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Rates of Conformational Changes in the Anion Radicals of Bianthrones[1]

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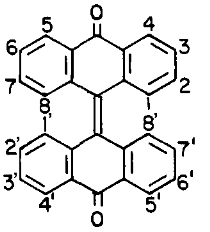
Abstract: Bianthrone and its 3,3′-dimethyl, 3,3′-dimethoxy, and 1,1′-dimethyl derivatives were studied by pulse radiolysis in *i*-PrOH–water solutions. One-electron reduction of the low-temperature A form of each of these bianthrones leads to the formation of the anion radicals $A^{-}\cdot$ which then undergo a conformational change into $B^{-}\cdot$, the anion radical of the high-temperature B form. Subsequently, $B^{-}\cdot$ undergoes second-order disproportionation to yield B and BH^{-} (bianthronyl). The absorption spectra of $A^{-}\cdot$ and $B^{-}\cdot$ exhibit maxima around 560 and 460 nm, respectively. The rates of the conformational change $A^{-}\cdot \rightarrow B^{-}\cdot$ were found to be $7 \times 10^4\ s^{-1}$ for bianthrone and 3,3′-dimethylbianthrone, $1.7 \times 10^4\ s^{-1}$ for the 3,3′-dimethoxy derivative, and only $1.1 \times 10^3\ s^{-1}$ for the sterically hindered 1,1′-dimethylbianthrone.

Introduction

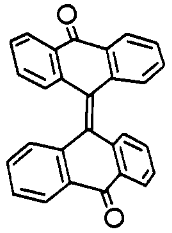
Bianthrone (**1**) is a thermochromic substance whose unusual properties have prompted many investigations.[2] At room temperature solutions of **1** are yellow, but as the temperature is increased a green color develops. This reversible process involves a thermal equilibrium between two distinct forms, A and B, where A is the low-temperature (yellow) form and B is the high-temperature (green) species. The B form of **1** and many of its derivatives is identical with one of the several species formed by photolysis.[2b]



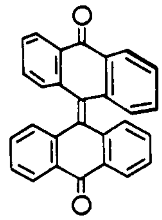
1

3,3'-dimethylbianthrone (2)
1,1'-dimethylbianthrone (3)
3,3'-dimethoxybianthrone (4)

The structures of the A and B forms have been studied extensively. The A form avoids the severe steric interactions between hydrogens at positions 1 and 8′ (and 1′ and 8) by adopting a structure with each anthrone system folded away from the other without twisting the connecting 9,9′ double bond. The most widely accepted structure of the B form enjoys two planar anthrone systems at the cost of considerable twisting (~57°) about the 9,9′ bond.[3]



A



B

Considerable equilibrium and kinetic information exists concerning the A ⇌ B transformation. Typically the enthalpy of B is 2–4 kcal/mol greater than that of A in **1** and derivatives[4] and activation energies of 13–15 kcal/mol are observed for the B → A process.[5] The equilibrium and rates of the *E,Z* isomerization of 2,2′-disubstituted anthrones have also been studied.[4,6] This reaction proceeds through B as an intermediate.

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(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy (P.N.) and by the National Science Foundation (D.H.E.). This is document No. NDRL-2250 from the Notre Dame Radiation Laboratory.

(2) The thermochromic and photochromic properties of **1** and related substances have been reviewed. See, for example: (a) Kortüm, G. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 391–403. (b) Bercovici, T.; Korenstein, R.; Muszkat, K. A.; Fischer, E. *Pure Appl. Chem.* **1970**, *24*, 531–65. (c) Margerum, J. D.; Miller, L. J. In "Techniques of Chemistry", Brown, G. H.; Ed.; Wiley-Interscience: New York, 1971; Vol. 3, pp 558–632. (d) Fischer, E. *Fortschr. Chem. Forsch.* **1967**, *7*, 605–41.

(3) Korenstein, R.; Muszkat, K. A.; Sharafy-Ozeri, S. *J. Am. Chem. Soc.* **1973**, *95*, 6177–81.

(4) Tapuhi, Y.; Kalisky, O.; Agranat, I. *J. Org. Chem.* **1979**, *44*, 1949–52.

(5) (a) Dombrowski, L. J.; Groncki, C. L.; Strong, R. L.; Richtol, H. H. *J. Phys. Chem.* **1969**, *73*, 3481–85. (b) Bercovici, T.; Fischer, E. *Isr. J. Chem.* **1969**, *7*, 127–33.

(6) Agranat, I.; Tapuhi, Y. *J. Org. Chem.* **1979**, *44*, 1941–8.

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Scheme I

$$\begin{tikzcd}
A \arrow[r, shift left, "e"] \arrow[d, shift left, "k_{AB}"] & A^{\overline{\cdot}} \arrow[l, shift left, "E^0_{1A}"] \arrow[d, shift left, "k^-_{AB}"] & \\
B \arrow[u, shift left, "k_{BA}"] \arrow[r, shift left, "e"] & B^{\overline{\cdot}} \arrow[l, shift left, "E^0_{1B}"] \arrow[u, shift left, "k^-_{BA}"] \arrow[r, shift left, "e"] & B^{2-} \arrow[l, shift left, "E^0_{2B}"]
\end{tikzcd}$$

$$K_{AB} = k_{AB}/k_{BA}$$
$$K^-_{AB} = k^-_{AB}/k^-_{BA}$$

By contrast, very little is known about the analogous $A \rightleftharpoons B$ structural changes in the anion radicals of bianthrone. The addition of an electron to the A form would be expected to diminish the double-bond character of the 9,9′ bond causing a reduction in the energy required to twist about that bond. Thus, it is expected that the anion radical may exist preferentially as a B-type structure, $B^{-}\cdot$. It is probably this species whose EPR spectrum has been reported.[7]

The postulated $A^{-}\cdot \rightleftharpoons B^{-}\cdot$ reaction is of key significance in understanding the mechanism of reduction of bianthrone. The electrochemical and spectroelectrochemical behavior[8] was quantitatively accounted for by Scheme I in which the reduction of the A form proceeds first to the A-like anion radical, $A^{-}\cdot$, which rapidly twists ($K_{AB}^- \gg 1$) to $B^{-}\cdot$ which in turn is rapidly reduced to B^{2-} because the potential for A reduction is more negative than E_{2B}^0.

It was not possible to confirm that the reduction proceeded by this pathway because the half-life of the reputed $A^{-}\cdot$ (<1.4 ms at −45 °C[8]) was apparently too short to permit its detection by electrochemistry. Thus a technique capable of forming $A^{-}\cdot$ and monitoring its conversion to $B^{-}\cdot$ on a shorter time scale is needed. The present paper reports results obtained by pulse radiolysis for bianthrone and three derivatives.

Experimental Section

Bianthrone[9] (**1**), 3,3′-dimethylbianthrone (**2**), 1,1′-dimethylbianthrone (**3**), and bianthronyl (**5**) were purchased from Aldrich. The synthesis of 3,3′-dimethoxybianthrone (**4**) has been described.[10] The 2-methoxy-9-anthrone precursor was prepared by the method of Blicke and Weinkauff[11] and **4** was recrystallized from mesitylene before use. The organic solvents used were either Baker Analyzed or Fisher Certified reagents and were used without further purification. The inorganic compounds were also Baker Analyzed Reagents. Water was purified by a Millipore Milli-Q system.

Solutions were freshly prepared before irradiation and were kept in the dark until the moment they entered the irradiation cell. The bianthrones were first dissolved in either dioxane or THF and then diluted with *i*-PrOH and finally with alkaline water. This procedure was chosen because direct dissolution of the bianthrones in *i*-PrOH or *i*-PrOH-H_2O mixtures was very slow. The dioxane or THF was added to facilitate the preparation of solutions and also to enhance the solubility. Acetone (1%) was added as an electron scavenger. Potassium hydroxide was introduced into the solvent mixture via the water portion. The addition of base was considered necessary in order to avoid protonation of the anion radicals, which would interfere with observation of the conformational changes.

The solutions were deoxygenated by bubbling with pure N_2 (Linde, oxygen free grade). These solutions, with concentrations of the bianthrones $\leq 5 \times 10^{-4}$ M, were stable in the dark for several hours, the time required to carry out the radiolysis experiments.

Steady-state radiolysis was carried out in a Gammacell 220 ^{60}Co source with a dose rate of 3×10^{17} eV g^{-1} min^{-1}. Irradiation times were of the order of minutes. Optical absorption spectra of the solutions before and after irradiation were recorded with a Cary 219 spectrophotometer. The kinetic spectrophotometric experiments were carried out with a revised version of the computer-controlled apparatus described previously.[12] Pulses of 7 MeV electrons and of 5–10 ns duration times from an ARCO LP-7 linear accelerator supplied energy to the solution to produce 2–4 μM totoal radical concentration per pulse. Solution was passed through the cell between pulses to supply a fresh sample for each pulse. The monitoring light source was a Xenon lamp. Narrow bandpass filters were used to protect the solution from unnecessary illumination. All experiments were carried out at room temperature, 21 ± 1 °C.

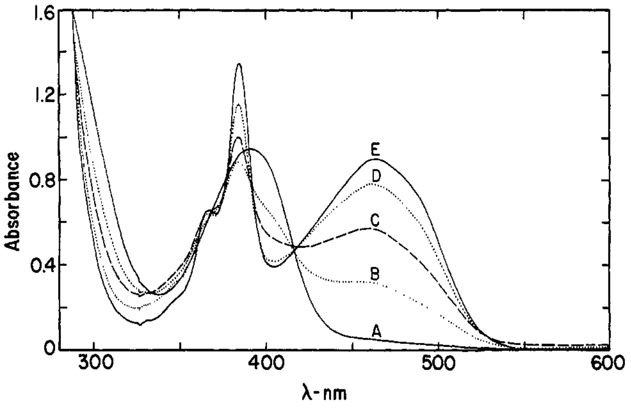

Figure 1. Optical absorption spectra of bianthrone and its radiolytic product. A solution of 2.5×10^{-4} M bianthrone in 10% THF, 70% *i*-PrOH, 1% acetone, and 19% pH 12 water was bubbled with N_2. (A) Spectrum before irradiation. (B, C, D, E) Spectra after 5, 10, 15, and 20 min irradiation in a γ source, dose rate = 3×10^{17} eV g^{-1} min^{-1}. Optical path length 3 mm. Curve E is identical with the spectrum of bianthronyl in the same solvent mixture after equilibrtion (see text).

Results and Discussion

The action of radiation on the solvent mixtures used in the present work produces predominantly the $(CH_3)_2\dot{C}OH$ radical in the following steps.[13] Radiolysis of *i*-PrOH produces solvated electrons, $(CH_3)_2\dot{C}OH$, and $(CH_3)_2CH\dot{O}$. The alkoxyl radicals react with *i*-PrOH to form $(CH_3)_2\dot{C}OH$. Radiolysis of water produces H, OH, and e_{aq}^-. The H and OH also react with *i*-PrOH to produce $(CH_3)_2\dot{C}OH$ by hydrogen abstraction. Solvated electrons react with acetone to yield $(CH_3)_2\dot{C}O^-$ (which protonates into $(CH_3)_2\dot{C}OH$, pK_a = 12). Thus most of the primary radicals of radiolysis are converted within a fraction of a microsecond into the reducing radical $(CH_3)_2\dot{C}OH$. This is accompanied by a small amount of the similarly reducing radicals from dioxane or THF. All these radicals will then react with the bianthrones (A form) to produce the anion radicals.

$$(CH_3)_2\dot{C}OH + A \rightarrow (CH_3)_2CO + H^+ + A^{-}\cdot \qquad (1)$$

The pK_a for protonation of $A^{-}\cdot$ is expected[14] to be between 7 and 9 so that in the alkaline solutions used $A^{-}\cdot$ will remain unprotonated. It will then undergo conformational changes (reaction 2) and/or decay into final products by second-order radical–radical reactions (reaction 3).

$$A^{-}\cdot \rightarrow B^{-}\cdot \qquad (2)$$

$$2B^{-}\cdot \rightarrow B + B^{2-} (\xrightarrow{H^+} BH^-) \qquad (3)$$

Steady-state radiolysis of bianthrone shows bleaching of the 390-nm absorption of this compound accompanied by buildup of product absorptions at 384 and 463 nm (Figure 1). The isosbestic points are not perfect, but nevertheless they show a reasonable conversion of bianthrone into products. The final spectrum E in fact resembles that of B^{2-} observed previously[8] but is blue shifted, probably because it is a protonated form BH^-. This was confirmed by examining a solution of bianthronyl (BH_2, **5**) in the same solvent mixture. A spectrum identical in shape and in intensity with curve E, Figure 1, was found after tautomeric and acid–base equilibria had been reached in the alkaline solution (~90 min

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(7) Agranat, I.; Rabinovitz, M.; Falle, H. R.; Luckhurst, G. R.; Ockwell, J. N. *J. Chem. Soc. B* **1970**, 294–8.

(8) Olsen, B. A.; Evans, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 839–43.

(9) The parent name used by Chemical Abstracts for **1** and derivatives is 10-(10-oxo-9(10*H*)-anthracenylidene)-9(10*H*)-anthracenone.

(10) Bergmann, E. D.; Loewenthal, E. *Bull. Soc. Chim. Fr.* **1952**, 66–72.

(11) Blicke, F. F.; Weinkauff, O. J. *J. Am. Chem. Soc.* **1932**, *54*, 1460–4.

(12) Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129.

(13) See, e.g.: Brault, D.; Neta, P. *J. Am. Chem. Soc.* **1981**, *103*, 2705.

(14) Judging from the pK_a values for the para (4), ortho (5), and meta benzosemiquinone (7) and the pK_a values for acetophenone (10) and benzophenone (9.2) ketyl radicals.

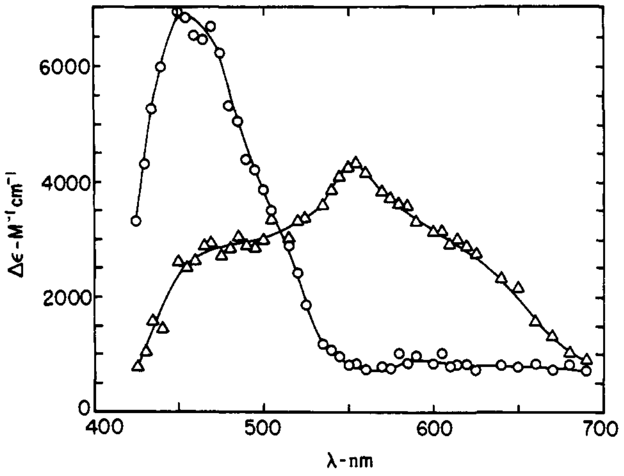
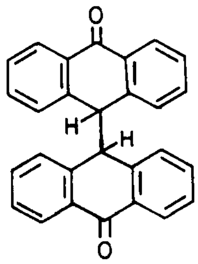


Figure 2. Transient absorption spectra in the pulse radiolysis of bianthrone. The solution contained 3.9 × 10^{-4} M bianthrone in 10% THF, 69% *i*-PrOH, 20% aqueous 0.25 M KOH, and 1% acetone and was bubbled with N_2. The spectra were monitored 4–5 μs (Δ) and 25–30 μs (O) after the pulse. The extinction coefficients were calculated with use of KSCN dosimetry and assuming a yield of G = 6 radicals/100 eV.

after preparation of solution, under nitrogen and in the dark). Thus, the product of radiolysis is the two-electron reduction product **5**, probably present as an anion, BH^-.


5

The initial yield of this product, estimated from Figure 1, is G = 3.0. Since the yield of reducing radicals is expected to be $G \approx 6$, this finding is consistent with the disproportionation mechanism (reaction 3).

Pulse radiolysis experiments with bianthrone show formation of the product absorption at 460 nm within ~3 ms. At shorter time scales, reactions 1 and 2 can be followed. This is clearly demonstrated by Figure 2, where the transient spectrum monitored 25–30 μs after the pulse is found to be very different from the initial spectrum monitored 4–5 μs after the pulse. Figure 3 shows several kinetic traces at 460 and 550 nm which indicate the occurrence of the two steps. At 430–510 nm the two reactions cause two consecutive absorption buildups which, unfortunately, are not fully resolved. The resolution is limited by the rate of reaction of $(CH_3)_2\dot{C}OH$ with bianthrone and the limited solubility of this compound. At 530–650 nm, however, the initial buildup is followed by a decrease in absorption and thus gives a clearer distinction between the two processes (see traces at 550 nm in Figure 3). Using the decay portion of traces such as 3 and the same intervals of traces such as 4 we calculate a first-order rate constant $k = (7 \pm 1.5) \times 10^4\ s^{-1}$ for the transformation of the initial spectrum with $\lambda_{max} \approx 555$ nm into the spectrum with $\lambda_{max} \approx 455$ nm observed at longer times. The rate constant for the reaction of $(CH_3)_2\dot{C}OH$ with bianthrone cannot be determined accurately because this reaction is rapidly followed by the second process, but it is estimated to be (3–10) × $10^8\ M^{-1}\ s^{-1}$ (see below). The rate of the second process was independent of the dose/pulse and appears to be independent of the concentration of bianthrone. The concentration could not be increased beyond ~5 × 10^{-4} M. Decreasing the concentration slowed down the first step and caused greater overlap of the two processes, but did not appear to lower the rate of the second process. These findings, and the results described below for substituted bianthrones, lead to the conclusion that the rate of 7 × $10^4\ s^{-1}$ can be assigned to the conformational change (reaction 2).

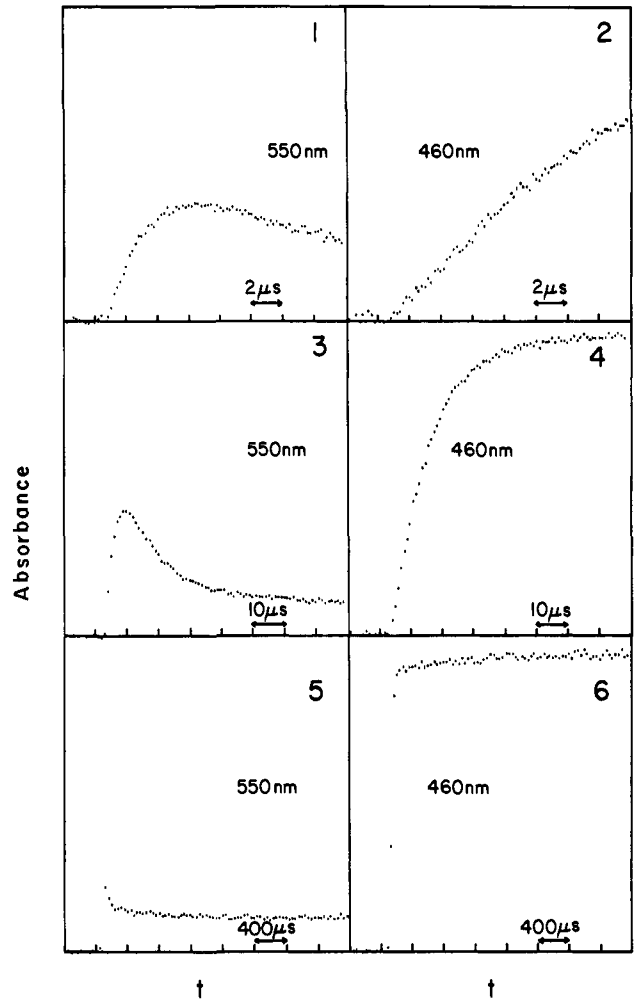


Figure 3. Kinetic traces obtained upon pulse radiolysis of bianthrone. The solution contained 2.6 × 10^{-4} M bianthrone in 10% dioxane, 70% *i*-PrOH, 20% pH 12 water, and 0.2% acetone and was bubbled with N_2.

Experiments with 3,3′-dimethylbianthrone gave very similar results to those described above, both in spectra (similar to Figure 2) and in kinetics, $k = 7 \times 10^4\ s^{-1}$. The spectrum of the final reduction product monitored after γ radiolysis was also very similar to that shown in Figure 1.

The behavior of 3,3′-dimethoxybianthrone (Figure 4) was slightly different. At 460 and 550 nm the expected buildup and decay were observed as in the previous compounds. However, in the region of 700 nm considerable bleaching was observed which cannot be accounted for on the basis of reaction 2. Since 3,3′-dimethoxybianthrone contains ~4% of the B form at room temperature[15] and since the B form exhibits broad absorption around 740 nm, the bleaching observed at this wavelength region probably indicates the occurrence of reaction 4. This is a route for converting $A^-\cdot$ into $B^-\cdot$ in addition to reaction 2, and its rate should

$$A^-\cdot + B \rightarrow A + B^-\cdot \qquad (4)$$

depend on [B]. In order to examine this possibility, the rates of buildup at 460 nm, decay at 520 nm, and bleaching at 730 nm were examined as a function of concentration. The results indeed show a linear dependence of the pseudo-first-order rate on the concentration of 3,3′-dimethoxybianthrone. The intercept of the line gives 1.7 × $10^4\ s^{-1}$ assignable to reaction 2, and the slope gives

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(15) Estimated in DMF solutions assuming that the extinction coefficient of the B form is independent of substitution. Olsen, B. A., Ph.D. Thesis, University of Wisconsin, 1980.

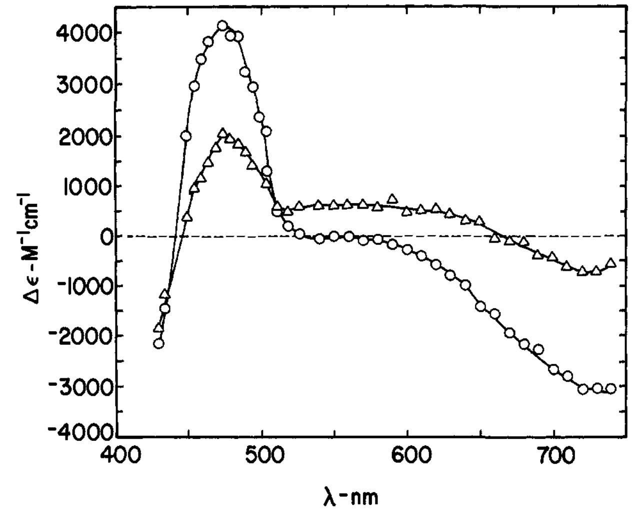

Figure 4. Transient absorption spectra in the pulse radiolysis of 3,3′-dimethoxybianthrone. Conditions as in Figure 3. Spectra were monitored 20 μs (Δ) and 200 μs (O) after the pulse.

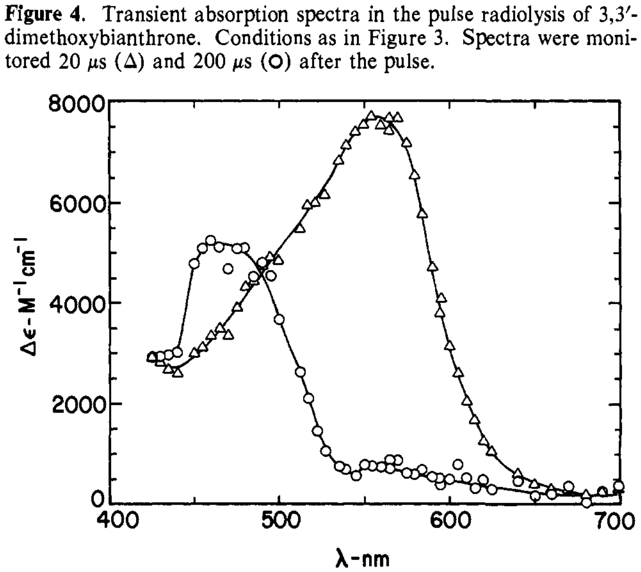

Figure 5. Transient absorption spectra in the pulse radiolysis of 1,1′-dimethylbianthrone. Solution contained 1 × 10^{-4} M substrate in 10% THF, 69% *i*-PrOH, 20% 0.25 M aqueous KOH, and 1% acetone and was bubbled with N_2. Spectra were monitored 100–150 μs (Δ) and 2.5–3.0 ms (O) after the pulse.

a second-order rate constant of 4.8 × 10^9 M^{-1} s^{-1} (assuming the bianthrone under study contains 4% of the B form). This rate constant is practically diffusion controlled, which is not surprising, since the difference between the one-electron reduction potentials of A and B is estimated to be nearly 1 V (see below). In contrast with this case, bianthrone and 3,3′-dimethylbianthrone contain only 0.2% and 0.6%, respectively, of their B forms and thus the contribution of reaction 4 in these cases is very small and was not observed. (It should be pointed out, however, that a certain batch of bianthrone exhibited a concentration effect on the rate of the $A^{-}\cdot$ decay which is probably owing to reaction with impurities, e.g., anthraquinone.)

The transient spectra observed with 1,1′-dimethylbianthrone are shown in Figure 5 and the results of the steady-state radiolysis in Figure 6. In this case, the initial reduction species $A^{-}\cdot$, with λ_{max} = 560 nm, has a much longer lifetime than the corresponding species from the other bianthrones and, therefore, its spectrum was experimentally fully developed to reach ϵ = 7700 M^{-1} cm^{-1} at 560 nm. With the previous bianthrones the 560-nm absorption was observable but was not fully developed owing to the overlap of a rapid reaction 2 with the formation reaction 1. For the same reasons, the rate constants for reaction 1 were not determined accurately with the previous bianthrones. However, for 1,1′-dimethylbianthrone k = 7 × 10^8 M^{-1} s^{-1} was determined for the initial reduction step (reaction 1). Similar rate constants are expected for the other bianthrones as well.

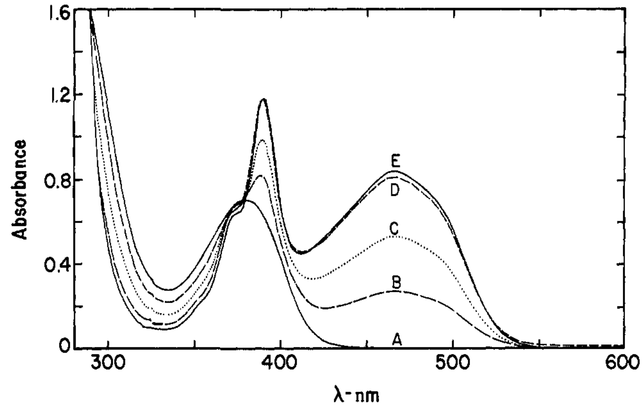

Figure 6. Optical absorption spectra of 1,1′-dimethylbianthrone and its radiolytic product. Solution contained 2.2 × 10^{-4} M substrate in solvent mixture as in Figure 5. Curves A, B, C, D, and E correspond to irradiation times of 0, 5, 10, 15, 20 min. Optical path length 3 mm.

Since the decay of $A^{-}\cdot$ of 1,1′-dimethylbianthrone was much slower than in the previous cases and took place over 3–5 ms, it is necessary to examine carefully whether this decay was a first-order or a second-order process. The experimental points were found to fit only a first-order rate law and, moreover, the rate of decay was independent of the dose/pulse, i.e., initial $A^{-}\cdot$ concentration from 1 to 5 × 10^{-6} M. The rate was determined to be (1.1 ± 0.1) × 10^3 s^{-1} and can be assigned to reaction 2 for 1,1′-dimethylbianthrone. In this compound, whose A form is present entirely as the *E* isomer,[6] the methyl groups exert strong steric hindrance between the two rings and thus make the conformational change very slow as compared with that of the previously discussed bianthrones.

It should be noted that the second-order decay, reaction 3, causes only small changes in the spectra with all the bianthrones studied. These changes are seen on the long time scale traces of Figure 3. The full spectra, at 100 μs and 3 ms after the pulse, were monitored with bianthrone and show only a slight shift upon decay, 10–20 nm to lower wavelengths with little change in peak absorbance. In the case of 1,1′-dimethylbianthrone, because reaction 2 is relatively slow, it was difficult to verify whether the spectrum observed at 4 ms after the pulse (Figure 5) represents $B^{-}\cdot$ or a mixture of $B^{-}\cdot$ and the final products.

In summary of the kinetic results, it is found that the conformational change, reaction 2, takes place with a rate of 7 × 10^4 s^{-1} with bianthrone and 3,3′-dimethylbianthrone, is slightly slower, 1.7 × 10^4 s^{-1}, with 3,3′-dimethoxybianthrone, but is much slower, 1.1 × 10^3 s^{-1}, with the sterically more hindered 1,1′-dimethylbianthrone. However, all these rates are too rapid to be observed by the electrochemical technique used previously.[8]

For bianthrone, the $A^{-}\cdot \rightarrow B^{-}\cdot$ rate constant of 7 × 10^4 s^{-1} corresponds to a $\Delta G^{\ddagger}$ of 10.8 kcal/mol at room temperature (assuming the preexponential factor is $kT/h = 6 \times 10^{12}$ s^{-1}) which is about half the value observed[8] for the analogous transformation (A → B) in the neutral species, 20.2 kcal/mol. This is due to a reduced resistance to twisting about the 9,9′ bond in the anion radical as compared to the neutral forms. Very similar fractional changes are noted in $\Delta G^{\ddagger}$ calculated at room temperature for cis→trans isomerization of the parent (37 kcal/mol[16]) and anion radical (16 kcal/mol[17]) of diesters of maleic acid and for the parent (43 kcal/mol[18]) and anion radical (21 kcal/mol[19]) of stilbene. It is concluded that the rate constant attributed to $A^{-}\cdot \rightarrow B^{-}\cdot$ is of the expected order of magnitude.

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There is also a large difference in equilibrium constant between the neutral and anion radical states of bianthrone. In the neutral form $K_{AB} = [B]/[A] = 2 \times 10^{-3}$ in dimethylformamide at room temperature.[8] By contrast, $K_{AB}^- = [B^-\cdot]/[A^-\cdot]$ must be very large since the present experiments show that $B^-\cdot$ is strongly favored. An estimate of K_{AB}^- would be of interest because it is governed in part by the release of steric interaction experienced on going from the doubly folded A form to the twisted B form.

K_{AB}^- may be calculated from standard electrode potentials and K_{AB} by eq 5 (see Scheme I for definitions). Both K_{AB} and E_{1B}^0

$$\ln K_{AB}^- = \ln K_{AB} + (nF/RT)(E_{1B}^0 - E_{1A}^0) \qquad (5)$$

(−0.195 V vs. SCE) are available[8] but E_{1A}^0 cannot be measured directly by electrochemical techniques because the reduction of A is irreversible. As stated earlier, the reduction is thought[8] to proceed by the ECE pathway (electrochemical step/chemical step/electrochemical step), $A \rightarrow A^-\cdot \rightarrow B^-\cdot \rightarrow B^{2-}$. Assuming that the rate constant for $A^-\cdot \rightarrow B^-\cdot$ is independent of solvent, the value determined in the present work may be combined with the peak potential observed at a given scan rate in dimethylformamide[8] to calculate E_{1A}^0, using the theoretical relationships[20,21] for an ECE process in cyclic voltammetry. The value so obtained is −1.14 V vs. SCE. It may be regarded as a lower limit because the theory pertains to the limit of a very rapid electron-transfer reaction at the electrode and any sluggishness in electron transfer will cause the calculated value to be too negative. When placed in eq 5, a value of $K_{AB}^- = 2 \times 10^{13}$ is obtained indicating that the free energy of $A^-\cdot$ exceeds that of $B^-\cdot$ by 18 kcal/mol.

The fact that $A^-\cdot \rightarrow B^-\cdot$ ~70 times slower for 1,1′-dimethylbianthrone than for bianthrone itself seems quite reasonable in view of the steric bulk of the methyl groups. The same effect of 1,1-disubstitution is also found for the $A \rightarrow B$ process in the parent bianthrones.

This latter statement may seem to contradict the repeated observation[4,22] that 1,1′-disubstitution does not impede the reverse $B \rightarrow A$ process, the reaction whose rate can be measured in the bianthrones. The principal effect of substituents bulkier than fluorine[23] is to destabilize the B form sufficiently to prevent thermochromism, i.e., the energy difference is too large to permit formation of a significant concentration of B at temperatures up to decomposition. Thus 1,1′-disubstitution severely decreases K_{AB} while having little effect on k_{BA}. Consequently, k_{AB} must be decreased by substitution in the 1-positions. Apparently these same effects are found in the anion radicals.

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Comparison of Proton- and Electron-Transfer Equilibria and Rates for Tetraalkylhydrazines

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Abstract: Relative electron-transfer equilibria for 17 tetraalkylhydrazines (R_4N_2) were determined by measurement of their standard potentials for oxidation ($E^{\circ\prime}$) and rates of electron loss by measurement of their standard heterogeneous electron-transfer rate constants (k_s) determined from their cyclic voltammograms. These data are compared with equilibrium and rate constant measurements for proton transfer between R_4N_2 and salicylic acid. All measurements were in dimethyl sulfoxide containing 0.1 M tetraethylammonium perchlorate. Similar trends are found for electron and proton transfer; the most basic R_4N_2 examples are the most easily oxidized and the fastest both to protonate and lose an electron. The proton transfers run under these conditions show anomalous Brønsted behavior; the rate of protonation of R_4N_2 is about twice as sensitive to change of the R groups as is the equilibrium constant, and the rate of deprotonation consequently becomes slower as the reaction becomes more exothermic. A Brønsted-like plot for electron transfers was constructed by estimating the electron-transfer rate constants for all R_4N_2 at the same potential (called k_0); electron transfer also gives anomalous Brønsted behavior for R_4N_2. The electron-transfer rate has been previously shown to be far faster in anti lone pair conformations than in gauche ones, so that electron transfer from acrylic R_4N_2 involves a prior conformational equilibrium to the unstable but rapidly oxidized anti form. It is suggested that a similar gauche to anti conformational change precedes proton transfer under our conditions, and is a major contributing factor to the anomalous Brønsted behavior of R_4N_2.

In a preliminary communication,[1] we reported equilibrium constant and rate constant data for the proton-transfer reactons of tetraalkylhydrazines (R_4N_2) with salicylic acid (HSal), as shown in eq 1, for several α-unbranched examples (alkyl substituents all $R'CH_2$–). The rate constant k_f was measured by a chro-

$$R_4N_2H^+ + Sal^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R_4N_2 + HSal \qquad (1)$$

$$K = k_f/k_b$$

noamperometric technique developed for this work[2] in which the potential is stepped to a region where R_4N_2 oxidizes rapidly but the other components of eq 1 are electrochemically inert, and the kinetic current determined. Both the rate and equilibrium constants for eq 1 prove to be quite sensitive to alkyl group structure, and it was proposed that hydrazine conformational effects are reponsible for this sensitivity. We report here additional proton-transfer data for compounds having α-branched alkyl groups (alkyl substituents $R'R''CH$–) and compare the equilibrium and rate constants for proton transfer (eq 1) with those for electron transfer, eq 2, determined by cyclic voltammetry in the same solvent system, dimethyl sulfoxide (Me_2SO) containing 0.1 M

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