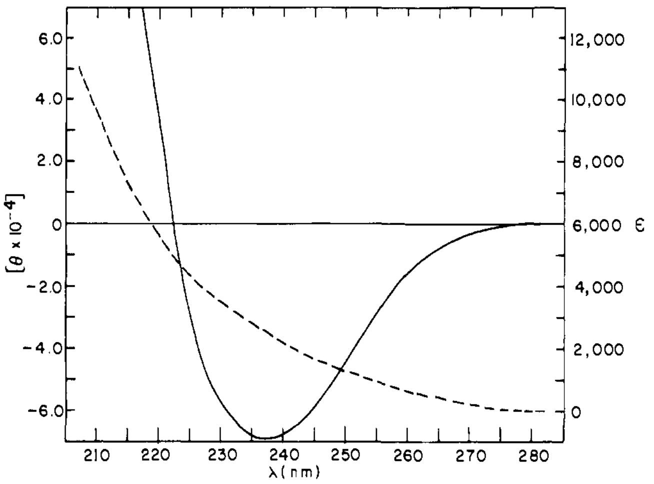
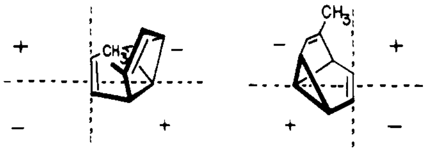


Figure 2. UV (- - -) and CD (—) spectra of (+)-**2*** (hexane solution).

deviations which are not predictable at our present state of knowledge.

The principal absorption band in (+)-**2a*** shall be considered in the present discussion as due to a $\pi \rightarrow \pi^*$ transition, although its precise spectroscopic assignment remains uncertain. Analysis of Figure 2 indicates that the sign of the CD curve due to this transition can be predicted by applying the Scott and Wrixon octant rule[15] to the outer semibullvalene framework in either of the two projection formulas (A and B) which do not position the methyl group in the noncontributory *z* plane of a left-handed Cartesian coordinate diagram. In A, the methyl group and its attached double bond are positioned in a front octant which is negative; the rear octant features which characterize B generate the identical result. Thus, the effect of methyl perturbation on the chiroptical properties of the semibullvalene nucleus is dissignate.[16]



A (front octant)   B (rear octant)

Although this analysis nicely correlates the negative Cotton effect of (+)-**2a*** with its absolute configuration, it has assumed that the double bonds in semibullvalene behave as isolated olefinic linkages. However, at least one theoretical analysis has raised the issue of dominant through-space interaction in molecules of this type.[17] Consequently, as additional chiral semibullvalenes become available, it may prove necessary to refine matters through application of coupled oscillator theory.[18,19]

Acknowledgment. This work was supported in part by the National Institutes of Health and the National Science Foundation.

Supplementary Material Available: Final atomic (Table I) and anisotopic thermal parameters (Table II), bond lengths (Table III), and bond angles (Table IV) for (+)-**7*** (3 pages). Ordering information is given on any current masthead page.

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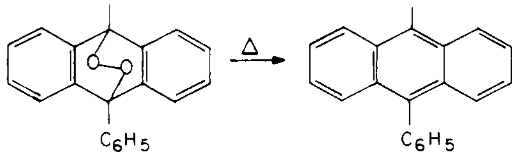
Magnetic Isotope Effect on the Thermolysis of 9,10-Diphenylanthracene Endoperoxide as a Means of Separation of ^{17}O from ^{16}O and ^{18}O

Sir:

In principle, magnetic fields will influence any chemical process involving a change in electron spin multiplicity.[1] The experimental question to be answered involves the magnitude of magnetic effects in cases of interest. Intersystem crossing (ISC, singlet-triplet or triplet-singlet) of organic radical pairs[2] (or diradicals)[3] has been shown to be sensitive to magnetic fields resulting from laboratory fields[4] and from nuclear magnetic moments.[5] When ISC of a radical pair is competitive with chemical or physical processes (which do not involve ISC), the efficiency of these processes will depend on magnetic fields. The observation of a magnetic isotope and/or a magnetic field effect on a chemical reaction is impressive evidence in support of radical pair or a diradical intermediate along the reaction pathway. A significant laboratory magnetic field effect was observed[6] on the relative yields of singlet ($^1O_2$) and triplet ($^3O_2$) oxygen produced from the thermolysis of 9,10-diphenylanthracene endoperoxide (DPA-O_2) as shown in eq 1.



$$+ \alpha\,{}^1O_2 + (1 - \alpha)\,{}^3O_2 \quad (1)$$

The (simplified) mechanism shown in eq 2 was employed to interpret the basis of the influence of magnetic fields on the

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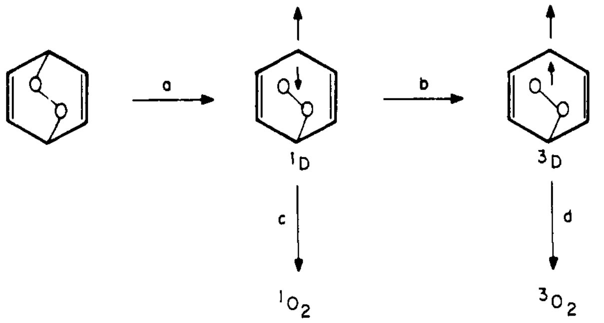
Table I. Yield of $^1O_2$ Formation and Isotopic Composition in the Thermolysis of DPA-O_2

yield of $^1O_2$[a]			composition of nontrappable O_2,[e] ^{17}O	solvent	magnetic field
^{16}O[b]	$^{17,18}O$[c]	^{18}O[d]			
0.37 ± 0.02	0.34 ± 0.01	0.37 ± 0.01	0.380 ± 0.005	$CHCl_3$[f]	0.5 G
0.32 ± 0.01	0.31 ± 0.01	0.31 ± 0.01	0.368 ± 0.002	$CHCl_3$[f]	10 kG
			0.369 ± 0.001	$CHCl_3$, dioxane	(control[g])
0.32 ± 0.01	0.28 ± 0.02	0.32 ± 0.02	0.376 ± 0.001	dioxane[f]	0.5 G
0.27 ± 0.02	0.23 ± 0.01	0.28 ± 0.02	0.376 ± 0.002	dioxane[f]	12 kG

[a] The yield of $^1O_2$ is defined as the ratio of disappearance of tetracyclone to the appearance of DPA.[6] The yield is derived directly from the mixed isotopic oxygen containing DPA employed; i.e., no adjustment in yield is made for the differing percents of ^{16}O, ^{17}O, and ^{18}O in the starting DPA-O_2. The error given is the standard deviation derived from a minimum of eight independent samples, each sample measured once. [b] The initial isotopic composition is 99.8% ^{16}O. [c] The initial isotopic composition is 60% ^{18}O, 37% ^{17}O (and 3% ^{16}O). [d] The initial isotopic composition is 92% ^{18}O, 4% ^{17}O (and 4% ^{16}O). [e] $DPAO_2$ (0.02 M) containing 36.9% ^{17}O in degassed solution was thermolyzed at 90 °C. Typically, the conversion was >90%. The molecular oxygen generated was analyzed on a JEOL-JMS-07 mass spectrometer. The error limits refer to the standard deviation derived from four independent samples, each sample being measured four times. The signal (voltage) was converted to frequency with a 1-MHz V/F converter (Analog Devices). The frequency was stored and integrated with a Tracor Northern TN-1710 Multichannel Analyzer. The setup provides an accuracy, 0.05%, calibrated with natural abundance CO_2 and O_2. [f] Molecular oxygen produced from the thermolysis of $DPAO_2$ in the presence of tetracyclone. [g] Molecular oxygen produced from thermolysis of $DPAO_2$ in the absence of tetracyclone.

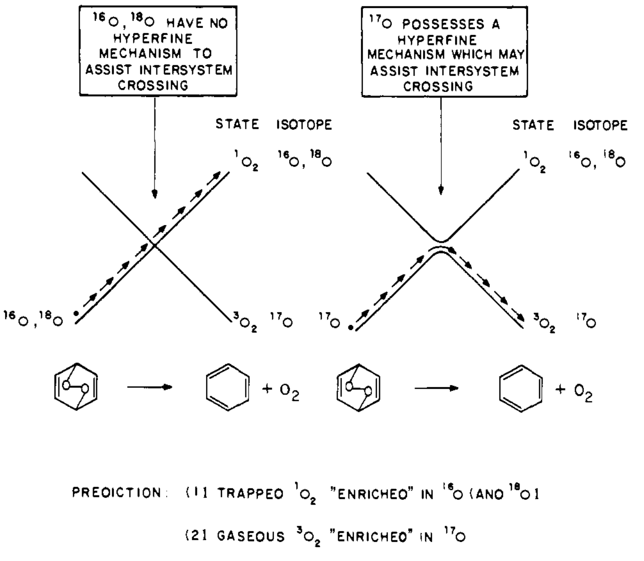
thermolysis of DPA-O_2. The key intermediate is the diradical ^1D which may undergo ISC to ^3D (step b), a process that is competitive with elimination of $^1O_2$ (step c).



(2)

Magnetic isotopes will influence the competition between step b and step c (eq 2). Consider (Scheme I) the difference between ^1D species containing ^{17}O (a magnetic isotope) and ^1D species containing ^{16}O and/or ^{18}O (nonmagnetic isotopes). As molecules approach the diradicaloid structure (near the surface crossing),[7] those possessing a ^{17}O nucleus will have a higher probability of undergoing intersystem crossing than molecules possessing only ^{16}O and/or ^{18}O nuclei. Since ^{17}O-containing molecules will undergo ISC from ^1D to ^3D more efficiently, *$^1O_2$ will be produced less efficiently and $^3O_2$ will be produced more efficiently from ^{17}O-containing molecules than from molecules containing only ^{16}O and/or ^{18}O nuclei!* Thus, if a selective and efficient trap of $^1O_2$ is present, *the "untrappable" O_2 produced by thermolysis of DPA-O_2 will be enriched in ^{17}O!*

Scheme I



To test the validity of these ideas, DPA-O_2 enriched in ^{17}O was synthesized and thermolyzed in the presence and absence of $^1O_2$ traps.

Two types of measurements were made: (a) the ^{17}O and (^{16}O + ^{18}O) content of untrappable oxygen was analyzed by mass spectrometry and (b) the yield of trapped $^1O_2$ was evaluated by quantitative determination of the amount of reacted acceptor when DPA-$^{16}O_2$, DPA-$^{18}O_2$ or DPA-$^{17}O_2$ were employed. From Table I it can be seen that the yield of $^1O_2$ formation is smaller for ^{17}O-containing DPA-O_2. The fact that both DPA-^{16}O and DPA-^{18}O produce the *same* yield of $^1O_2$, while DPA-^{17}O produces less $^1O_2$ rules out a significant mass isotope effect as the basis for different quantum yields. The observation that the results change quantitatively when reactions are run in a laboratory magnetic field confirms the conclusion that a magnetic spin isotope effect is operating.

Since the amount of reacted trap is monitored in the yield measurements they only provide an *indirect* test of the isotopic enrichment. A *direct* measurement involves determination of the isotopic composition of the untrappable molecular oxygen produced in the thermolysis of DPA-O_2. Table I lists the isotopic composition of untrapped molecular oxygen produced from thermolysis of DPA-O_2 in $CHCl_3$ and in dioxane. Since a small amount (1–2%) of ^{16}O was invariably present in these samples owing to contamination with oxygen from air (99.8% ^{16}O) the analysis of oxygen composition is based on the mass peaks, 36, 35, 34, and 33 only. The results demonstrate that the untrappable molecular oxygen is indeed enriched in ^{17}O relative to the control sample.

In summary, our results are consistent with the postulate that the thermolysis of DPA-O_2 produces a mixture of $^1O_2$ and $^3O_2$ as primary products via an initial singlet diradicaloid intermediate (^1D) which can either fragment to yield $^1O_2$ or intersystem cross to yield a triplet diradicaloid (^3D) that can fragment to yield $^3O_2$. When the singlet diradicaloid possesses an ^{17}O atom that can interact, via hyperfine coupling, with an electron spin, the rate of intersystem crossing $^1D \rightarrow {}^3D$ is accelerated relative to the rate for singlet diradicaloids that possess only ^{16}O or ^{18}O atoms. The experimental manifestations of this magnetic isotope effect are a lower quantum yield for $^1O_2$ formation in ^{17}O-enriched DPA-O_2 and a selective isotopic enrichment of ^{17}O in the untrappable molecular oxygen generated in the thermolysis of DPA-O_2. To the best of our knowledge, these results represent the first report of selective separation of a "middle" isotope by a chemical process.[8] It is surprising to conclude that ISC of a relatively small diradical will be influenced by hyperfine coupling. It may be that the observed effect is, in fact, due to the hyperfine interaction in a small population of diradicals that have a structure for which electron exchange between the radical centers is very small. If this is true, then reduction of the exchange interaction might strongly enhance the magnitude of the observed effect.

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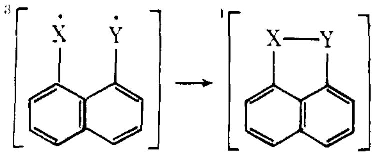
On the Mechanism of Intersystem Crossing and Ring Closure of the Triplet 1,8-Naphthoquinodimethane Biradical

Sir:

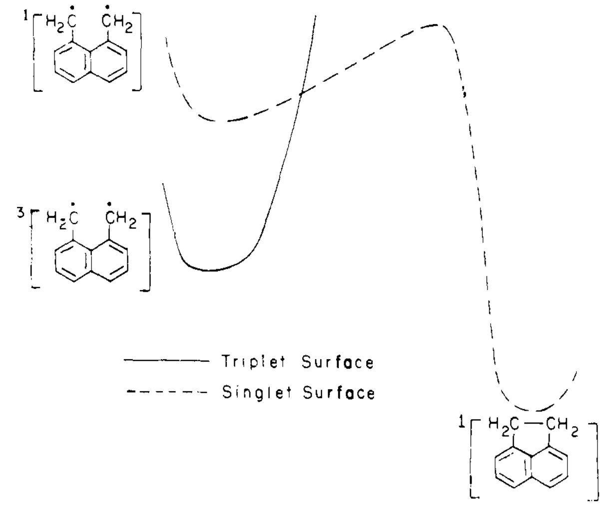
Triplet biradical intermediates are implicated in many photochemical[1] and chemiluminescent reactions.[2] They can decompose intramolecularly to stable singlet products by several processes such as ring closure, fragmentation, and disproportionation. Intersystem crossing (ISC) from the triplet to a singlet spin state may occur prior to (Scheme I) or concurrent with (Scheme II) chemical reaction of the triplet biradical. With the notable exception of the Closs and Doubleday[3] CIDNP study of Norrish type 1 acyl biradicals, very little is known about the mechanism of the crucial ISC step. It therefore seemed worthwhile to prepare various perinaphthalenediyls (**1**) and measure their absolute rate of ring closure. In this manner geometric variation in the biradicals might be minimized as substituent effects were examined. We herein report the results of such a study on the parent hydrocarbon biradical (**1a**) and its tetradeuterio derivative (**1b**).



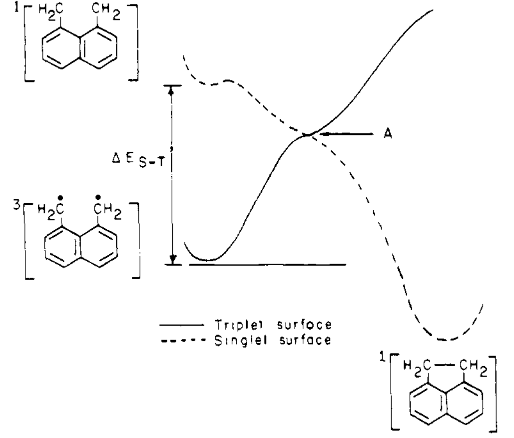
1

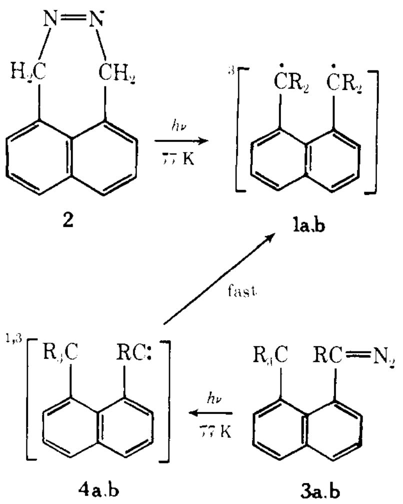
a, X = Y = CH_2; b, X = Y = CD_2

Scheme I



Scheme II





(a) R = H; (b) R = D

1,8-Naphthoquinodimethane was first observed by Pagni[4] by the photolysis of azo compound **2**. It can also be prepared by low-temperature photolysis of diazo compound **3** in 2-methyltetrahydrofuran (2MTHF) or hexafluorobenzene.[5] The hypothetical carbene intermediate **4a** was not observed, even at 4 K. As primary isotope effects may be exceptionally large at cryogenic temperatures, particularly if tunneling processes are involved, it was hoped that **4b** might be sufficiently long lived to afford ESR detection.[6] The synthesis of **3b** is shown in Scheme III (isotopic purity of the tosyl hydrazone, 75.6% d_4, 18.2% d_5, 3% d_6, and 4% d_7, as determined by mass spectroscopy). Photolysis of **3b** ($\lambda > 350$ nm) at 10 K produced a strong spectrum of the tetradeuterio biradical ($|D/hc| = 0.022$

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