1/2}$, defined as the time at which R_1 equals 0.5, is a superior method for distinguishing between mechanisms. The $R_1-t_{1/2}$ curves for all mechanisms pass through a common point (time = $t_{1/2}$) and then diverge so that data taken at times equal to several $t_{1/2}$ differ substantially. This is demonstrated by the two theoretical curves in Figure 5 for mechanisms which differ only by the inclusion of the disproportionation side equilibrium in the otherwise identical EEC mechanism.

Kinetic data obtained by double potential step chronoamperometry using the working curve which takes into account eq 3 are summarized in Table I and shown graphically in Figure 5. The important feature in Figure 5 is that the experimental data measured out to times as great as $7t_{1/2}$ fit the curve including the fast equilibrium, which lies significantly above the curve for the unperturbed EEC mechanism. The rate constants were calculated from the relationship $k_{\text{app}} = 1.24/t_{1/2}$, which comes from the simulation. Due to the difficulty in obtaining meaningful data for the temperature dependence of eq 3, we have used the constant value 2.17 for K_3 obtained by analysis of the voltammetric peak in the absence of the kinetic perturbation. Therefore, the resulting rate constants do not only reflect the configurational change but also contain a contribution from the deviation of the actual value of K_3 from 2.17. Comparison of lucigenin with compounds of related structure for which the temperature dependence of ΔE° is known²⁷ suggests that the maximum deviation, at 23°C , of K_3 from 2.17 amounts to approximately 50%, decreasing with decreasing temperature. Thus, the k_{app} values resulting from the present investigation can be used as good estimates for the real values of k_p . The fact that the rate constants observed were only slightly dependent on concentration further supports the validity of our mechanism assignment. The apparent reaction order in finite difference form²⁸ for the data at the two concentrations was found to be 1.2 ± 0.2 while the simulation predicted a value of ~ 1.4 . The activation energy (16.4 kcal/mol, expressed in these units to facilitate comparison with related data) obtained from the analysis of the Arrhenius plots (Figure 6) does, like the rate constants, contain a contribution from the temperature dependence of K_3 . However, the value of E_a is only moderately dependent on variations in K_3 , the 50% mentioned above giving rise to a deviation of only 1.5 kcal/mol in E_a . Thus, we are justified in discussing the measured activation energy in terms of the configuration change alone.

The geometry of a system related to B^{2+} , 9,9'-bianthryl, has been investigated in detail by spectroscopic methods.²⁹⁻³¹ In

(24) U. Svanholm, B. S. Jensen, and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 907 (1974).

(25) J. Phelps and A. J. Bard, *J. Electroanal. Chem.*, **68**, 313 (1976).

(26) M. Mastragostino, L. Nadjo, and J.-M. Savéant, *J. Electroanal. Chem.*, **13**, 721 (1968).

(27) F. Ammar and J.-M. Savéant, *J. Electroanal. Chem.*, **47**, 115 (1973).

(28) B. M. Bezilla, Jr., and J. T. Maloy, *J. Electrochem. Soc.*, **126**, 579 (1979).

analogy, the angle between the two planar tricyclic ring systems of B^{2+} is expected to be close to 90° . This indicates that the gain in resonance energy associated with a rotation around the central bond to lower angles is insufficient to overcome the steric interaction introduced between hydrogen atoms in positions 1,8 and 1',8'. For neutral B the gain in energy associated with the formation of a formal double bond between the ring systems is much more important, and thus the equilibrium angle for this species is expected to be significantly smaller than 90° . A molecular model demonstrates, assuming the tricyclic rings to be planar in the neutral molecule as well as in the dication, that the nonbonded interactions become serious, the H-H distance being close to twice the van der Waals radius, when the angle approaches 45° , and thus it is expected that the equilibrium angle in the neutral molecule is somewhat greater than this value. The cation radical is expected to attain the lowest energy by adopting an angle somewhere between these values, since an electron distribution involving a double bond between the ring systems is of lesser importance for this system. Thus, the stepwise introduction of two electrons into B^{2+} is associated with a successive decrease in the dihedral angle from 90° to approximately 50° . However, the activation energy for this rotation is negligible, and thus no effect is expected to be observed by conventional electrochemical techniques. In accordance with this view, two consecutive, reversible, one-electron transfers are observed by cyclic voltammetry for the reduction of B^{2+} to B. The important question remains as to how the transformation of B to A takes place.

Valuable information on the activation energy encountered during a simple rotation around the central bond in such systems can be gained from studies on the rate of racemization of optically active 9,9'-bianthrils. Thus, it was found that heating 2,2'-bis-(methoxycarbonyl)-9,9'-bianthryl in dimethyl phthalate under nitrogen at 220°C for 6 h resulted in no change in the rotation.³² By application of the Arrhenius equation, assuming the frequency factor for this process to be close to that observed for 1,1'-binaphthyls, the value of the activation energy was estimated to be greater than 42 kcal/mol. However, when the experiment was carried out in triglyme in the presence of oxygen, 83% racemization was observed after only 1.5 h. It was suggested that this difference was due to the reversible addition of oxygen or a species derived from oxygen attack on the solvent to one of the anthracene units, resulting in a more tetrahedron-like arrangement around one of the central carbon atoms in the latter case. Bearing in mind the relatively low activation energy, 16.4 kcal/mol, that we observed for the configurational change $B \rightarrow A$, it seems likely on comparison with the above discussion that this process does not take place as a simple rotation around the central bond but must involve a more complicated change in the molecular geometry. The same conclusion was arrived at for the transformation of the B form to the A form for bianthrone.³³ For the B form, it was found that the equilibrium dihedral angle between the two planar halves of the molecule was close to 57° . The strain potential energy curve increases dramatically as the angle approaches 40° , and below this angle a configuration in which the two anthracene units are folded along the 9-10 axis is more stable. This latter configuration is identical with the A form when the angle equals 0° .³⁴ A rough estimate of the activation barrier for the transformation was calculated as being equal to the energy at the intersection of the potential energy curves of the two forms. The value obtained in this manner was close to 20 kcal/mol, in reasonably good agreement with the results previously reported for bianthrone and

alkyl bianthrone, which all fall in the range 13-15 kcal/mol.³⁵⁻³⁷

The activation energy that we observe for the conversion of B to A, 16.4 kcal/mol, suggests in analogy that this process involves the folding of the tricyclic systems at an early stage in the reaction. It may even be that the equilibrium structure of B includes a slight folding in the tricyclic rings in contrast to the results obtained for bianthrone. However, the present system differs from bianthrone in an important way. The angle at the 10-position decreases from 120° to a lower value on going from the planar structure to a folded geometry. This decrease is opposed by the carbonyl group in the bianthrone but is facilitated by the tertiary amino group in the biacridylidene system. The angles for the unstrained conformers are 120° and 107° for the carbonyl and the tertiary amino groups, respectively. Molecular models demonstrate clearly how the folding of the tricyclic systems decreases the steric hindrance to rotation. While rotation of a planar system forces the interacting hydrogen atoms to move along the same path, the process of folding allows one of the hydrogen atoms of one ring, i.e., H_1 , to pass between H_1' and H_8' of the other ring and so forth, resulting in an overall lowering of the activation energy for rotation as compared to planar systems.

For lucigenin the energy of the π system varies only a little with the structural changes allowed at room temperature, i.e., variation of the dihedral angle between 90° and approximately 50° . Thus, electron transfer takes place only to molecules close in energy to the stable dication, and the voltammetric response is that expected for a reversible system. In this respect the behavior of B^{2+} is at variance with that observed for COT in which the ring flattening is associated with a considerable variation of the LUMO energy.³⁸ After injection of the two electrons, the activation energy for the configurational change is low enough so that the reaction proceeds rapidly at room temperature, the overall process being of the EEC type.

The situation for the oxidation of A to B^{2+} is different. In this case the cation radical is formed in the energetically unfavorable A configuration, and a fast conversion of $A^{\cdot+}$ to $B^{\cdot+}$ ensues, accelerated by the release of steric strain. The cation radical in configuration B is then formed at a potential where further oxidation to B^{2+} occurs readily. Thus, the oxidation of A is best described as a simple ECE process, where we do not make the distinction between heterogeneous and homogeneous electron transfer in the second E step.

We can generalize at this point using the configuration of the cation radical as a reference. For a two-electron process where the cation radical is the intermediate oxidation state, the reaction will be of the EEC type if the preferred configuration of the cation radical resembles that of the substrate and of the ECE type if the configuration of the cation radical resembles that of the product. In the lucigenin case, reduction fits the first category (EEC) while oxidation of 10,10'-dimethyl-9,9'-biacridylidene falls in the latter category (ECE). The overall EEC-ECE (or ECE-EEC) scheme for a full cycle apparently is applicable to many systems belonging to this class of compounds, i.e., bianthrone^{35,39,40} and dithioxanthylene,⁴¹ as well as compounds with more exotic structures such as bis[α -(1',2'-dithio-3'-ylidene)phenacyl]s⁴² and might as well be operative for 1,3-dimethylenecyclobutanes,⁴³ although the voltammetry of the latter system was suggested to be consistent with an ECE path in both directions. These and

(35) Z. R. Grabowski and M. S. Balasiewicz, *Trans. Faraday Soc.*, **64**, 3346 (1968).

(36) T. Bercovici and E. Fischer, *Isr. J. Chem.*, **7**, 127 (1969).

(37) L. J. Dombrowski, C. L. Groncki, R. L. Strong, and H. H. Richtol, *J. Phys. Chem.*, **73**, 3481 (1969).

(38) The voltammetric behavior of COT will be the subject of a following paper in this series.

(39) Z. R. Grabowski, B. Czochralska, A. Vincenz-Chodkowska, and M. S. Balasiewicz, *Discuss. Faraday Soc.*, **45**, 145 (1968).

(40) M. E. Peover, *Discuss. Faraday Soc.*, **45**, 177 (1968).

(41) P. T. Kissinger, P. T. Holt, and C. N. Reilley, *J. Electroanal. Chem.*, **33**, 1 (1971).

(42) C. T. Pedersen, V. D. Parker, and O. Hammerich, *Acta Chem. Scand., Ser. B*, **B30**, 478 (1976).

(43) M. Horner and S. Hünig, *J. Am. Chem. Soc.*, **99**, 6122 (1977).

(29) F. Schneider and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **72**, 1155 (1968); **74**, 624 (1970).

(30) M. Hoshino, K. Kimura, and M. Imamura, *Chem. Phys. Lett.*, **20**, 193 (1973).

(31) N. Nakashima, M. Murakawa, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **49**, 854 (1976).

(32) C. Koukotas and L. H. Schwartz, *J. Chem. Soc., Chem. Commun.*, 1400 (1969).

(33) R. Korenstein, K. A. Muszkat, and S. Sharafy-Ozeri, *J. Am. Chem. Soc.*, **95**, 6177 (1973).

(34) This angle is rather poorly defined since it is not between planar ring systems.

similar systems are under further investigation.

Experimental Section

Lucigenin, as the nitrate salt, was a commercial sample and was recrystallized from ethanol before use. The counterion is electroinactive in the potential range studied and did not influence the voltammetric results. Cells, electrodes, reference electrodes, and voltammetric instrumentation were as previously described.^{44,45} Beckman platinum-bottomed

electrodes (No. 39273) were used as working electrodes for cyclic voltammetry.

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(44) E. Ahlberg, B. Svensmark, and V. D. Parker, *Acta Chem. Scand., Ser. B*, **B34**, 53 (1980).

(45) O. Hammerich and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 4289 (1974).

Electron-Transfer Chemistry of the Merostabilized 3,5,5-Trimethyl-2-morpholinon-3-yl Radical

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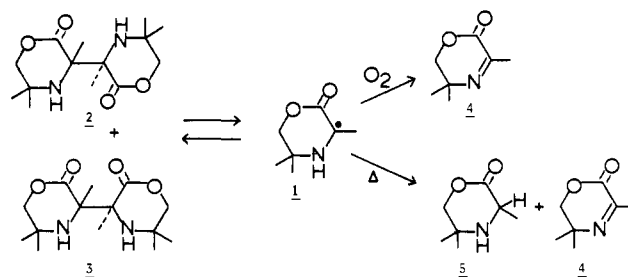
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Abstract: Reductions of 5,6-dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one (**6**) to 5,5-dimethyl-3-phenyl-2-morpholinone (**8**), 2-benzoyl-4,4-dimethyl-2-oxazoline (**9**) to 2-(hydroxyphenylmethyl)-4,4-dimethyl-2-oxazoline (**10**), 4-(diphenylmethylene)-2,5-cyclohexadienone (**12a**) to diphenyl(*p*-hydroxyphenyl)methane (**14a**), 4-[bis(4-hydroxyphenyl)methylene]-2,5-cyclohexadienone (**12b**) to tris(*p*-hydroxyphenyl)methane (**14b**), benzil (**17**) to benzoin, and substituted benzils (**17a-c**) to substituted benzoin by 3,5,5-trimethyl-2-morpholinon-3-yl radical are described. Intermediate radicals 5,5-dimethyl-3-phenyl-2-morpholinon-3-yl (**7**), diphenyl(*p*-hydroxyphenyl)methyl (**13a**), and tris(*p*-hydroxyphenyl)methyl (**13b**) are characterized by EPR spectroscopy. Kinetic analyses of the reductions of **6**, **9**, **17**, and **17a-c** are described, and mechanisms and rate laws are shown in Schemes II, III, and VII. Reduction reactions most likely occur by electron transfer. Evidence for electron transfer includes an isotope effect for disproportionation of **1** equal to 1.10 ± 0.09 , correlation of the logarithm of the relative rates of reduction of benzils with σ^+ with a ρ of 1.7 ± 0.1 , and observation of electron transfer from **1** to tetracyanoethylene, dianisylloxammonium perchlorate (**21**), and paraquat (**20**).

Radicals bearing electron-donating and electron-withdrawing substituents have unusual stability and persistence. The synergistic effect of this substitution has been described by Katritzky and co-workers as merostabilization,¹ by Balaban and co-workers in terms of push-pull stabilization,² and by Viehe as a captodative substituent effect.³ The preparation, stability, and reactivity of these radicals have been recently reviewed by Viehe and co-workers.⁴ The only mode of reactivity described is basically radical combination. We report in detail our results, previously communicated,⁵ on the one electron-transfer reactivity of an aminocarboxy-substituted free radical, 3,5,5-trimethyl-2-morpholinon-3-yl (**1**, Scheme I).

We have reported that 3,5,5-trimethyl-2-morpholinon-3-yl is formed when a mixture of the meso and *dl* dimers (**2** and **3**, respectively) of the radical are dissolved in benzene, chloroform, or ethanol solvent at ambient temperature.⁶ In chloroform solvent the ΔH° and ΔH^\ddagger for formation of **1** are 22 and 27 kcal/mol, respectively.^{6,7} The facility of bond homolysis and the persistence

Scheme I



of **1** have been discussed in terms of dipolar resonance stabilization of **1**.⁶ The methylmorpholinonyl radical **1** oxidizes in air to 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**4**) and disproportionates upon being heated at 80 °C to a 50:50 mixture of **4** and 3,5,5-trimethyl-2-morpholinone (**5**).

Results and Discussion

Reduction of 5,6-Dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one (6) by 3,5,5-Trimethyl-2-morpholinon-3-yl (1). A mixture of the meso and *dl* radical dimers **2** and **3** reacts with 5,6-dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one (**6**) in degassed methanol solvent to give a new radical species characterized by EPR spectroscopy as 5,5-dimethyl-3-phenyl-2-morpholinon-3-yl (**7**). The EPR spectrum shows a *g* value of 2.00399 and the

(1) Baldock, R. W.; Hudson, P.; Katritzky, A. R.; Soti, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1422.

(2) Balaban, A. T.; Caproin, M. T.; Negoita, N.; Baican, R. *Tetrahedron* **1977**, **33**, 2249.

(3) Stella, L.; Janousek, R.; Merényi, R.; Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1978**, **17**, 691.

(4) Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, **18**, 917.

(5) Burns, J. M.; Wharry, D. L.; Koch, T. H. *J. Am. Chem. Soc.* **1979**, **101**, 2750.

(6) Koch, T. H.; Olesen, J. A.; DeNiro, J. *J. Am. Chem. Soc.* **1975**, **97**, 7285.

(7) Bennett, R. W.; Wharry, D. L.; Koch, T. H. *J. Am. Chem. Soc.* **1980**, **102**, 2345.