

Electron Transfer Reactions Accompanied by Large Structural Changes. II. Rates and Activation Parameters for the Interconversion of Bianthrone Isomers

OLE HAMMERICH^a and VERNON D. PARKER^b

^a Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark and ^b Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

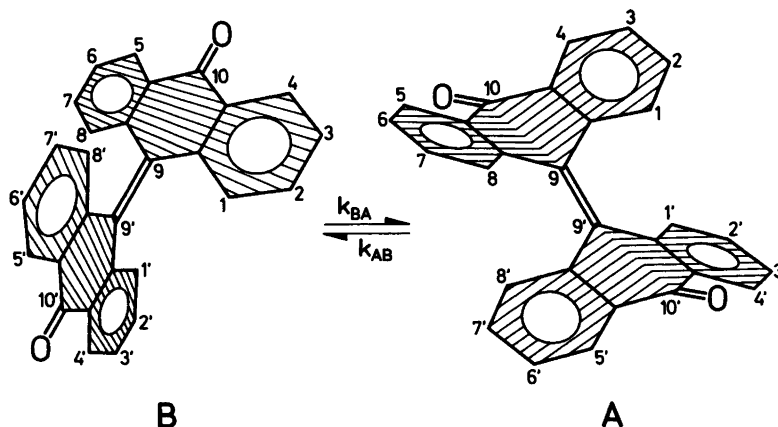
Two-electron reduction of bianthrone and treatment of bianthranyl with ethoxide ion lead to the formation of the stable bianthrone dianion. Oxidation of the dianion proceeds stepwise, first to the anion radical and then to the neutral molecule, both with configurations (B) similar to that of the dianion, but different from that of the most stable form (A) of bianthrone. The kinetics of the configuration

change $B \xrightarrow{k_{BA}} A$ were studied in *N,N*-dimethylformamide (DMF) by derivative cyclic voltammetry over the temperature range +4 to +37 °C with rate constants ranging from 1 to 20 s⁻¹. The activation energy for the transformation was found to be equal to 15.3 kcal/mol. The kinetics of the reverse process,

$A \xrightarrow{k_{AB}} B$, could be studied in DMF by polarography over the temperature range +15 to +70 °C. The

value of k_{AB} extrapolated to +25 °C was found to be equal to 0.022 s⁻¹ with an activation energy of 18.1 kcal/mol. The pre-exponential factors for the two processes are identical within the experimental error and lead to an activation entropy of -7 cal/deg mol.

We have recently determined the rate constant, k_p , and the activation energy for the reaction (1), where DMA(A) and DMA(B) refer to the stable and meta-stable structures of 10,10'-dimethyl-9,9'-biacridylidene.¹ The meta-stable form was observed directly



Scheme 1.

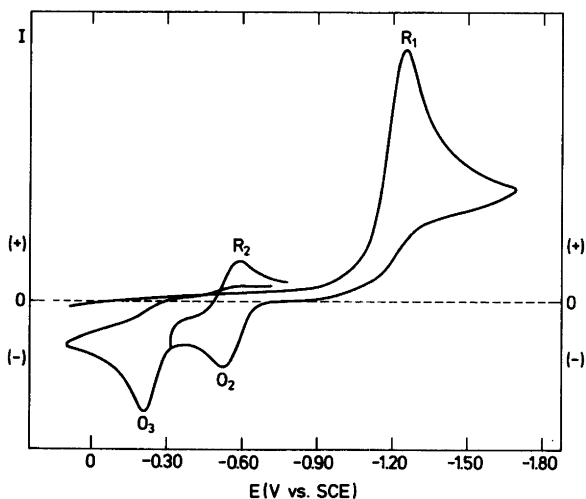


Fig. 1. Cyclic voltammogram for the reduction of bianthrone A, (1 mM) in DMF containing Bu_4NBF_4 (0.1 M). Voltage sweep rate = 100 mV/s.

by cyclic voltammetry at low temperatures and k_p was found to vary in the range $3-300 \text{ s}^{-1}$ in the temperature interval -20 to $+23^\circ\text{C}$. It was

suggested that a number of other apparently "slow" electron transfer reactions probably also involve fast electron transfer followed by slow intramolecular geometry changes. In this paper we describe the rates and activation parameters for the inter-conversion of the structural modifications, A and B, of bianthrone in DMF solution (Scheme 1). The meta-stable form B is formed *via* the dianion from reduction of A at an electrode. The dianion of B (2) is oxidized stepwise first to the anion radical (3), without configuration change and then to B (4) which undergoes configuration change to A (5).



The configurational change had previously been studied by Grabowski and Balasiewicz² using polarographic and voltammetric techniques in

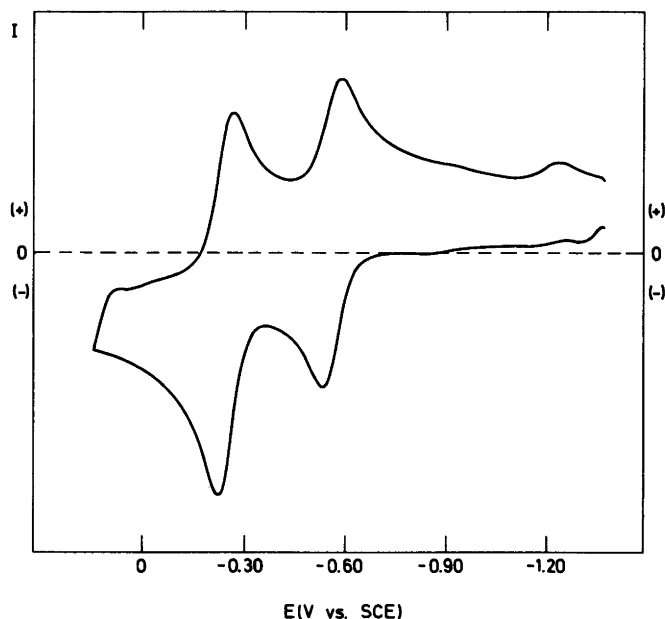


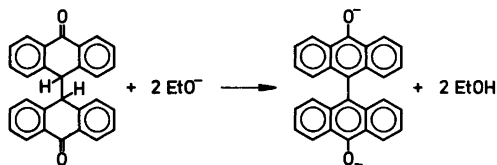
Fig. 2. Cyclic voltammogram for the oxidation of bianthrone dianion, B^{2-} , produced by reduction of A during a potential step to -1.35 V . Solvent is DMF containing Bu_4NBF_4 (0.1 M). Voltage sweep rate = 20 V/s.

aqueous 75–80 % phenol solutions. This study² was complicated by the fact that both products and intermediates interact significantly with the protic solvent system and thus the rate constants as well as the activation parameters reflect contributions from these interactions. Near the end of this investigation we also became aware of a spectroelectrochemical study by Olsen and Evans³ concerned with the rate of the configuration change $B \rightarrow A$ in DMF. The latter report was not addressed to the problem of the activation involved in reaction (5) which we consider to be the area of most general interest in these systems.

RESULTS

Cyclic voltammetric studies. The voltammetric behaviour of A under aprotic conditions has previously been reported.^{3–4} The results of this study are in close agreement with those obtained by Olsen and Evans³ and are illustrated in Figs. 1 and 2. During the first negative potential scan the reduction of A to B^{2-} was observed as a single cathodic peak, R_1 (-1.24 V vs. SCE, Fig. 1). The anodic counterpart of R_1 was absent on the reverse scan and instead, two peaks, O_2 (-0.53 V) and O_3 (-0.21 V), were observed due to the oxidation of B^{2-} to $B^{\cdot-}$ and B, respectively. No evidence for the primary intermediate formed at R_1 was found at sweep rates up to 1,000 V/s. When the scan was reversed again between O_2 and O_3 , R_2 (-0.59 V) corresponding to the reduction of $B^{\cdot-}$ to B^{2-} was observed. The reduction of B to $B^{\cdot-}$ was not observed at low sweep rates (0.02–1 V/s) due to conversion of B to A. Thus, the voltammetric behavior of A is totally consistent with eqns. (2)–(5).

To demonstrate unambiguously that the oxidation peaks O_2 and O_3 are in fact due to B^{2-} and $B^{\cdot-}$, a solution of B^{2-} in DMF was made from bianthrone by treatment with sodium ethoxide dissolved in ethanol (Scheme 2). Cyclic voltammetric analysis of this solution resulted, as ex-



Scheme 2.

pected, in a voltammetric pattern similar to that depicted in Fig. 1. During the scan in the negative direction a shoulder corresponding to the reduction of B to $B^{\cdot-}$ was barely discernible, while the two major reduction peaks were R_2 and R_1 due to reduction of $B^{\cdot-}$ and A, respectively. When the sweep rate was increased to 20 V/s two reversible couples, O_3/R_3 and O_2/R_2 , for the $B^{\cdot-}/B$ and $B^{2-}/B^{\cdot-}$ redox systems were observed, while R_1 had almost vanished. A similar result (Fig. 2) was obtained from a solution of A when the potential was first stepped to -1.35 V, where A is converted to B^{2-} , followed by a sweep at 20 V/s. These experiments demonstrate that the conversion of B to A is a process with a rate constant of the order of a few reciprocal seconds at room temperature.

Derivative cyclic voltammetric (DCV) studies. Due to problems with establishing base-lines for the measurement of peak current ratios, cyclic voltammetry is somewhat qualitative for kinetic studies. The precision problems can be overcome by derivative techniques and DCV has recently been presented as a quantitative kinetic technique.⁵ The method involves the measurement of R'_1 (I'_b/I'_f) which is the ratio of the first derivative peaks on the backward and forward scans of the cyclic voltammograms. As in ordinary cyclic voltam-

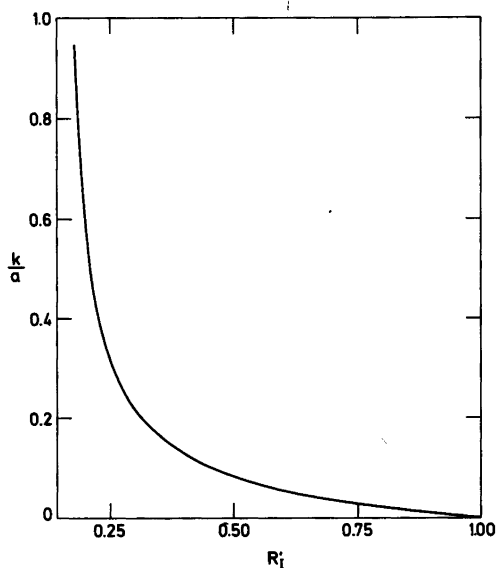


Fig. 3. Derivative cyclic voltammetry working curve for the EC mechanism (constructed from theoretical data provided by Dr. E. Ahlberg).

metry, rate constants are obtained by comparing experimental data with theoretical data corresponding to the mechanism of the reaction. For the EC mechanism, this comparison is made using the working curve illustrated in Fig. 3.

There is a special problem associated with the measurement of k_{BA} [eqn. (5)] connected with the fact that B is not the initial intermediate formed at the electrode. The normal mode to apply DCV is as a two-segment waveform where the intermediate is formed in the first half-cycle and converted back to substrate in the second. In this case a three-segment waveform is required, (i) the generation of B^{2-} , (ii) oxidation of B^{2-} in two consecutive steps and (iii) the reduction of B and $B^{\cdot-}$. Since the kinetic step involves the unimolecular reaction of B (5) any competing reactions of B will be reflected in the value of R'_1 . The reaction of B with B^{2-} [eqn. (6)] is favorable with an equilibrium constant of the order of 10^5 as demonstrated by Olsen and Evans.³ However, this reaction only involves a change in oxidation state and thus has no effect on the peak

currents in cyclic voltammetry. Reactions analogous to (6) are always present when we deal with multiple



electron transfers and peak current ratios are unity for all couples in spite of favorable equilibrium constants such as K_6 . Thus, it is not necessary to consider (6) as a competing reaction when carrying out DCV studies. On the other hand, the concentration profile of B is enormously affected by (6) and kinetic studies carried out by spectroelectrochemistry must take this into account.³

Two different approaches were used to generate B^{2-} . The first involved a waveform consisting of a step to a potential where A is reduced at a diffusion controlled rate followed by a normal two-segment triangular waveform encompassing the $B^{2-}/B^{\cdot-}$ and the $B^{\cdot-}/B$ couples. The input waveform and the normal and differentiated response curves are illustrated in Fig. 4. The second approach involved keeping the initial potential more negative than necessary to reduce A and a normal triangular wave to get the cyclic response. The latter method involves the continuous generation of B^{2-} and worked remarkably well.

Results using the potential step-cyclic method are summarized in Table 1. The values of k/a where k

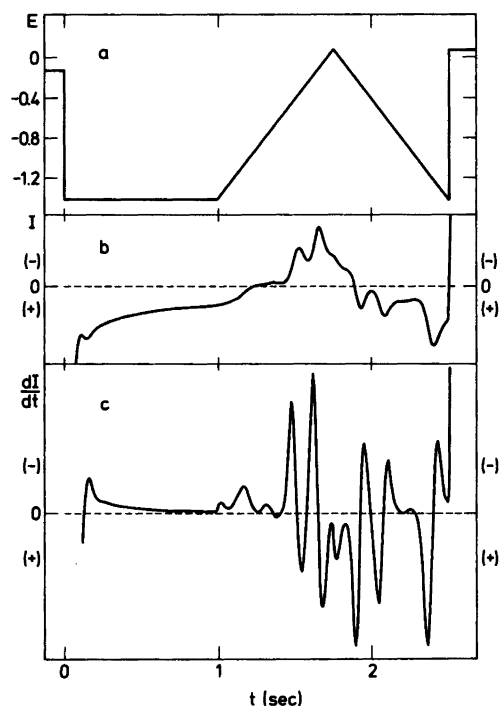


Fig. 4. Kinetic analysis of the configuration change $B \rightarrow A$ by derivative cyclic voltammetry. (a) Input waveform, (b) normal response curve and (c) differentiated response curve.

Table 1. Derivative cyclic voltammetry data for the kinetics of the configuration change of meta-stable bianthrone.

$v/V s^{-1}$	$t/^\circ C$	R'_1^a	k_{BA}/a	k_{BA}/s^{-1}
20	37	0.74	0.027	20
10	37	0.61	0.051	19
5	37	0.49	0.080	15
10	28	0.85	0.016	6.2
5	28	0.70	0.035	6.7
2	28	0.44	0.102	7.9
1	28	0.36	0.156	6.0
2	14	0.68	0.036	2.9
1	14	0.57	0.057	2.3
0.5	14	0.41	0.119	2.4
1	4	0.76	0.024	1.0
0.5	4	0.66	0.041	0.86
0.2	4	0.44	0.101	0.85

^aThe ratio of the first derivative peak heights on the backward and forward scans of a cyclic voltammogram.

Table 2. Test for concentration dependence in the kinetics of the bianthrone reduction.^a

$v/\text{mV s}^{-1}$	$R'_1{}^b$	Multiples of $v_{\frac{1}{2}}$
0.50 mM bianthrone		
690	0.620(0.005)	2.0
345	0.502(0.002)	1.0
173	0.404(0.003)	0.5
1.00 mM bianthrone		
700	0.645(0.002)	2.0
350	0.501(0.002)	1.0
175	0.343(0.002)	0.5
2.00 mM bianthrone		
720	0.682(0.002)	2.0
360	0.502(0.001)	1.0
180	0.338(0.002)	0.5

^a Measurements in DMF containing Bu_4NBF_4 (0.1 M) at a platinum electrode at 6.4 °C. ^b The sweep rate was first adjusted to give the ratio as close to 0.500 as possible and then measurements were made at that sweep rate and two others. The numbers in parentheses are the standard deviations in ten measurements.

is the first order rate constant assuming a simple EC mechanism and $a = nFv/RT$ were obtained from the working curve shown in Fig. 3. There do not appear to be any systematic trends in the data with respect to the sweep rate (v) which is an indication of a good fit to the working curve. The rate constants at the four different temperatures provided an Arrhenius activation energy (E_a^{BA}) equal to 15.0 kcal/mol* and a frequency factor ($\log A^{\text{BA}}$) equal to 11.8 with a correlation coefficient of -0.996.

The alternative measurement method resulted in the data in Table 2 where $v_{\frac{1}{2}}$ indicates the value of v when R'_1 is equal to 0.500. From the working curve, the relationship between k and $v_{\frac{1}{2}}$ was found to be (7). The theoretical values of R'_1 at 0.5, 1.0 and 2.0 times $v_{\frac{1}{2}}$ are equal to 0.35, 0.50 and 0.67 while

$$k = 0.078 (Fv_{\frac{1}{2}}/RT) \quad (7)$$

the experimental values at 3 concentrations were equal to 0.36 (± 0.03), 0.50 (± 0.00) and 0.65 (± 0.03). Here again, the experimental data agree well with

* Expressed in these units to facilitate comparison with related data. 1 cal = 4.184 J.

the theoretical data for the simple EC mechanism. The reason that the values are exact at $v_{\frac{1}{2}}$ equal to 1.0 is that the experiments were conducted by first fine-tuning the sweep rate to give R'_1 equal to 0.500 before making the other measurements.

It has recently been shown that apparent activation energies can be obtained directly from experimental v values without the necessity of using a working curve. The method involves measuring R'_1 at one temperature and then making changes in the temperature while fine-adjusting v to hold R'_1 constant.⁶ The activation energy can then be determined directly from (8) where v_c refers to the

$$\ln(v_c/T) = (-E_a/R)(1/T) + c \quad (8)$$

value of the sweep rates necessary to hold R'_1 constant. Since in this case the value of R'_1 selected for the analysis was 0.500, eqn. (7) can be used to calculate the rate constants as well and these are listed in Table 3. The value of E_a^{BA} obtained in this set of experiments, 15.3 kcal/mol ($r = -0.9998$) agrees quite closely with the other determination.

Polarographic studies. For the reverse process, $A \xrightarrow{k_{\text{AB}}} B$, the rate is too low for analysis by derivative cyclic voltammetry and instead the process was investigated via the kinetic current observed during polarography of A in DMF as was done in aqueous phenol by Grabowski and Balaziewicz.²

The application of kinetic currents in polarography for the determination of rate constants has been adequately discussed by Meites.⁷ For the present case the relationship between the kinetic current, i_k , and the diffusion current, i_d , is given by expression (9) where t is the drop time of the

$$\frac{i_k}{i_d - i_k} = 0.81 \cdot \frac{k_{\text{AB}}}{k_{\text{BA}}} \cdot t^{\frac{1}{2}} \quad (9)$$

capillary. One important consequence of this equation is that neither k_{AB} nor the associated activation parameters can be determined independently of

those for the back reaction i.e. $B \xrightarrow{k_{\text{BA}}} A$. Since k_{BA} was not measured at temperatures (50–70 °C)

necessary for the reaction $A \xrightarrow{k_{\text{AB}}} B$ to proceed at an appreciable rate, we found it more convenient to eliminate the rate constants in eqn. (9) by introduction of (10) and (11), which, under the assumption that E_a^{AB} and E_a^{BA} do not vary significantly between

Table 3. Derivative cyclic voltammetric activation energy determination for the conversion B→A.

$t/^\circ\text{C}$	T^{-1}/K^{-1}	$v_c/\text{V s}^{-1}$	$\ln(v_c/\text{V s}^{-1})$	R_1^a	$k_{\text{BA}}/\text{s}^{-1b}$
6.4	0.00358	0.300	-1.204	0.501(0.004)	0.97
15.2	0.00347	0.710	-0.342	0.495(0.006)	2.2
21.8	0.00339	1.30	0.262	0.498(0.004)	4.0
32.8	0.00327	3.29	1.191	0.500(0.003)	9.8

^aThe numbers in parentheses are the standard deviations in ten measurements after fine-tuning the sweep rate to give $R_1^a=0.50$. ^bWhen $R_1^a=0.500$, $k_{\text{BA}}=906$ (v_c/T).

-20 and 70 °C, ultimately leads to expression (12). Thus, a plot of $\log [i_k/(i_d - i_k)]$ vs. $1/T$ should result

$$k_{\text{AB}} = A^{\text{AB}} \exp(-E_a^{\text{AB}}/RT) \quad (10)$$

$$k_{\text{BA}} = A^{\text{BA}} \exp(-E_a^{\text{BA}}/RT) \quad (11)$$

$$\log\left(\frac{i_k}{i_d - i_k}\right) = \log(0.81 t^{\frac{1}{2}} \frac{A^{\text{AB}}}{(A^{\text{BA}})^{\frac{1}{2}}}) + \frac{E_a^{\text{BA}}}{2.303 \cdot 2RT} - \frac{E_a^{\text{AB}}}{2.303 \cdot RT} \quad (12)$$

in a straight line with the slope equal to $(E_a^{\text{AB}} - 2E_a^{\text{BA}})/(2.303 \cdot 2R)$ and the intercept equal to $\log[0.81 t^{\frac{1}{2}} A^{\text{AB}}/(A^{\text{BA}})^{\frac{1}{2}}]$. The polarographic results are summarized in Table 4. A plot of $\log[i_k/(i_d - i_k)]$ vs. $1/T$ gave a straight line ($r = -0.966$) with a slope of -2305K and the intercept equal to 5.86. By introduction of the values found for E_a^{BA} and A^{BA} and $t = 1.6$ s, the corresponding values for the conversion of A to B can be calculated to be $E_a^{\text{AB}} = 18.1$ kcal/mol and $\log A^{\text{AB}} = 11.6$.

DISCUSSION

The cyclic voltammetric results are in agreement with the common observation^{1-4,8-9} that ion radicals and more highly charged ions of overcrowded ethylenes have configurations which differ

considerably from those of the parent compounds. Accordingly, the initial formation of the anion radical, $A^{\cdot-}$, in the first cathodic wave, R_1 , is followed by a configuration change to $B^{\cdot-}$. The process is fast and effectively irreversible, which may be attributed to the release of steric strain associated with the conversion.¹⁰⁻¹¹ The absence of current for the oxidation of $A^{\cdot-}$ to A even at 1000 V/s indicates that the conversion of $A^{\cdot-}$ to $B^{\cdot-}$ is a process with a rate constant greater than about 10^4 s⁻¹. Once formed, $B^{\cdot-}$ is further reduced to $B^{2\cdot-}$ at the applied potential. No oxidation peak corresponding to the primary intermediate formed at R_1 as reported by Peover⁴ could be observed. It has recently been suggested³ that the oxidation current observed by Peover might have been due to superoxide ion resulting from reduction of oxygen present as an impurity. For the full cycle $A \rightarrow B^{2\cdot-} \rightarrow A$ the sequence of electron transfer steps, E, and chemical steps, C, i.e. configuration changes, follows the scheme ECE-EEC which was also proposed for the analogous transformations of lucigenin.¹ The cyclic voltammetric results can be generalized as follows: For a single scan, the reduction reaction will be of the ECE type if the starting material and the ion radical have different preferred configurations, and the EEC scheme will be followed if they have similar preferred configurations. Similar behavior is expected if the initial reaction is an oxidation.

Table 4. Polarographic data for the kinetics of the conversion A→B.

$t/^\circ\text{C}$	T^{-1}/K^{-1}	$i_k/(i_d - i_k)^a$	$\log [i_k/(i_d - i_k)]$
70.1	0.00291	0.15 (0.06)	-0.82
60.8	0.00299	0.08 (0.02)	-1.10
51.0	0.00309	0.06 (0.02)	-1.22

^aThe numbers in parentheses are the standard deviations in three measurements.

The difference between E_a^{AB} and E_a^{BA} , which corresponds to the enthalpy difference between A and B, amounts to 3.1 kcal/mol. This value is in good agreement with ΔH -values measured by visible spectroscopy for bianthrone,¹⁰ 3.4 ± 0.2 kcal/mol, and 3,3'-bis(methoxycarbonyl)bianthrone,¹⁰ 2.4 ± 0.2 kcal/mol.

The transformation of B to A for bianthrone and a series of substituted bianthrone has been studied by photochemical techniques, where advantage was taken of the possibility to convert the A form to B by illumination after which the thermal reaction back to A can be studied.¹²⁻¹³ Activation barriers in the range 13–15 kcal/mol were found almost independent of the nature and position of the substituents in good agreement with the value, 15.3 kcal/mol, from this study. To our knowledge the activation energy for the reverse process A→B in aprotic media has not been reported for the unsubstituted bianthrone. However, introduction of substituents in the bianthrone molecule may result in compounds which can be resolved into Z and E forms and the interconversion of such isomers involves as the first step a transformation of the A form to B. The activation energy associated with the process can conveniently be measured by NMR coalescence experiments. This approach was taken in a study of two substituted bianthrone, 2,2'-dimethylbianthrone and 2,2'-bis(trifluoromethyl)bianthrone.¹⁴ For the dimethyl derivative, the signals due to the methyl groups in the ¹H NMR spectra were found to coalesce at 357 K in CDBr₃, corresponding to a ΔG^\ddagger value of 20.0 ± 0.5 kcal/mol. The corresponding value for the trifluoromethyl substituted bianthrone was found to be 21.3 ± 0.2 kcal/mol from the coalescence of the ¹⁹F NMR signals at 414 K. Our value of 18.1 kcal/mol for E_a^{AB} corresponds to a ΔG^\ddagger value at 357 K of 19.7 kcal/mol assuming the value of ΔS^\ddagger to be -7 cal/deg mol (see later). Since the methyl groups in the 2 and 2' positions are only expected to play a minor role in determining the height of the activation barrier, the above values of 20.0 kcal/mol at 357 K is probably a good estimate for unsubstituted bianthrone as well and thus our value (19.7 kcal/mol) must be considered to be in satisfactory agreement with that expected on the basis of the related work.

The implications of these relatively small activation barriers for the structure of the transition state have been discussed thoroughly elsewhere^{1,11} and need not be repeated here. It is sufficient to

point out that an activation energy in the range 15–18 kcal/mol leads to the conclusion that the transformation between the A and B forms does not proceed as a simple rotation of planar ring systems around the central bond, a process for which the activation energy is expected to be higher than 42 kcal/mol.¹⁵ Instead the process involves considerable folding of the central ring systems by which the passage of the interacting hydrogen atoms in positions 1 and 1' (8 and 8', respectively) is greatly facilitated.

A noteworthy result of the present work is the observation that the pre-exponential factors A^{AB} and A^{BA} are identical ($\log A \sim 11.7$) within experimental error. From the knowledge of A the activation entropy, ΔS^\ddagger , can be calculated from eqn. (13) which is easily derived by introduction of $\ln A = \ln k + E_a/RT$ in a common expression¹⁶ for ΔS^\ddagger . Calculated in this way ΔS^\ddagger was found to be equal to -7 cal/deg mol.

$$\Delta S^\ddagger = 2.303R[\log(A/T) - 10.753] \quad (13)$$

The observation of identical or almost identical values of ΔS^\ddagger for the two steps of equilibrium (5) is a natural consequence of the small difference in free energy between two forms which at the same time are of very similar structure. The interconversion of the A and B forms of bianthrone and several closely related systems is a reaction strongly resembling the racemization of optically active biaryls, a process for which, of course, ΔH equals zero and ΔS^\ddagger has the same value in both directions. Data have been published for the racemization of a series of optically active binaphthyls¹⁷ relevant in the present context and which show trends very similar to those observed for bianthrone. For the interconversion of the *d* and *l* forms of 8,8'-bis(methoxycarbonyl)-1,1'-binaphthyl an E_a of 22 kcal/mol and a ΔS^\ddagger of -7.5 cal/deg mol were found, values which clearly illustrate the similarity pointed out above. Also for this and similar reactions the possibility of a folded transition state in analogy to that for bianthrone¹¹ and 10,10'-dimethyl-9,9'-biacridylidene¹ has been discussed.¹⁷⁻¹⁸

Comparison of the rates for the interconversion of A and B in aqueous phenol² and anhydrous DMF (this study) demonstrates that the reaction proceeds significantly more slowly in the protic solvent system. Recalculated to the common temperature, 25 °C, the values are the following: k_{AB} (aq.phenol) $\cong 0.7 \times 10^{-2} \text{ s}^{-1}$, k_{AB} (DMF) = $2.2 \times$

10^{-2} s^{-1} and $k_{\text{BA}}(\text{aq.phenol}) \cong 0.6 \text{ s}^{-1}$, $k_{\text{BA}}(\text{DMF}) = 5.2 \text{ s}^{-1}$. The origin of this difference should primarily be sought in the significant difference in ΔS^\ddagger observed in the two solvent systems: $\Delta S^\ddagger(\text{aq.phenol}) = -20 \text{ cal/deg mol}$, $\Delta S^\ddagger(\text{DMF}) = -7 \text{ cal/deg mol}$. It was suggested² that the very negative value of $\Delta S^\ddagger(-20 \text{ cal/deg mol})$ had its origin in an activated complex possessing some additional linkage between the two tricyclic ring systems through positions 1 and 1' (or 8 and 8'). However, in the light of the present view on the transition state structure¹¹ together with the much smaller value of ΔS^\ddagger observed under aprotic conditions, we feel that this interpretation may be questioned and that the low value found in aqueous phenol more likely reflects an increased ordering of the protic solvent system in the transition state as compared to DMF. This point is presently under investigation and results will be reported separately.

EXPERIMENTAL

The instrumentation for cyclic voltammetry and derivative cyclic voltammetry was as earlier described.^{5,19-20} Polarography was carried out using conventional equipment and the drop time was controlled by a Juul Electronics drop timer.

Electrodes for CV and DCV were either Beckman Platinum buttons (No. 39273) or constructed from this ($\varnothing = 0.5 \text{ mm}$) platinum wire sealed into soft glass after which the electrode surface was electroplated with mercury. Reference electrodes were made according to the design reported by Moe.²¹

Bianthrone was a commercial sample (EGA-CHEMIE) and was used without further purification. Bianthrone was prepared by a literature procedure²² and recrystallized three times from benzene-ethanol (1/1) prior to use.

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