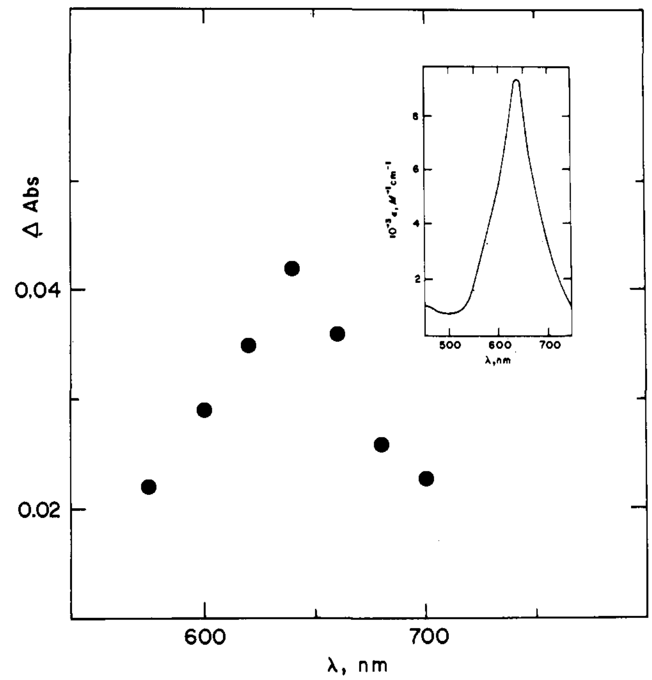

Figure 1. Spectrum of the transient observed 600–800 ns after the 530-nm laser pulse; [$Ru(bpy)_3^{2+}$] = 5×10^{-5} M, [$Co^{II}L$] = 8×10^{-3} M, [HA^-] = 0.5 M, pH 8.1, 25 °C. Shown in the insert is the spectrum of $Co^I[Me_6[14]dieneN_4]$ reported in ref 11.

efficient compared with that of the Eu(II) system, the ascorbate system is important because it represents a photochemically driven upconversion of ~20 kcal mol^{-1}.

The reduction of other substrates may prove of greater value than the photoreduction of water. Here we have demonstrated the photoproduction of a Co(I) species that undergoes oxidative-addition of a hydronium ion. It should be possible to photogenerate catalysts which undergo other oxidative-addition reactions. The feasibility of this alternative is supported by work of Fleischer and Krishnamurthy[27] who report the catalytic reduction of acetylene to ethylene and the stoichiometric reduction of N_2 to NH_3 by a Co(I) porphyrin in aqueous solution. Current efforts in these laboratories are directed toward the identification of systems in which photochemically initiated hydrogenation of such substrates can be carried out.

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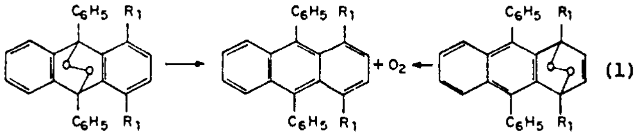
Thermolysis of Anthracene Endoperoxides. Concerted vs. Diradical Mechanisms. Microscopic Reversibility in Endothermic Chemiluminescent Reactions

Sir:

Thermolysis of 9,10-anthracene endoperoxides **1** and **2** and of 1,4-anthracene endoperoxides **3** and **4** results[1-4] in nearly quantitative (>95%) production of molecular oxygen and the parent anthracene (eq 1). For the thermolysis of anthracene endoperoxides **1–4** we have measured (1) the yields of both singlet[5] and triplet molecular oxygen, (2) the activation parameters,[6] and (3) the reaction enthalpies,[7]



1 (R_1 = H)
2 (R_1 = CH_3)
5 (R_1 = H)
6 (R_1 = CH_3)
7 (R_1 = OCH_3)
3 (R_1 = CH_3)
4 (R_1 = OCH_3)

From Table I it is noted that each reaction is *endothermic*. Nonetheless, the chemiluminescent process to generate $^1O_2$ reaches efficiencies approaching 100% for **3** and **4**. Thus, the bulk of the energy for formation of $^1O_2$ comes from activation energy and not reaction exothermicity. From Table I it is found that a correlation exists between $\Delta S^{\ddagger}$ for the thermolyses and the yield of $^1O_2$; a high positive value of $\Delta S^{\ddagger}$ (9,10-endoperoxides) correlates with a low yield of $^1O_2$ and a near-zero (or slightly negative) value of $\Delta S^{\ddagger}$ (1,4-endoperoxides) correlates with close to a quantitative yield of $^1O_2$.

Consider Figure 1 which displays a schematic representation of the pertinent energy surfaces corresponding to the reaction coordinate for eq 1. According to theoretical calculations,[4] a singlet-triplet surface crossing is expected along the reaction

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Table I. Reaction Enthalpies,[a] Activation Parameters,[b] and Singlet Oxygen Yields[c] for the Thermolyses of Endoperoxides **1-4**

compd	ΔH, kcal/mol	$\Delta E^{\ddagger}$, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$^1O_2$, yield, %	solvent
1	+5	33.2 ± 0.2	15.4 ± 0.1	32.5 ± 0.2	9.6 ± 0.5	35	dioxane
		32.1 ± 0.2	14.9 ± 0.1	31.4 ± 0.2	7.3 ± 0.5	35	chlorobenzene
2	+3	32.5 ± 0.3	14.9 ± 0.2	31.8 ± 0.3	7.4 ± 0.8	50	dioxane
		30.3 ± 0.4	13.7 ± 0.3	29.6 ± 0.4	2 ± 1	75	chlorobenzene
3	+8	30.5 ± 0.3	13.0 ± 0.2	29.8 ± 0.3	−1.8 ± 0.8	95	dioxane
4	+1	24.8 ± 0.3	13.0 ± 0.2	24.2 ± 0.2	−0.3 ± 0.7	95	dioxane

[a] Reaction enthalpy of thermolysis of solid endoperoxide measured by differential thermal analysis.[7] [b] Activation parameters derived from Arrhenius plots of the first-order rate constants for appearance of anthracene product (monitored by UV analysis).[6] [c] Yield of $^1O_2$ determined by quantitative trapping with tetracyclone. Trapping experiments run at 90 °C.[5]

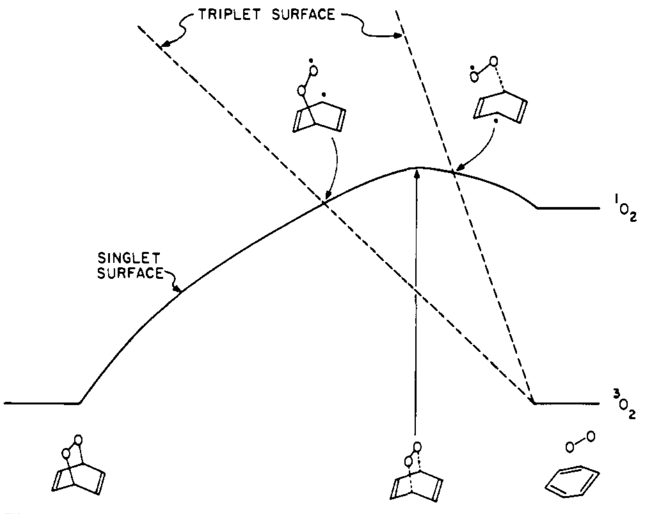

Figure 1. Qualitative reaction profile for the thermolysis of the endoperoxide of an aromatic hydrocarbon.

coordinate for the *concerted* thermolysis of endoperoxides. It is reasonable to expect that for certain endoperoxides a greater or lesser tendency toward concerted transition states will exist and that the expected singlet-triplet crossing may occur at structures that come earlier or later than the concerted transition state structures. From our experimental data, 1,4-endoperoxides are interpreted as decomposing via a concerted mechanism since quantitative yields of $^1O_2$ are produced. This conclusion is supported by the similarity of the value of $\Delta S^{\ddagger}$ for a "classical" concerted fragmentation, the retro [4 + 2] cycloaddition of dicyclopentadiene[8] to the values found for 1,4-endoperoxide thermolysis ($\Delta S^{\ddagger} = -1$ and ~ -2 eu, respectively). There is little opportunity to generate effective spin-orbit coupling anywhere along the reaction coordinate for a concerted reaction (no one-center, odd-electron structures);[9] thus, *the system never leaves the lowest energy singlet surface, and $^1O_2$ is produced quantitatively.* In the case of **3** and **4**, nearly 90% of the activation energy required to initiate reaction is retained as electronic excitation energy in $^1O_2$. This suggests that the transition state occurs late in the thermolysis of 1,4-endoperoxides. In the case of 9,10-endoperoxides, the breaking of a single C-O bond evidently occurs competitively with or preferentially to completely concerted bond breaking. As a result, a greater diradicaloid character results as the system proceeds along the reaction coordinate, and more effective spin-orbit coupling is available because of developing one-electron character on an oxygen atom. In the region of the singlet-triplet surface crossing, the system now has a better opportunity to "jump" to the lowest energy triplet surface as a result of the enhanced spin-orbit interaction which results from one-center interactions.[9] The conclusion of a greater contribution of a diradicaloid structure to the transition state is supported by the similarity of the values of $\Delta S^{\ddagger}$ for a "classical" diradical fragmentation, the retro [2 + 2] cycloaddition of cyclobutane[8] and the values found for 9,10-endoperoxide thermolyses ($\Delta S^{\ddagger} \sim +9$ and $\sim +7$ eu, respectively).

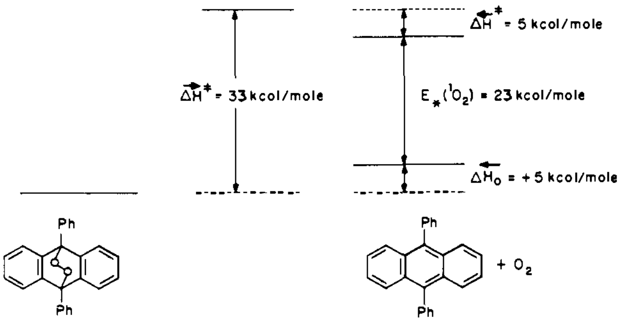

Figure 2. Energy diagram for 9,10-diphenyl-9,10-anthracene endoperoxide.

In the case of 9,10-diphenylanthracene endoperoxide (9,10-DPAO_2), construction of a complete energy diagram (Figure 2) for the reaction 9,10-DPAO_2 → DPA + $^1O_2$ is possible since the energy for $^3O_2 \rightarrow {}^1O_2$ excitation is known (~23 kcal/mol),[10] the activation energy of reaction of $^1O_2$ and DPA has been determined to be +5 kcal/mol,[11] and the heat of reaction of 9,10-DPAO_2 → DPA + $^3O_2$ has been evaluated to be +5 kcal/mol.[7] It is clear that the inefficiency in formation of $^1O_2$ from 9,10-DPAO_2 is not simply a function of reaction energetics, since the transition state for thermolysis is higher in energy than the $^1O_2$ + DPA product state. Our data for 9,10-DPAO_2 are consistent with the postulate that the chemiluminescent thermal generation of $^1O_2$ from 9,10-DPAO_2 and the photochemical addition of $^1O_2$ to DPA are related by microscopic reversibility: i.e., $\overrightarrow{\Delta H}^{\ddagger} = \overleftarrow{\Delta H}_0 + \overleftarrow{\Delta H}^{\ddagger} + E(^3O_2 \rightarrow {}^1O_2)$.

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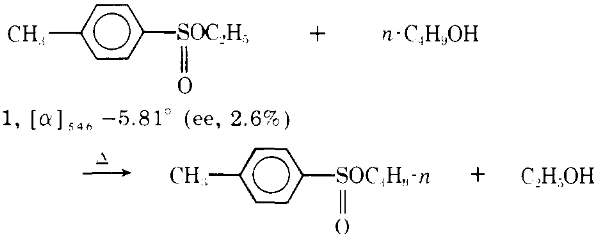
Nucleophilic Substitution at Sulfur. Kinetic Evidence for Inversion of Configuration at Sulfinyl Sulfur in Acid-Catalyzed Transesterification of Sulfinates

Sir:

In 1925 Phillips[1] prepared for the first time optically active levorotatory ethyl *p*-toluenesulfinate (*1*) and *n*-butyl *p*-toluenesulfinate (**2**) by kinetic resolution taking place when (−)-octanol-2 was heated with two molecular proportions of either racemic ethyl or *n*-butyl *p*-toluenesulfinate. Moreover, he stated that thermal transesterification of (−)-**1** with 1-butanol gives (+)-**2**. If one assumes, as Phillips did, that both (−) esters **1** and **2** obtained from kinetic resolution have the same configuration around sulfur, it follows that the conversion of (−)-**1** into (+)-**2** should occur with inversion of configuration. These experiments are considered to be the earliest evidence of the stereochemical course of substitution at chiral sulfur center.

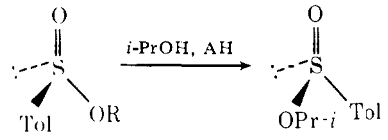


(−)-1, $[\alpha]_{546}$ −5.81° (ee, 2.6%)

(+)-**2**, $[\alpha]_{546}$ +0.32° (ee, 0.1%)

Recently, considerable progress has been made[2-5] in the synthesis of optically active sulfinates as well as in the determination of their optical purity and chirality at sulfur. This cast a new light on the experiments described by Phillips. First of all, the stereospecificity of the reaction shown above is extremely low (it does not exceed 5%), although, in accord with the original assumption by Phillips, the conversion of (−)-**1** into (+)-**2** is, indeed, accompanied by inversion.[6] However, in our hands the reaction of (−)-**1**, $[\alpha]_{589}$ −25.7°, with 1-butanol performed under the conditions described by Phillips resulted always in the formation of the completely racemic sulfinate ester **2**. Therefore, the desirability of exploring other experimental approaches to establish the steric course of the transesterification reaction of sulfinates was obvious.

Taking into account that hydrolysis of certain sulfinates and sulfites can be catalyzed by acids,[7] we have first investigated the stereochemistry of the reaction between optically active alkyl *p*-toluenesulfinates **3**, **4**, and **5** and isopropyl alcohol in the presence of strong acids (AH) like CF_3COOH, CF_3SO_3H, and $PhSO_3H$. The reaction was carried out at room temperature in isopropyl alcohol solution using equimolar amount of acid in respect to sulfinate. When the reaction was complete (see Table I) the usual workup (quenching with water, extraction, neutralization) gave isopropyl *p*-toluenesulfinate (**6**) which was isolated by distillation in yields of over 80%. The results obtained are summarized in Table I.



3, R = CH_3
4, R = $CH_2{=}CHCH_2$
5, R = $CH{\equiv}CCH_2$

6

As inspection of the results in Table I shows that, in contrast to the nonstereospecific reaction of **3**, sulfinate esters **4** and **5** undergo transesterification with predominant inversion of configuration, though the stereospecificity of these conversions was low. The highest stereospecificity (40%) of the reaction was observed for **5** in the presence of trifluoromethanesulfonic acid. In this context, it is interesting to note that both the acidic catalyst and the leaving alkoxy group have an influence on the stereospecificity of the considered reaction.

Most probably the great extent of racemization observed is due to the competitive symmetrical alkoxy-alkoxy exchanges in the starting and produced sulfinates. However, another possible way to account for these results is to assume that transesterification of sulfinates proceeds by an addition-elimination mechanism involving a dialkoxysulfurane intermediate which racemizes via permutational isomerization.[8]

In order to provide more rigorous evidence supporting the inversion in the transesterification of sulfinates as well as to gain better insight into mechanism of this reaction, we utilized the classical approach used by Hughes[9] to establish that inversion of configuration accompanies S_N2-type substitution. This approach, which consists of the comparison of the rate of racemization with that of isotopic exchange, has recently been successfully applied to phosphorus[10] and silicon[11] chemistry.

To this end we have (a) synthesized optically active sulfinate **3** containing ^{14}C in the methoxy group by the asymmetric reaction shown in eq 1 and (b) measured the rate of racemization of **3** and isotopic methoxy-methoxy exchange in methanol in the presence of trifluoroacetic acid.

The racemization and isotopic exchange measurements[12] were carried out under exactly the same conditions using a methanol solution of sulfinate (+)-**3** (12.37×10^{-2} mol/L) and trifluoroacetic acid (17.52×10^{-2} mol/L). The results obtained are shown in eq 2.

Table I. Acid-Catalyzed Reaction of (−)-*S*-Alkyl *p*-Toluenesulfinates with Isopropyl Alcohol

compd	starting sulfinate		catalyst	reaction time, h	sulfinate **6**		stereospecificity
	$[\alpha]_{589}$,	ee, %			$[\alpha]_{589}$, deg	ee, %	
3	−19.35	9.3	CF_3SO_3H	75	0	0	0
4	−15.6	10.7	CF_3COOH	98	0	0	0
4	−15.6	10.7	CF_3SO_3H	18	+2.0	1	9.2
4	−15.6	10.7	$C_6H_5SO_3H$	2.5	+1.7	0.9	7.9
5	−4.4	4.0	CF_3COOH	72	+0.3	0.15	3.8
5	−24.2	21.7	CF_3SO_3H	41	+17.6	8.7	40

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