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Oxidation and Reduction Properties of Anthraquinocyclopropanes and Anthraquinocyclopropenes

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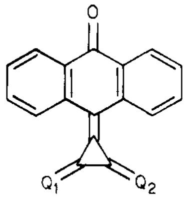
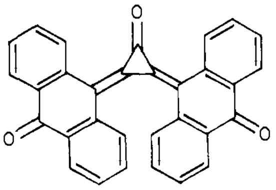
Abstract: Tris(9-anthron-10-ylidene)cyclopropane (**3**) and the related anthraquinocycloalkanes (**1**, **2**, **4**, and **5**) where one or more anthrone group has been replaced by 4-oxo-3,5-di-*tert*-butyl-2,5-cyclohexadiene can be involved in two different redox cycles with their dihydro analogues, **6–10**. The free-radical and anion radical intermediates in the oxidation of the dihydro compounds to their quinonoid forms have been studied by electron spin resonance. The hyperfine splitting constants for the anion radicals of these and related quinonoid compounds are rationalized by molecular-orbital calculations. Cyclic voltammetry was used to determine the reduction potentials of **1–5**. Spectrophotometric titration of **6–9** to their corresponding dianions is described.

In the preceding paper[2] we presented the synthesis and spectroscopic properties of a new family of compounds, the anthraquinocyclopropanes, **1–5**, and their dihydro analogues the anthraquinocyclopropenes. Compounds **1–5**, like other quinones, can be involved in two different redox cycles. These are illustrated in Scheme I, where A equals any of **1–5**. Under neutral conditions the dihydro compounds AH_2 can undergo oxidation first to the neutral monoradicals AH· and then to the fully oxidized forms, A. Alternatively the dihydro compounds may be deprotonated to the dianions A^{2-}, which can undergo oxidation to A. The intermediate one-electron product in the latter couple is the semiquinone anion radical $A^{-}\cdot$.



1–3



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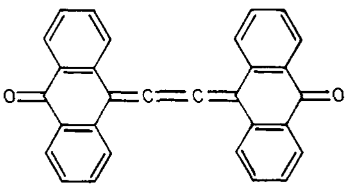

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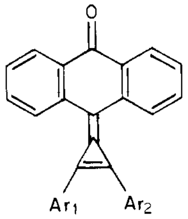
1, $Q_1 = Q_2$ = 4-oxo-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-ylidene
2, Q_1 = 4-oxo-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-ylidene;
  Q_2 = 9-anthron-10-ylidene
3, $Q_1 = Q_2$ = 9-anthron-10-ylidene

In this paper we describe the spectrophotometric titration of AH_2 to A^{2-}, the study of the A to A^{2-} redox couple by cyclic voltammetry, and electron spin resonance investigations of the intermediate anion radicals $A^{-}\cdot$ and monoradicals AH·.

Spectrophotometric Titrations

The dihydroxy compounds **6–8** were titrated spectrophotometrically with base (diazabicyclononane in THF or NaOH in MeOH) in order to study the equilibria between these compounds and their anions.[3] Compounds **6** and **7** show fully reversible deprotonation to the dianion upon stepwise addition of the necessary 2 equiv of base. Further addition of base has no effect on the spectrum, and the original spectra can be regenerated upon addition of acid. Figure 1 shows the spectrophotometric titration of **6**. Isosbestic points are maintained, indicating that these anthraquinocyclopropenes are deprotonated directly to the dianion, and that the intermediate monoanion is unstable with respect to the dihydro and dianion forms. This is fully analogous to the behavior of the reduced forms of the triquinocyclopropanes.[4-8]



6, $Ar_1 = Ar_2$ = 4-hydroxy-3,5-di-*tert*-butylphenyl
7, Ar_1 = 4-hydroxy-3,5-di-*tert*-butylphenyl;
  Ar_2 = 9-hydroxy-10-anthryl
8, $Ar_1 = Ar_2$ = 9-hydroxy-10-anthryl

Compound **8** behaves quite differently not only from **6** and **7** but from all related compounds studied previously.[4-8] When **8** is titrated (NaOH in methanol), isosbestic points are not maintained, although the titration is fully reversible. The spectrophotometric curves suggest that the monoanion as well as the dianion is present in the solution. Relative to the dianion and neutral molecule, the monoanion is apparently more stable for **8** than for other related compounds. This may be due to steric destabilization of the dianion of **8**, which cannot approach the planar form in which maximum delocalization could occur. In the monoanion, steric effects would be much less pronounced because negative charge is delocalized over only two of the anthracene rings. The anthracene ring which is still protonated can be twisted out of the plane of the rest of the molecule, relieving steric strain.

Reduction Potentials by Cyclic Voltammetry

The reduction of the anthraquinocyclopropanes **1–5** to their dianions was examined by using cyclic voltammetry. Two-wave reduction cycles were observed for each compound. As an ex-

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[1] (a) Research Laboratories, 3M Co. (b) University of Wisconsin.

[2] Benham, J. L.; West, R.; Norman, J. A. T. *J. Am. Chem. Soc.*, preceding paper in this issue.

[3] Bis(9-hydroxyanthryl)cyclopropenone (**9**) does not titrate reversibly because the dianion decomposes rapidly in solution. Bis(9-hydroxyanthryl)acetylene (**10**) was not obtained pure and so could not be studied.

[4] West, R.; Zecher, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 161.

[5] West, R.; Zecher, D. C.; Koster, S. K.; Eggerding, D. *J. Org. Chem.* **1975**, *40*, 2295.

[6] Koster, S. K.; West, R. *J. Org. Chem.* **1975**, *40*, 2300.

[7] Wendling, L. A.; Koster, S. K.; Murray, J. E.; West, R. *J. Org. Chem.* **1977**, *42*, 1126.

[8] Komatsu, K.; West, R.; Beyer, D. *J. Am. Chem. Soc.* **1977**, *99*, 6290.

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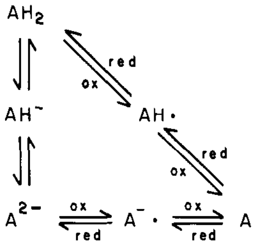
Scheme I



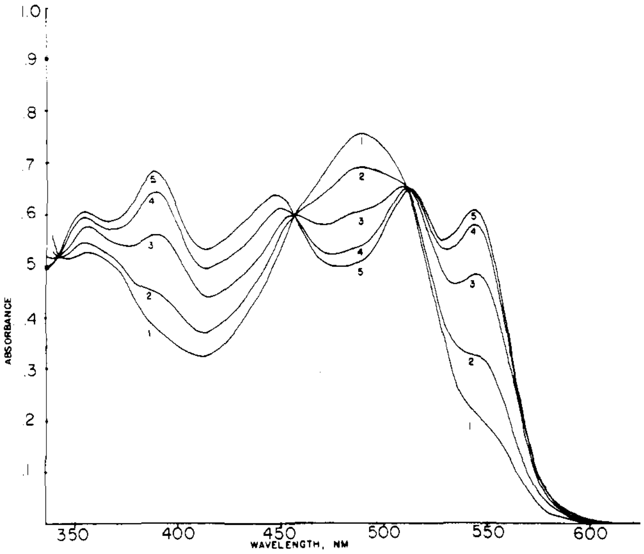


Figure 1. Spectrophotometric titration of **6**, 0.002 M in methanol, with aqueous NaOH. Curves 1, 2, 3, 4, and 5 represent additions of 0, 0.5, 1.0, 1.5, and 2.0 equiv of NaOH, respectively.

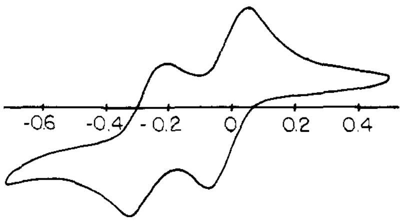


Figure 2. Cyclic voltammogram of **3**, 0.001 M in acetonitrile.

Table I. Reduction Potentials by Cyclic Voltammetry (V vs. SCE)

compd	$E_{1/2}$[b] first wave	$E_{1/2}$[b] second wave	ref
1	+0.02	−0.27	this work
2	+0.05	(−0.27)[c]	this work
3	+0.02	−0.28	this work
TQCP[a]	+0.05	−0.33	6
4	+0.05	(−0.32)[c]	this work
DQCPO[a]	+0.13	−0.34	6
5	−0.42	−0.61	this work
DQE[a]	−0.37	−0.63	this work

[a] See text for identification of these compounds. [b] Average of cathodic and anodic peak potentials of cyclic voltammograms. [c] Irreversible waves.

Table II. Predicted and Observed Proton Hyperfine Splitting Constants for Anion Radicals

	a_{H_i}, G	
	calcd	obsd
1	a, 1.473	1.676 (2 H)
	b, 0.364	1.257 (2 H)
	c, 1.352	0.419 (4 H)
	d, 0.297	
	q, 0.023	
2	1, 1.131	
	b, 0.266	1.08 (8 H)
	c, 1.05	
	d, 0.241	
	q, 0.112	
3	a, 0.835	1.08 (6 H)
	b, 0.176	1.05 (6 H)
	c, 0.787	
	d, 0.179	
4	a, 0.638	1.4 (4 H)
	b, 0.109	1.2 (4 H)
	c, 0.680	
	d, 0.188	
5	a, 0.666	1.0125 (8 H)
	b, 0.048	0.162 (4 H)
	c, 0.820	
	d, 0.132	

ample, the cyclic voltammogram of **3** is shown in Figure 2. The observed reduction potentials are shown in Table I, compared with those for other members of the polyquinocycloalkane family.

Compounds **1**–**3** are powerful oxidizing agents, with first reduction waves at +0.02 to +0.05 and second waves at ~−0.27 V vs. saturated calomel. The analogous benzoquinonoid compound tris(4-oxo-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-ylidene) cyclopropane (TQCP) shows quite similar values;[9] the compounds **1**–**3**, which contain one or more anthroquino groups, are marginally more easily reduced, especially in the second reduction step. These potentials are similar to those of other organic compounds useful as oxidizing agents: cf. chloranil, 0.0 and −0.78 V, and DDQ, +0.57 and −0.32 V.

The diquinocyclopropanone compound **4** also shows $E_{1/2}$ values quite close to those for TQCP and **1**–**3**. Compound **4** is, however, a somewhat poorer oxidizing agent than its benzoquinonoid analogue, bis(4-oxo-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-ylidene)cyclopropanone (DQCPO), particularly in the first reduction step.[9] This difference in ease of reduction may be associated with the increased stability of **4** compared to DQCPO.

Finally, the cumulene derivative **5** has reduction potentials quite similar to those for its benzoquino analogue, bis(4-oxo-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-ylidene)ethylene (DQE). However, both of these compounds, which lack a central ring, are much less easily reduced than the three-membered-ring compounds. Lower electron affinities for **5** and for DQE than for other polyquinocycloalkanes are consistent with molecular-orbital calculations,[2] which predict both compounds to have higher energies for the LUMO than do other molecules in their respective series.

Electron Spin Resonance of Anion Radicals

Previous studies have shown the usefulness of electron spin resonance spectroscopy in the study of electron distribution in polyquinocycloalkane anion radicals.[4-8] Anion radicals could be obtained by oxidation of the dianions A^{2-} (Scheme I) or reduction of the quinones **1**–**5**. In practice producing the anion radicals by electrolytic reduction of degassed solutions of **1**–**5** in tetrahydrofuran proved most convenient. The radical anions are generally very stable, persisting unchanged for many hours at room temperature.

The Hückel molecular orbitals discussed previously were used to calculate predicted values of proton hyperfine splitting constants, using the method of McLachlan.[10,11] These are given in Table II together with the observed values of splitting constants. In earlier studies of benzoquinocycloalkane anion radicals, the

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(9) Komatsu, K.; West, R. *J. Chem. Soc., Chem. Commun.* **1976**, 570.

(10) McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.

(11) (a) A value of $Q = 28$ was used in the McConnell equation $a_H = Q\rho_c$. As in the Hückel MO calculations, the value of β_{CC} for the bond joining the anthraquino group to the central ring was reduced from 1.0 to 0.8 in compounds **2**–**4** to take account of possible twisting of the anthraquinone rings due to steric interaction. This change, however, makes very little difference in the pedicted a_H values. (b) Compound **9** is the dihydro derivative of **4**.

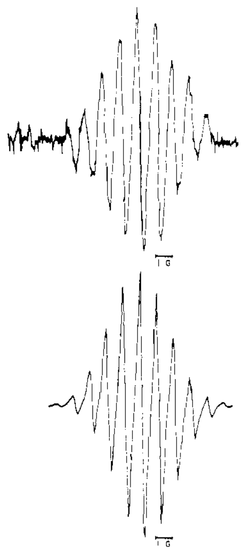
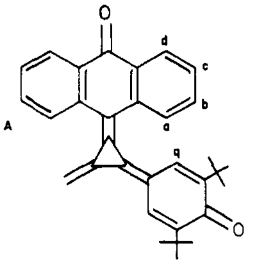


Figure 3. ESR spectrum of anion radical $\mathbf{3}^{-}\cdot$ (above) and computer simulation (below).

McLachlan calculations gave surprisingly good semiquantitative agreement with observed constants.[5] In the anthraquinonoid anion radicals, which are certainly nonplanar, quantitative agreement is generally poorer. However, the calculations are nevertheless quite useful for predicting qualitative trends and aiding in interpretation of the spectra.

As the data in Table II show, for each of the anthraquino anion radicals two of the ring carbons (a and c in structure A) are predicted to have high and nearly equal spin densities. The protons attached to these carbons are therefore expected to give rise to relatively large, nearly equal splitting constants. The other two sets of protons, b and d, are predicted to give much smaller splitting constants. The anion radical ESR spectra are all interpretable on the basis of these predictions.



The more symmetrical compounds which produce simpler ESR spectra will be treated first. Compound **3** gives upon electrolytic reduction an anion radical whose ESR spectrum is an apparent nine-line pattern, having relative line intensities 1:1.8:3.2:5.0:6.7...(Figure 3). The spectrum can be simulated as the central nine lines of an 11-line pattern obtained from two sets of six equivalent hydrogens having nearly the same coupling constants (1.08 and 1.05 G). The splittings can therefore be assigned to the equivalent sets of a and c protons of $\mathbf{3}^{-}\cdot$. Splittings due to the b and d protons are probably lost in the line width.

The ESR spectrum of the anion radical of **4** also gives a nine-line pattern, which can be simulated by assuming that spin coupling takes place from two sets of four equivalent hydrogens with hyperfine splitting constants of 1.4 and 1.2 G (Figure 4). The couplings can again be assigned to the a and c protons. Just as with **3**, the other proton couplings are not observed, consistent with theoretical prediction.

The ESR pattern for the anion radical of **5** is somewhat more complicated. The spectrum is again assignable as a nine-line pattern which can be assigned to splitting from the a and c protons. However, in this anion radical the a and c proton couplings are coincidentally equivalent. As a result a smaller splitting of 0.16 G is also observable, probably due to the b or d protons.

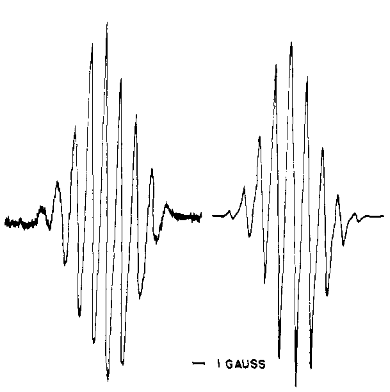


Figure 4. ESR spectrum of anion radical $\mathbf{4}^{-}\cdot$ (left) and computer simulation (right).

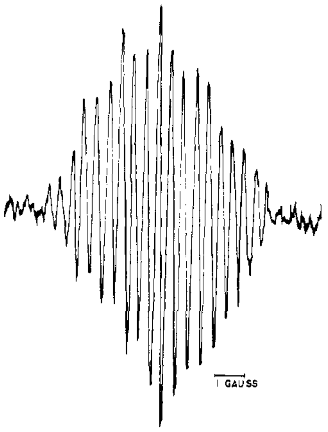


Figure 5. ESR spectrum of anion radical $\mathbf{1}^{-}\cdot$.

In compounds **1** and **2**, which contain benzoquino as well as anthraquino groups, the MO calculations predict that most of the spin density should reside in the anthraquino moieties (Table II). The splittings due to the protons on the benzoquinonoid groups (q in structure A) are predicted to be very small. Electrolytic reduction of **2** gives an anion radical showing an apparent nine-line pattern, with $a_H = 1.08$ G. We assign this splitting to nearly equivalent coupling by the eight a and c protons on the two anthraquino rings. The anion radical of **1** produces a more complex ESR spectrum consisting of 19 nearly equally spaced lines (Figure 5). Several slightly different values of hyperfine splitting constants give approximate simulations to the observed spectrum. The best simulation was obtained by using splitting constants of 1.68 (2 H), 1.2 (2 H), and 0.419 G (4 H). The two large splittings can be assigned to the a or c hydrogens and the smaller splittings to the b and d hydrogens with coincidentally nearly equal coupling.

Among the observed splitting constants in Table II, the largest values are found for the anion radical of **1**, the species which contains only one anthraquino group. Compound **2** shows much lower splitting constants, consistent with spreading of the spin density over two anthaquino moieties. Anion radical $\mathbf{3}^{-}\cdot$ shows proton hyperfine splittings almost equal to those in $\mathbf{2}^{-}\cdot$. The data, however, do not support a model for **3** where the unpaired electron is delocalized over only two of the anthraquinone rings, as this would give line intensities quite different from those observed (Table I and Figure 3). The splittings must nevertheless reflect differences in geometry with $\mathbf{3}^{-}\cdot$ more distorted from planarity than $\mathbf{2}^{-}\cdot$.

Anion radicals $\mathbf{4}^{-}\cdot$ and $\mathbf{5}^{-}\cdot$ show intermediate values for proton splitting constants. The rather low value for the principal splitting in $\mathbf{5}^{-}\cdot$ is predicted from the calculations; the calculations fail, however, to predict the relatively high a_H values found for $\mathbf{4}^{-}\cdot$.

Electron Spin Resonance Spectra of Monoradicals

As shown in Scheme I, oxidation of dihydro compounds AH_2 under neutral conditions may take place through the neutral

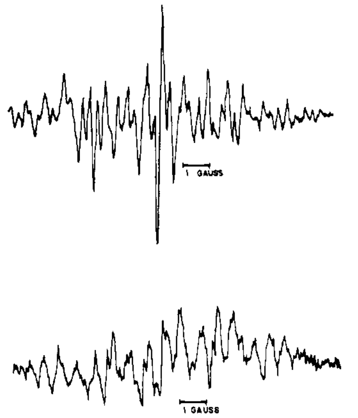
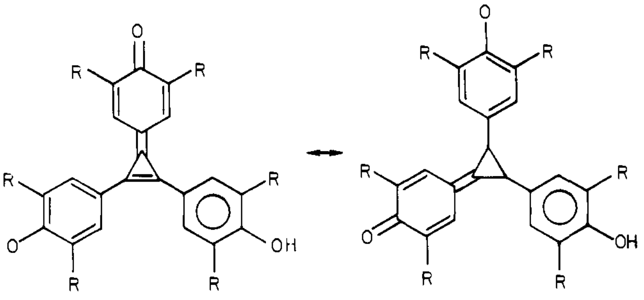


Figure 6. ESR spectrum of monoradicals from oxidation of **6** (above) and **7** (below).

semiquinone-type radicals AH·. In order to detect these intermediates, compounds **6**–**9**[11a] were oxidized with less than 1 equiv of PbO_2, and the resulting solutions were studied by ESR spectroscopy. An ESR spectrum was observed for each compound for the signals were rather weak, indicating that the monoradicals are relatively unstable with respect to the forms AH_2 and A. Similar results have been observed for other polyquinocycloalkanes.

Compounds **6**–**9** all gave quite similar ESR spectra upon partial oxidation. Typical spectra are shown in Figure 6. Exact simulations were not obtained, but the spectra are approximately simulated by assuming coupling to four dissimilar sets of two protons, with splitting constants of about 3.4, 3.0, 0.9, and 0.8 G. The large values for coupling constants are consistent with distribution of spin density over a small number of carbon atoms, rather than over several rings as in the anion radicals. We conclude that in the monoradicals of **6**–**9** the unpaired electron is *localized in a single anthroxy ring.*[12]

Localization of spin density in one anthroxy ring is expected for the monoradical of **9**. In the monoradicals from **7** and **8**, however, resonance structures can be written which would lead to delocalization over two equivalent anthroxy rings. Such delocalization is in fact observed for the corresponding monoradicals in the TQCP series, **11**. Restriction of the unpaired electron to one anthroxy moiety in the monoradicals from **7** and **8** may result from steric effects. Rotation of the anthroxy group out of the plane of the three-membered ring may relieve considerable strain in these species.



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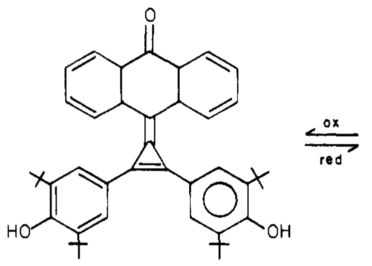
The monoradical **12** produced by oxidation of **6** is especially interesting. Compound **6** itself is entirely in the tautomeric form in which both phenyloxy groups were protonated and the anthracene group is quinonoid. However, upon oxidation, the ESR spectrum of the radical indicates that the unpaired electron is again associated with the anthracene moiety. The stable form of the monoradical may therefore be the one (**12a**) in which a phenyl ring is quinonoid, with unpaired electron restricted to the anthracene ring by steric effects.[13]



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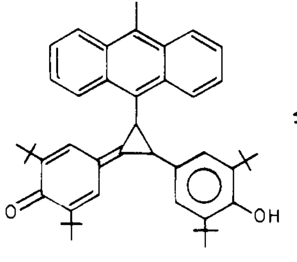
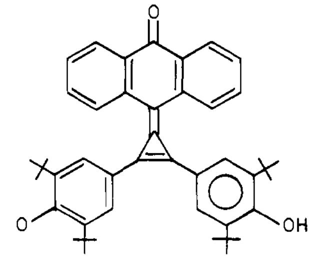


12a



12b

Experimental Section

General Procedures. Spectra were recorded by means of the following instruments: ultraviolet-visible, Cary 14; ESR, Varian 4502-13; cyclic voltammetry, Princeton Applied Research Model 170 or 169 electrochemistry system.

ESR electrolysis experiments were carried out with the use of a 300-V battery source with the current kept at <0.1 μA. The *g* values of all observed radicals were measured with the use of double cavity techniques and potassium nitrodisulfanate (Fremy's salt) as a standard.

Spectrophotometric Titrations. The base titrations of **6**–**9** were carried out by the following method. Aqueous NaOH (0.10 N) was added in 0.10-mL aliquots by use of a micropipet to a well-stirred solution of 0.02 mmol of **6** in 100 mL of spectrograde methanol. The UV–visible spectrum was recorded after each addition of the base, and the sample solution was returned to the main batch. No spectral change (beyond experimental error) was observed after the addition of 0.04 mmol of base. Addition of 0.04 mmol of HCl regenerated the original spectrum for **6**–**8**. The original spectrum of **9** could not be regenerated, indicating decomposition during the titration. Electronic spectrum for the dianion of **6**: λ_{max} (methanol) 360 nm (log ε 4.14), 393 (4.29), 447 (4.17), 520 (4.17), 550 (4.14). **7**: 360 (4.12), 370 (4.11), 505 (4.36), 537 (4.48), 576 (4.59). **8**: 367 (1.18), 440 (4.04), 460 (4.03), 542 (4.42), 580 (4.48). **9**: 372 (4.0), 445 (3.966), 540 (4.04), 580 (3.93).

Compound **6** was similarly titrated by using 0.1 N DBN in THF. The electronic spectrum of the dianion of **6** shows λ_{max} (log ε) 320 nm (4.30), 348 (4.08), 405 (4.27), 470 (4.31), 510 (4.30), 570 (sh, 3.95).

Electrolytic Generation of Anion Radicals. A few milligrams of the oxidized material (**1**–**5**) with a small amount of $(n\text{-Bu})_4N^+ClO_4^-$ was placed in an electrolytic cell. A small piece of glass wool was placed between the electrodes to slow diffusion. The cell was evacuated and THF (distilled from $LiAlH_4$ and stored over sodium/potassium anthracene) was distilled into the cell. The solution was degassed twice and the

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[12] The ESR spectrum obtained upon oxidation of **8** is weak and poorly resolved, but the line spacings are similar to those observed for the other compounds in the series.

[13] If **12b** were present, splitting from the protons in the phenyl ring would proably not be detected, since the spin density at the proton-bearing carbons is predicted to be low. However, in this structure the unpaired electron would be delocalized over a large number of carbon atoms, and therefore the splitting constants should be smaller than those observed.

cell placed in the ESR cavity. A minimal current was passed through and scanning begun.

The radical signal was observed by using the line-sharpening technique of Glarum.[14] Coupling constants have been reported in Table II. Measured *g* values: **3**, 2.003 79; **4**, 2.003 98; **5**, 2.003 55.

Generation of Neutral Monoradicals. Sample (**6–9**) (6 mg) and 2 mg of PbO_2 were weighed together and manually mixed with a spatula. Approximately one-third of this mixture was placed in an ESR cell, with about 1 mL of dry xylene. The cell was purged thoroughly with nitrogen and placed in the ESR cavity. A weak signal was generally observed, which could not be enhanced by variations in the temperature conditions. The *g* values of the monoradicals derived from oxidation of **8** and **9** were determined to be 2.003 84 and 2.003 76 ± 0.0001, respectively.

Cyclic Voltammetry. A three-electrode cell was used, having platinum wire working and auxiliary electrodes and a saturated calomel reference electrode. Sample solutions were 1 mM in anthraquinoid compounds with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte in dichloromethane which had been dried and distilled over P_2O_5. For compounds **1**, **3**, and **5**, each wave satisfied the reversibility criteria for the electrode process:[15] the ratio of cathodic and anodic peak currents, i_{pc}/i_{pa}, becomes close to unity as the scan rate is decreased, and a plot of peak current vs. the square root of the scan rate is linear passing through the origin for both cathodic and anodic peaks. Compound **2** satisfied the reversibility criteria for the first reduction wave, but accurate values for the peak currents for the second reduction wave could not be obtained. Compound **4** also satisfied the reversibility criteria for the first reduction wave, but failed to meet the criteria for the second wave.[16] For all of the compounds, the separation between cathodic and anodic peaks decreased with slower scan rates for both waves reaching minimal values of 0.08–0.1 V. Thus electron transfer must be somewhat slower than the fast transfer which occurs in completely reversible cases.[17]

Acknowledgments. This work was supported by Grant CHE76-80374 from the National Science Foundation.

Supplementary Material Available: Cyclic voltammetric data (2 pages). Ordering information is given on any current masthead page.

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(14) Glarum, S. H. *Rev. Sci. Instrum.* **1965**, *36*, 771.

(15) Adams, R. "Electrochemistry at Solid Electrodes"; Marcel Dekker: New York, 1969. Nicholson, R.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(16) Full data from the cyclic voltammograms are available on microfilm upon request.

(17) For a typically reversible case, the peak separation is expected to be 0.058 V independent of scan rate.

Chemiluminescent Thermolysis of α-Peroxylactones

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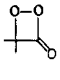
Abstract: A comprehensive study of the chemiluminescent decomposition of three α-peroxylactones (dimethyl α-peroxylactone (**1**), phenyl *n*-butyl α-peroxylactone (**2**), and diphenyl α-peroxylactone (**3**)) has been undertaken. Each compound decomposes to yield CO_2 and the corresponding ketone in high yield. The chemiluminescent species produced in these reactions have been characterized by a number of different measurements including spectral distribution of direct chemiluminescence, lifetimes, energy transfer, activation parameters, and photochemical reactions. Excited state chemiexcitation efficiencies have also been evaluated. It is shown that a combination of conventional kinetic measurements and "step analysis" of the chemiluminescence intensity provides a means of evaluating the activation energies for the deactivation paths of electronically excited states that precede the emission step responsible for chemiluminescence. The latter activation energies may also be monitored directly in some cases by measurement of excited-state lifetimes as a function of temperature. The agreement between the activation energies generated from chemiluminescence data and direct photoexcitation measurements is within the experimental error. The results for **1** are compared to those for tetramethyldioxetane (**4**) (both produce electronically excited acetone) and are found to be in excellent agreement.

Introduction

Investigation of the energetics, kinetics, activation parameters, and chemiexcitation parameters of decomposition of 1,2-dioxetanes has provided a wealth of information concerning chemiluminescence mechanisms.[1] The overwhelming proportion of published work deals with 1,2-dioxetanes, and only brief reports of α-peroxylactones have appeared,[2] possibly because of the difficulties of synthetic entries into this family of high energy content molecules. As a result of our recent discovery that α-peroxylactones may be conveniently synthesized by reaction of ketenes and phosphite ozonides,[3] we have been able to initiate a comprehensive study of the chemiluminescent decomposition of these important high-energy compounds. Our goals in this investigation were (a) to identify the excited-state species; (b) to quantify the chemiexcitation parameters; (c) to evaluate the activation parameters for the decomposition of dimethyl α-peroxylactone (**1**), phenyl *n*-butyl α-peroxylactone (**2**), and diphenyl peroxylactone (**3**); (d) to determine the activation energy for decay of the excited-state species involved in the chemiluminescence process; (e) to compare the excitation parameters of **1** and tetramethyldioxetane (**4**); and (f) to evaluate the activation parameters for the decomposition of **4** in the gas phase.



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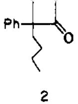

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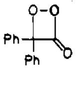

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We report here our progress toward achieving these goals and show how a combination of chemiluminescence measurements and

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