optically pure $(+)_D Co(en)_3^{3+}$ is produced in 50% en and 26% pure in 100% en. They tried to explain these results in terms of a mechanism involving direct substitution of a complex nature. However, we feel the data are better explained in terms of electron-transfer catalysis by $Co(en)_3^{2+}$. Busch et al. noted, in fact, that some Co^{II} is produced when KCoEDTA is dissolved in ethylenediamine.

When KCoEDTA was dissolved in 50% en, we found, in accord with the previous work, the production of $Co(en)_3^{3+}$ within a short time. However, in the presence of added H_2O_2 or EDTA, the reaction did not proceed significantly in several hours. Moreover, added $Co(ClO_4)_2$ accelerated the reaction.

Thus we propose the mechanism

$$CoEDTA^- + Co(en)_3^{2+} \rightarrow Co(en)_3^{3+} + CoEDTA^{2-} \quad (1)$$

$$CoEDTA^{2-} + 3en \rightarrow Co(en)_3^{2+} + EDTA^{4-} \quad (2)$$

Note that only $\sim 1 \times 10^{-4}$ M Co^{II} is necessary for a 5-minute half life. The stereoselectivity demonstrated for reaction 1 leads to the stereoselectivity of the overall reaction.

It remains to be learned whether significant discrimination will be observed in systems where both reactants carry charges of the same sign.

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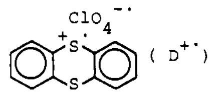
Formation of Sulfinyl Oxide and Singlet Oxygen in the Reaction of Thianthrene Cation Radical and Superoxide Ion

Sir:

Recently much attention has been focussed on photooxygenation via a non-singlet-oxygen mechanism.[1] Some of the cases have been suggested to involve an electron-transfer process to produce the substrate cation radicals and/or superoxide ion in photosensitized oxygenation with α diketones,[1,2] Rose Bengal,[3] or 9,10-dicyanoanthracene (DCA).[4] Foote has originally proposed that the oxidation proceeds through the direct coupling of substrate cation radicals and the superoxide ion.[5] This sequence was applied to the DCA-sensitized oxygenation of alkenes and sulfides.[4a] However, it seems to us that these ion radicals may undergo annihilation by electron transfer from the superoxide ion to cation radicals to produce singlet oxygen which gives indirect oxidized products rather than direct coupling to produce dioxetanes or peroxy intermediates (eq 1).[6,7]

$$D^{+\cdot} + O_2^{-\cdot} \begin{array}{l} \nearrow DO_2 \\ \searrow D + {}^1O_2 \end{array} \quad (1)$$



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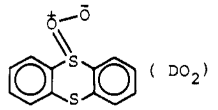

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On the other hand, more recently, Tang[8] and Landis[9] have proposed a new route for non-singlet-oxygen photooxygenation, in which the cation radical reacts with triplet oxygen and propagates radical-chain oxidation for the Barton's reagent[10] catalyzed oxygenation of dienes, such as ergosteryl acetate, and for the photosensitized oxygenation of azines, respectively. Especially, the former case is clearer because of definite implication of cation radicals in the reaction system.

Therefore, to elucidate the possibilities of the oxidation through direct coupling of the cation radical and superoxide ion, it is necessary to use both stable ion radicals. Now this communication reports the first example in which the reaction of the sulfur cation radical and superoxide anion radical gave, not only singlet oxygen by the annihilation reaction, but also direct coupling.

We initiated our investigation using the thianthrene cation radical perchlorate (**1**)[11] and KO_2 as the superoxide anion radical. The reaction of **1** and KO_2 to give sulfinyl oxide (**2**)[12] is evidenced by the change in products as a function of added diphenyl sulfide, which was the original method used by Foote[12a] and Martin.[12c] In a typical experiment, 1–2 mmol of **1** and 4 mmol of KO_2 in 50 cm^3 of acetonitrile were added to the freeze–pump–thaw flask, separately, and the flask was evacuated. The solution of **1** was then transferred into the suspension of KO_2. The color of the solution of **1** (violet, λ_{max} 546 nm) soon disappeared with vigorous evolution of oxygen. The evolved oxygen was measured by manometer and the reaction mixture was analyzed by GLC. Two products, thianthrene and thianthrene 5-oxide, were obtained in comparable yields, but thianthrene 5,5-dioxide unexpectedly was not detected. Treatment of an acetonitrile solution of 20 mmol of diphenyl sulfide and 4 mmol of KO_2 with a solution of 1 mmol of **1** rapidly gave 17% diphenyl sulfoxide with a comparable yield of thianthrene 5-oxide. Parallel studies with Na_2O_2 were also carried out under similar conditions. The yields of thianthrene 5-oxide were half of those in the absence of diphenyl sulfide (see Table I).

Reference to Table I indicates that, at least from a stoichiometric viewpoint, both the annihilation and direct coupling reactions occur. If the annihilation prevails, thianthrene and oxygen may be produced in quantitative yields. In the presence of diphenyl sulfide, thianthrene 5-oxide formation is apparently suppressed (entry III and V), and the yield of thianthrene is concomitantly increased. Furthermore, the yields of thianthrene 5-oxide and diphenyl sulfoxide are approximately equal. Under these conditions, **1** is inert to oxygen, and thianthrene and diphenyl sulfide are not oxidized with KO_2 or Na_2O_2. These results could be explained in terms of complete interception of sulfinyl oxide **2** by diphenyl sulfide. The mechanism is outlined in Scheme I. Hence, the reaction of **2** with thianthrene obtained from the annihilation reaction was readily diverted by diphenyl sulfide. The intermediate **2** was also produced by the reaction of peroxide ion (O_2^{2-}) with **1**, but the

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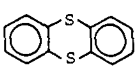
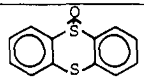
Table I. Reaction of Thianthrene Cation Radical Perchlorate (**1**) with KO_2 and Na_2O_2[a]

Entry	System	Products Yields (%)[b)]			
				Ph_2SO	O_2
I	H_2O	46	54		
II	KO_2	43	47		55
III	KO_2+excessPh_2S	80	15	17	50
IV	Na_2O_2	59	34		23
V	Na_2O_2+excessPh_2S	75	14	21	0

[a] The reaction was carried out with 1–2 mmol of thianthrene cation radical perchlorate (**1**), 4 mmol of KO_2 or Na_2O_2, and 20 mmol of Ph_2S in MeCN. [b] Average of two experiments.

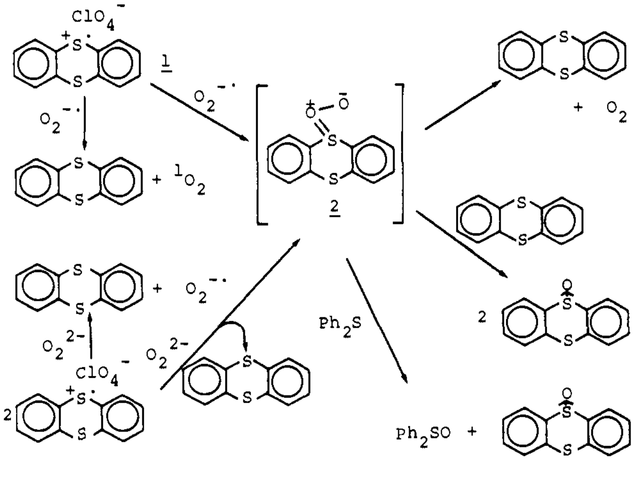
yields of thianthrene 5-oxide and oxygen definitely decreased (entry IV), compared with those of entry II. This seems to be because 2 equiv of **1** is consumed in generating intermediate **2** (Scheme I). Furthermore, entry V shows that oxygen does not evolve when diphenyl sulfide is present in the reaction system, in contrast to entry III. It can be seen that oxygen was formed only by the decomposition of sulfinyl oxide **2**; so the addition of diphenyl sulfide completely suppressed the evolution of oxygen in entry V. On the other hand, the oxygen in entry II may be formed from both decomposition of sulfinyl oxide **2** and the annihilation by superoxide ion ($O_2^-\cdot$).

Competitive co-oxidation of pairs of para-monosubstituted diphenyl sulfides with **2** showed such a sulfinyl oxide to be electrophilic, with a ρ value of -0.94, while similar co-oxidation of these sulfides with diethyl sulfinyl oxide produced by Rose Bengal sensitized photooxygenation gave a ρ value of -0.61.[12f]

We now try to take an evidence of singlet oxygen formation spectroscopically in the reaction of **1** and KO_2 or Na_2O_2. Because of being both the most electrophilic and nucleophilic in the system, the chemical trapping method is not suitable.[13] If our mechanism is correct, the oxygen produced by the reaction of **1** with KO_2 is expected to be singlet oxygen, but not in the reaction with Na_2O_2.

An acetonitrile suspension of a large excess of KO_2 or Na_2O_2 to the cation radical **1** was transferred to a quartz cell in a new type of spectrometer[14] and, in the dark, an acetonitrile solution 0.1 M in cation radical **1** was slowly added to the solution through a capillary tube to maintain generation of oxygen without vigorous bubbling. The solution was not stirred during spectral analysis.

Scheme I



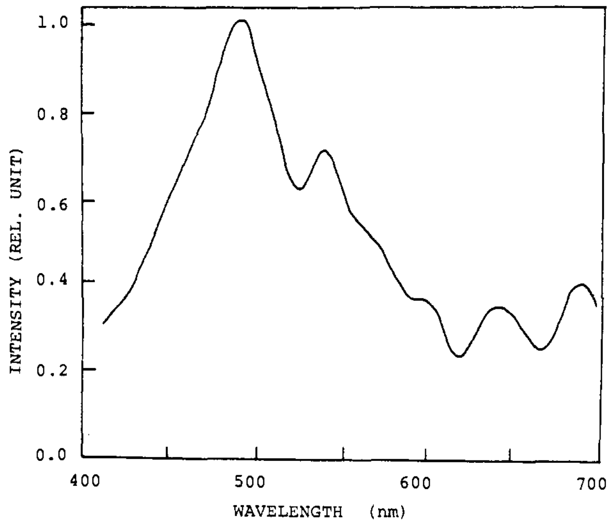


Figure 1. Emission spectrum observed in the reaction of thianthrene cation radical perchlorate (**1**) with KO_2.

Consequently, we obtained a strong emission from the reaction of **1** and KO_2, but no detectable emission from the reaction of **1** and Na_2O_2, supporting our mechanism. The intensity of emission is in proportion to the evolution of oxygen and the disappearance of color of **1** and is not detectable after their completion, in spite of a large excess of KO_2 used.[15] The emission spectrum in the reaction of **1** and KO_2 is shown in Figure 1. In this spectrum, five characteristic peaks around 480, 530, 580–600, 630, and 680 nm are distinguishable, so that the spectrum has a resemblance to that of the singlet oxygen luminescence spectrum previously reported, except for the different intensities of the peaks.[16d,17] The emitter would not be the singlet state of thianthrene because of the small energy of the annihilation reaction.[18] Actually, the emission maximum of thianthrene was not observed at 434 nm in present spectrum.[20] We believe that the use of spectroscopy for the determination of the formation of singlet oxygen by the annihilation reaction was not reported previously.[21]

It is noteworthy that the cation radical and superoxide anion radical underwent not only the annihilation reaction, but also the direct coupling reaction.

Acknowledgment. The authors gratefully acknowledge Professor Christopher S. Foote for helpful discussions.

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(18) The singlet state of thianthrene is 2.48 eV,[20] but the energy of annihilation, ΔH°, is ~1.84 eV according to[19] $\Delta H^\circ = eE^\circ(A/A^-\cdot) - eE^\circ(D/D^+\cdot) + 0.16$ eV where $E^\circ(A/A^-\cdot)$ for oxygen is −0.75 V vs. SCE and $E^\circ(D/D^+\cdot)$ for thianthrene is +1.25 V vs. SCE.

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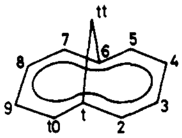
Aromatic Protonation. 6.[1] The Rearranged Ion of Monoprotonated 1,6-Methano[10]annulene. Evidence for the Presence of a Cyclopropylcarbinyl Cation Moiety

Sir:

The protonated aromatic hydrocarbon 1,6-methano[10]-annulene (**1**)[2] is, in view of its methano bridge, a potential source of cyclopropylcarbinyl cations. We reported that treatment of **1** with FSO_3H-SbF_5-SO_2ClF at −120 °C yields the stable monocation **2**, but that, on raising the temperature to −60 °C, the dication **3**, containing the cyclopropyldicarbinyl dication moiety **4**, is formed.[1] A decade ago Winstein and Warner reported on the monocation **2**, using FSO_3H, and briefly indicated a slow rearrangement to another species at −60 °C.[3] We now report on the rearrangement of **2** to the stable cation **5**, containing the cyclopropylcarbinyl moiety **6**. Addition of **1** in SO_2ClF to a solution of FSO_3H-SO_2ClF (1:1 v/v) at ca. −100 °C in an NMR tube resulted in an orange-colored solution of **2**. At −60 °C ion **2** rearranges slowly (in ~1 h) to ion **5** (dark red), as was established by NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **5** are shown in Figure 1, and the chemical shifts, coupling constants, and assignments[4] are compiled in Table I.



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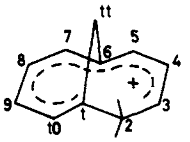

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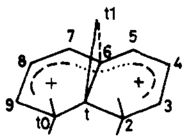

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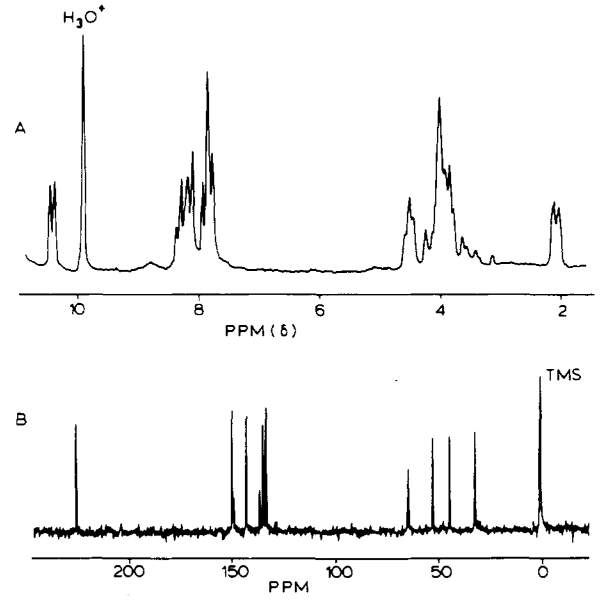
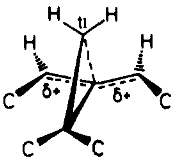


Figure 1. ^1H NMR (100 MHz) spectrum (A) and ^{13}C proton noise decoupled NMR spectrum (B) of ion **5** in FSO_3H-SO_2ClF at −60 °C.



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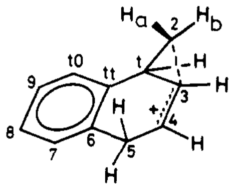

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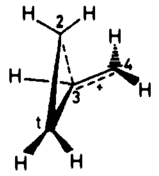

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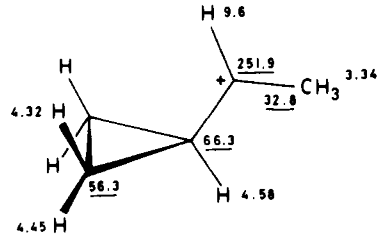
Both the ^1H and ^{13}C NMR spectra show three types of signals, viz., the aliphatic ones, those of a disubstituted benzene moiety,[5] and one of the carbocationic center. Comparison of the aliphatic ^1H and ^{13}C NMR data with those of, e.g., the bisected ions **7**[6] and **8**[7] reveals the presence in **5** of a cyclopropylcarbinyl cation moiety.



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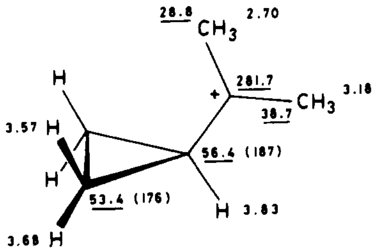

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The rearrangement of **2** to **5** may be rationalized in terms of ring closure (in **2**) between C(1) and C(6) after which the bridge methano group wanders over the "naphthalenium" skeleton probably via a [1,2] and subsequent [1,4] sigmatropic shift (see Scheme I), although two subsequent [1,3] shifts cannot be ruled out a priori. Quenching of the ion solution of

0002-7863/80/1502-4528$01.00/0