Secondary Bicyclic Peroxide Cation Radicals

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Cyclic voltammetry data are reported for nine secondary bicyclic peroxides with the oxygens in a two-atom bridge: the [2.2.1], [4.2.1], [5.2.1], [2.2.2], [3.2.2], and [4.2.2] systems (4–9, respectively) and the syn-1-bridge bromo peroxides in the [2.2.1], [3.2.1], and [4.2.1] systems (10–12). The lifetimes of the radical cations decreased in the order 7^+ (no decomposition seen by CV) > 8^+ > 4^+ ≫ 5^+ > 6^+, 9^+ (no reduction wave seen by CV). Accurate $E^{\circ\prime}$ values could be measured only for 7 (2.27 V), 8 (2.35 V), and 4 (2.40 V) because of large ΔE_p values at fast scan rates or low temperatures. ESR spectra with resolved proton hyperfine splittings are reported for 4^+, 7^+, and 8^+.

We recently showed that bicyclic tertiary dialkyl peroxides **1** and **2** give long-lived enough radical cations at room temperature to allow observation of reduction waves in their cyclic voltammograms, so that their thermodynamically significant $E^{\circ\prime}$ values could be measured with reasonable accuracy.[1] Di-*tert*-butyl peroxide (**3**) cation
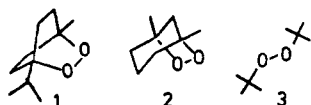
radical, in contrast, decomposed so rapidly at room temperature that only an irreversible oxidation wave was observed. Although 3^+ was longer lived at −78 °C, and both oxidation and reduction waves were observed, the difference in oxidation and reduction peak potentials, ΔE_p, was so large at low temperature that $E^{\circ\prime}$ could not be very accurately determined.

In this work we report the cyclic voltammetric behavior of nine secondary bicyclic peroxides **4–12**, compare their solution oxidation potentials with gas-phase ionization potential data from the literature,[2-5] and give ESR data for three secondary peroxide radical cations.
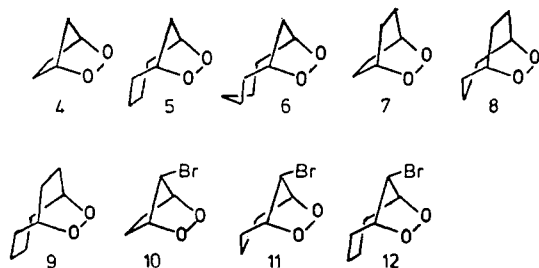
Results and Discussion

Electrochemistry. Peroxides oxidize above +2 V vs. SCE, and we observe large background currents in this range in methylene chloride. Following Parker,[6] we em-

ployed methylene chloride containing trifluoroacetic acid and trifluoroacetic anhydride (we used a 20:1:1 mixture by volume[7]) which presumably scavenges basic impurities; use of the 20:1:1 mixture allows scanning out to about 2.8 V vs. SCE before significant background current is observed. Of the compounds studied here, only **4** showed evidence for decomposition of the neutral compound. The peak current of the **4,4$^+$** oxidation wave was observed to decrease steadily over a period of tens of minutes, but since the decomposition products did not oxidize below 2.5 V vs. SCE, the position of the **4,4$^+$** oxidation wave could be measured. The radical cation reduction waves for **4, 7,** and **8** were observed even at 0.2 V/s scan rates, allowing accurate determination of $E^{\circ\prime}$. The most stable secondary peroxide radical cation studied was 7^+, which showed complete chemical reversibility (cation reduction wave as large as the neutral oxidation wave) at a 0.2 V/s scan rate. Complete chemical reversibility was observed for 8^+ at a 0.5 V/s scan rate, but 4^+ was not quite chemically reversible at this scan rate, so it has a shorter lifetime. Much shorter cation radical lifetimes were observed for **5, 6,** and **9**, and only **5** showed any reduction wave at all at room temperature, at a 20 V/s scan rate. All peroxides studied show quasi-reversible electrochemical behavior (modestly slow heterogeneous electron-transfer rate constants) so that large ΔE_p (peak-to-peak wave separation, $E_p^{ox} - E_p^{red}$) are observed at fast scan rates at room temperature and even at slow scan rates at low temperature. No chemical reversibility was observed for **9** even at −78 °C.

The relative lifetimes of peroxide radical cations make it clear that loss of a proton from carbon attached to oxygen (loss of an α-hydrogen) is the most rapid process for these species in the absence of special structural effects. No reversibility is observed for secondary peroxide cations unless a bicyclic structure holds the C–H$_\alpha$ bonds at a large angle to the axis of the spin-bearing p orbital at oxygen in the cation radical. Great increases in lifetime for heteroatomic radicals and radical ions having this structural feature have been noted previously, and the effect is called "Bredt's Rule kinetic protection".[8] Bridgehead olefins that

(1) Nelsen, S. F.; Teasley, M. F.; Kapp, D. L.; Wilson, R. M. *J. Org. Chem.* **1984**, *49*, 1845.

(2) Brown, R. S. *Can. J. Chem.* **1975**, *53*, 3439.

(3) Coughlin, D. J.; Brown, R. S.; Salomon, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 1533.

(4) Gleiter, R.; Schang, P.; Adam, W.; Eggelte, H. J.; Erden, I.; Bloodworth, A. J. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 223.

(5) Gleiter, R.; Dobler, W.; Eckert-Maksic, M.; Bloodworth, A. J.; Eggelte, H. J.; Cremer, D. *J. Org. Chem.* **1984**, *49*, 3716.

(6) (a) Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537. (b) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98.

(7) These peroxides show chemically irreversible oxidation in acetonitrile even in the presence of acid, presumably because of the greater basicity and/or nucleophilicity of the nitrile group than the chlorines of methylene chloride.

(8) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.
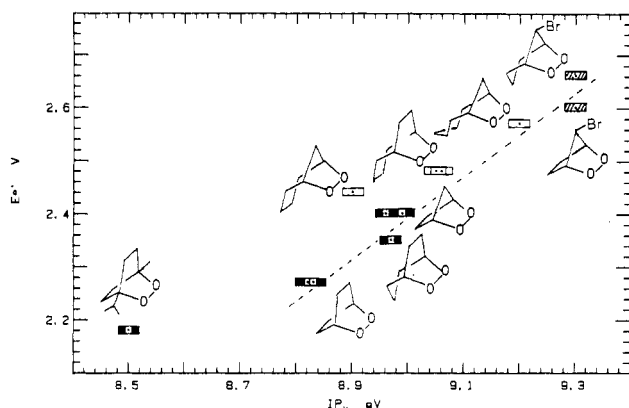
Figure 1. Plot of solution oxidation potential vs. vertical ionization potential for bicyclic peroxides (data of Table I). The filled rectangles represent $E^{\circ\prime}$ values and the open ones E_p^{ox} (0.2 V/s).

Table I. Cyclic Voltammetry[a] and Photoelectron Spectroscopy Data for Some Bicyclic Peroxides

compd	room temp		−78 °C		
	$E^{\circ\prime}$, V	ΔE_p, V	$E^{\circ\prime}$, V	ΔE_p, V	IP$_v$, eV
1[b]	2.18	0.10	2.14	0.16	8.50[c]
2[b]	2.29	0.09	2.3	0.40	
3[b]	E_p^{ox}	2.27 (irrev)	2.3	0.43	8.83[c]
4	2.40	0.12			8.99,[d] 8.96[e]
5	E_p^{ox}	2.44 (irrev)[g]	2.4	0.39	8.9[f]
6	E_p^{ox}	2.57 (irrev)[h]			9.2[f]
7	2.27	0.08	2.2_4	0.20	8.82,[d] 8.83[e]
8	2.35	0.10	2.3_4	0.36	8.97[d]
9	E_p^{ox}	2.48 (irrev)[h]	E_p^{ox}	2.68 (irrev)	9.05,[d] 9.06[e]
10	2.60[i]	0.15	2.7_5[i]	0.39	9.3[f]
11	2.66[i]	0.13	2.7_2[i]	0.35	9.3[f]
12			2.5_4[i]	0.17	9.2[f]

[a] CV conditions: solvent 20:1:1 $CH_2Cl_2/CF_3CO_2H/(CF_3CO)_2O$ 0.1 M in tetrabutylammonium tetrafluoroborate, at a Pt disk electrode; 0.2 V/s scan rate, vs. SCE. [b] From ref 1. [c] From ref 2. [d] From ref. 3. [e] From ref 4. [f] From ref 5. [g] Some reversibility seen at 20 V/s scan rate, ΔE_p = 0.42 V, $(E_p^{ox} - E_p^{red})/2 = 2.4_7$. [h] No reduction wave seen at 20 V/s scan rate. [i] Only a very small reduction wave was detected.

have a trans double bond in an eight-membered ring are isolably stable,[9] and bicyclic secondary peroxide cation radicals that contain the bridgehead hydrogens in an eight-membered ring are unstable on the CV time scale at room temperature, making the Bredt's Rule olefin analogy especially strong.

The lifetimes of the di-*tert*-alkyl peroxide cations studied indicated that C–O bond cleavage rates can be rate limiting for these species, which lack α-hydrogens. The bicyclic species 1^+ and 2^+ are both substantially longer lived than the acyclic 3^+, where CO bond stretching is not resisted by the structure. When the CO bond is further weakened by being allylic, the radical cation lifetime should become even shorter. Ascaridole (13), the 5,6-dehydro
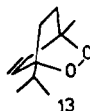
analogue of 1, shows no radical cation reduction wave even at −78 °C at a 20 V/s scan rate (E_p^{ox} 2.2 V at 0.2 V/s scan rate). It is certainly not clear whether the strained secondary cases 8^+ and 4^+ are decomposing by CO cleavage or α-hydrogen loss.

The 1-bridge bromo peroxides 10–12 showed poor behavior in the CV experiments. All three of our samples showed a broad, irreversible prewave peaking at about 2.35 V at a 0.2 V/s scan rate and at about 2.45 at 2 V/s scan rate. This prewave may represent a common impurity, although NMR indicated good purity of these samples. It might also be some sort of absorption wave. The cations from all three bromo peroxides were quite short-lived, none showing complete chemical reversibility, even at −78 °C. Only very small reduction waves appeared to be observed for 10^+ and 11^+ at room temperature, and the $E^{\circ\prime}$ values we quote should be considered tentative. The CV data are summarized in Table I.

Figure 1 shows a plot of electrochemical oxidation potentials measured in this work vs. vertical ionization potentials from the literature.[2-5] The filled rectangles show reversible $E^{\circ\prime}$ values determined in this work, while open ones represent irreversible E_p^{ox} (0.2 V/s scan rate) values. The rectangles for bromo peroxides 10 and 11 are hatched because of poor electrochemical behavior mentioned above. The uncertainty in IP$_v$ is underestimated by the horizontal size of the rectangles in Figure 1, which are shown at 0.02 eV. When two IP$_v$ measurements are

reported, both are plotted, but we do not show that IP$_v$ was only reported to 0.1 eV for 5, 6, 10, and 11.

The broken line in Figure 1 is a least-squares line through the five compounds that showed some room-temperature chemical reversibility. This line, $E^{\circ\prime} = 0.76_6 IP_v − 4.49$, has a maximum deviation in $E^{\circ\prime}$ from the data of 0.03 V and an r of 0.987, indicating a fair correlation of $E^{\circ\prime}$ with IP$_v$ for this limited series of compounds. The kinetically unprotected compounds 5, 6, and 9 show chemically irreversible oxidation, presumably because of rapid cation radical deprotonation. Kochi and co-workers[10a] discuss irreversible oxidation potentials for a series of 27 alkylated benzenes in detail, and make the point that different deprotonation rates for different R groups and numbers of R groups affect the irreversible E_p^{ox} values but only by about ±0.05 V. The situation appears to be similar here, and even plotting the irreversible E_p^{ox} data (open rectangles) along with the $E^{\circ\prime}$ data, as has been done in Figure 1, only makes the correlation have a little more scatter. Kochi and co-workers also point out that the slope in an $E^{\circ\prime}$ vs. IP$_v$ plot of 0.71 observed for their alkylated benzene data is principally caused by radical cation solvation energy differences. We note that the ditertiary peroxide 1, which is also plotted in Figure 1, has a rather higher $E^{\circ\prime}$ value than the disecondary peroxide line predicts (by 0.16 V). This is consistent with less efficient radical cation solvation for the ditertiary peroxide, which might be expected, as the bridgehead substituents could force solvent away from the formally half-positive oxygens. We see no evidence for different geometry reorganization energies for the peroxides studied here in our oxidation potential data. Because peroxide radical cations have a three-electron π-bond between the oxygens, they should resist twisting of the COOC angle θ from 0°. If the neutral form has a significant θ value, one might expect to see an increment in $E^{\circ\prime}$ corresponding to twisting θ to 0° in the $E^{\circ\prime}$ vs. IP$_v$ plot, because IP$_v$ is a vertical energy difference, while $E^{\circ\prime}$ is a measure of the adiabatic energy difference between cation radical and neutral species. Crystallographic studies[5] have shown that the neutral forms of 10 and 11 have small θ values (under 2°), while the 1-bridge syn bromide related to 5 has $\theta = 14 \pm 2°$ and that related

(9) (a) Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41–63. (b) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464–473.

(10) (a) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasimo, L.; Wrightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968. (b) Figure 2 plots the data of Table III, ref 10a, subtracting 0.24 V from the V vs. NHE entries convert to V vs. SCE.

Table II. ESR Data for Some Peroxide Radical Cations[a]

species	g factor	splitting constant, G (equiv of H) [assignment]
2^{+b}	2.0084	4.8_1 (2) [$H_{2ax,4ax}$], 0.7_1 (2) [$H_{2eq,4eq}$], 1.6_1 (1) [H_{8ax}], 0.4_9 (1), 0.2_5 (1), 0.1_5 (1), [6 H splitting under 0.05 G, LW[c] 0.12 G]
4^+	2.0094	9.9_5 (2) [$H_{5exo,6exo}$], 2.2_0 (1) [H_{7anti}], 1.1_0 (1) [H_{7syn}], 1.2_0 (2), ca. 0.3_6 (2) [LW 0.36 G]
7^+	2.0094	4.7_0 (4) [exo H_{5-8}], 1.1_8 (2) [$H_{1,4}$], ca. 0.2_7 (4) endo H_{5-8}], [LW 0.28 G]
8^+	2.0093	3.2_8 (2), 2.2_8 (2), 1.0_0 (2), [LW 0.45, 6 H unresolved]

[a] In 20:1:1 $CH_2Cl_2/CF_3CO_2H/(CF_3CO)_2O$ 0.1 M tetrabutylammonium tetrafluoroborate at -70 to -90 °C. [b] From ref 1. [c] Line width used in the simulation.
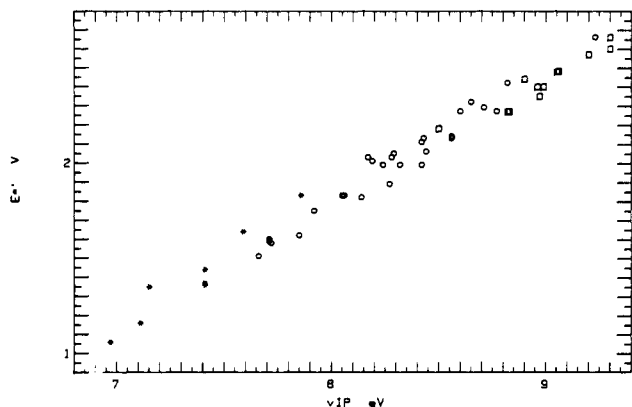

Figure 2. Plot of solution oxidation potential vs. vertical ionization potential for alkylated benzenes[10] (O), aromatic hydrocarbons[6b] (*), and peroxides (□).

to 6 has $\theta = 44 \pm 2°$ in the crystal. Any such effects are lost in the scatter of our data and thus appear not to be large.

Figure 2 compares the peroxide data of Figure 1 (as squares) with the alkylated benzene data of Kochi and co-workers[10a] (as circles,[10b] including their extrapolated benzene point), adjusted to the reference electrode used here, and the fused aromatic hydrocarbon data of Parker[6b] (as asterisks). We note that scatter in the three sets of data appears to be roughly comparable and is presumably related to radical cation solvation energy differences, which ought to differ somewhat from compound to compound. We think it noteworthy that although three different solvents are employed (CH_2Cl_2/TFA/TFAA, TFA/TFAA, and acetonitrile, respectively), the associated distributions in the $E°'$ vs. IP_v plot are quite similar. Geometry reorganization energies are certainly quite small for the large π-systems of Parker's fused hydrocarbons and are estimated to be only about 3 kcal/mol even for benzene.[10] We suggest that Figure 2 implies that geometry reorganization effects may be rather small for the peroxides as well, although the solvent change may cause a solvent stabilization effect that masks a larger geometry reorganization effect for the peroxides. The deviations of the five peroxides that showed some reversibility at 0.2 V/s from the line through the alkylated benzenes fall in the range -0.06 ± 0.04 V. Something is certainly causing the far slower heterogeneous electron-transfer rates for peroxides, which show substantial ΔE_p increases at fast scan rates and/or low temperatures, than for the aromatic systems, which do not. The two-atom π-system of the peroxides is appreciably smaller than the π-systems of either type of aromatic system and could well lead to larger outer sphere solvent reorganization energies. It is clear, however, that peroxides show far smaller geometry reorganization effects than do tetraalkylhydrazines, many of which would fall well over a volt lower than the hydrocarbons and peroxides in an $E°'$ vs. IP_v plot.[1] We attribute this to a much larger geometry reorganization energy for hydrazines. Significant

rehybridization occurs at the nitrogens of hydrazines upon electron removal, while peroxides, like aromatic compounds, lose an electron from a nearly purely p hybridized π-system.

ESR Spectra. The secondary peroxides which show chemically reversible oxidation by CV at low temperature (4, 7, and 8) give reasonably well-resolved ESR spectra under electrolytic oxidation conditions. Proton splitting constants derived from simulations of their ESR spectra are compared with those for 2^{+1} in Table II. The splittings for the H_γ hydrogens of 4^+ and 7^+ are the most revealing and will be discussed first. The small size of both single hydrogen C_7H splittings for 4^+ demonstrates that the spin-bearing orbital of the peroxide cation system is the expected $\pi^*(OO)$, so that the C_7H bonds lie in the nodal plane of the spin-bearing orbital.[11] These splittings for 4^+ (2.2 and 1.1 G) are slightly larger than those for the corresponding hydrogens of the hydrazine analogue with O replaced by NCH_3, 14^+ (1.7 and 0.8 G).[12] The largest

14   15
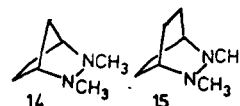
2 H splitting for 4^+ (9.9_5 G) and largest 4 H splitting for 7^+ (4.7_0 G) are clearly caused by the exo γ-hydrogens of the $(CH_2)_2$ bridges, which are in W-plan with the spin-bearing p orbitals at oxygen. Comparing these splittings with those of their hydrazine analogues, the W-plan splitting for 4^+ is about 2.1 times as large as that of 14^+ (4.8 G[12]), while that for 7^+ is about 1.8 times as large as the corresponding splitting for 15^+ (2.62 g[13]). The difference in W-plan splitting ratios for $4^+/14^+$ and $7^+/15^+$ is relatively small and quite possibly associated with pyramidiality differences in the hydrazine cations.[14] The observation of H_γ-W-plan splitting ratios of ≥ 1.8 for these O- and N-centered radical cations should be compared with the methyl H_β splitting ratio of 1.2_5 for $(CH_3)_2O^+$ in a matrix to $(CH_3)_2NH^+$ in solution.[15] The W-plan splitting

(11) For discussion of spin-labeled norbornyl derivative splitting constants, see: (a) Nelsen, S. F.; Travecedo, E. E.; Seppanen, E. D. *J. Am. Chem. Soc.* **1971**, *93*, 2913. (b) Russell, G. A.; Holland, G. N.; Chang, K.-Y.; Keske, R. G.; Mathox, J.; Chung, C. S. C.; Stanley, K.; Schmidt, K.; Blankespoor, R.; Kosugi, Y. *Ibid.* **1974**, *96*, 7237. (c) Russell, G. A.; Zeleta, M. *Ibid.* **1982**, *104*, 2318.

(12) Nelsen, S. F.; Weisman, G. R.; Hintz, P. J.; Olp, D.; Fahey, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 2916.

(13) Nelsen, S. F.; Landis, R. T., III. *J. Am. Chem. Soc.* **1973**, *95*, 6454.

(14) For discussion of a(N) and λ_m comparisons for tetraalkylhydrazines demonstrating that 14^+ and 15^+ are syn bent at nitrogen and that 14^+ is more bent at nitrogen than 15^+ see: Nelsen, S. F.; Blackstock, S. C.; Yumibe, N. Y.; Frigo, T. B.; Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 143. Bending at nitrogen mixes s character into the $\pi^*(N,N)$ orbital. Furthermore, bending in the exo and endo directions for 14^+ gives minima of different energy, while they are of the same energy for 15^+, where the two bridge are of the same size. The W-plan splittings observed for the hydrazines are time averages of structures bent different amounts in the two directions, making detailed consideration exceedingly complex.

(15) (a) Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1981**, *103*, 6994. (b) Danen, W. C.; Rickard, R. C. *Ibid.* **1972**, *94*, 3254.

ratio appears to be significantly more sensitive to the effect of replacing O by N than is the β splitting. The endo γ-hydrogens of 7^+ (a (4H) ca. 0.3 G) have a splitting only half as large as those of 15^+, demonstrating the complexity of interpreting such long-range splittings, which have multiple and canceling mechanisms for receiving small amounts of spin density.[16] We are unable to assign the smaller 2 H splittingss of 4^+ to position ($H_{1,4}$ (β) vs. endo $H_{5,6}$ (γ)). Although the bridgehead hydrogens lie significantly out of the nodal plane of the 3 e–π bond in the bicyclo[2.2.1]heptyl system so there should be a significant β splitting increment,, there is also a significant γ splitting increment in the opposite direction because of the nodal plane in the spin-bearing orbital.[11] It is noteworthy that the bridgehead splitting of 7^+ is an easily detectable 1.1_8 G, even though these hydrogens lie in the nodal plan of the p orbitals at oxygen. Stock and Wasielewski[17] showed that the bridgehead coupling in aniline cations in the 4′-aminobenzo- and 4′-aminotribenzobicyclo[2.2.2]octene cations are not zero, using pseudocontact shifts.

We do not think it is wise to attempt assignments of the splittings observed for 8^+, where only three of the five 2 H splittings were resolved, and the resolved ones only differ by a factor of three. We have not yet been successful at observing ESR spectra for the much shorter lived radical cations of either the bicyclic peroxides containing an eight-membered ring or the bromo peroxides.

Conclusions

Although dialkyl peroxides are thermodynamically extremely difficult to oxidize, their cation radical lifetimes in solution can exceed seconds. None are long-lived in acetonitrile, but some bicyclic peroxide radical cations are long-lived in CH_2Cl_2 (containing trifluoroacetic acid and anhydride to scavenge impurities). The lifetime order observed was 2^+, 7^+ (no cation decomposition observed) $> 1^+$, $8^+ > 4^+ \gg 5^+ > 6^+$, 9^+, 13^+ (no cation reduction wave observed). The much shorter lifetime when the bridgehead hydrogen is contained in an eight-membered ring implies that bridgehead deprotonation becomes rate limiting if large OCH, $\pi^*(OO)$ overlap can occur. The order of life-times observed for the bicyclo[2.2.2]octane derivatives is $7^+ > 1^+ \gg 13^+$. The CO bond strengths certainly decrease in this order, which is consistent with CO cleavage limiting lifetime when $C_\alpha H$ cleavage is precluded. The geometry reorganization increment to $E^{\circ\prime}$ of peroxides is certainly far smaller than for hydrazines, although both give three-electron π-bonded radical cations. It appears not to be much larger than for alkylated benzenes, although geometry reorganization and cation solvent stabilization effects have not been separated. The ESR spectra of 4^+ and 7^+ show that W-plan splittings are about twice as large for peroxides as for the related hydrazines 14^+ and 15^+, presumably because the $\pi^*(OO)$ orbital is stabilized relative to the $\pi^*(NN)$ orbital, so it mixes better with the σ-combination orbitals.

Experimental Section

The peroxides were prepared as previously described.[18] The cyclic voltammetry experiments were run as previously described.[8] The ESR spectrometer was a Varian E-15, and the electrochemical cell used to generate the peroxide radical cations was similar to that published by Ohya-Nishiguchi[19] except that heat-shrink tubing was used to insulate the central platinum electrode from the outer gold electrode. We estimate the errors in the splittings quoted in Table II to be about ± 0.05 G and the g factors to be good to ± 0.0002.

(16) For a review, see: King, F. W. *Chem. Rev.* 1976, *76*, 157.
(17) Stock, L. M.; Wasielewski, M. R. *J. Am. Chem. Soc.* 1973, *95*, 2743.

(18) Bloodworth, A. J.; Eggelte, H. J. *J. Chem. Soc., Perkin Trans. 1* 1981, 1375; *J. Chem. Soc., Chem. Commun.* 1982, 865.
(19) Ohya-Nishigushi, H. *Bull. Soc. Chem. Jpn.* 1979, *52*, 2064.