:lectron ground-state process), the complete retention of optical activity in **5** requires that **7** has been formed with complete inversion at the migrating carbon, as depicted in Scheme III.

This result is consistent with either of the two routes shown, i.e., a four-electron, ground-state, 1,3 sigmatropic shift of **6** to **7**, or a concerted, six-electron, excited-state di-π-methane isomerization of **5** to **7**.[9] It is inconsistent with a photochemical conversion of **6** to **7**, such as has been suggested for the cyclopentadiene phototransposition.[3] Since thermal 1,3 sigmatropic shifts in bicyclopentenes have likewise been ruled out,[10] the "conjugated di-π-methane" option for cyclopentadiene seems most attractive.[11] In fact, we now favor this alternative for the indene series as well, since all attempts to obtain NMR or UV spectral evidence for **6** have been without success. This is the case even upon photolysis at −90 °C, at which temperature rearrangement still occurs (albeit with reduced efficiency). More telling is the fact that the total photorearrangement of **5** has a $\phi \simeq 0.25$.[12] If one assumes that the inefficiency is solely due to competitive first-order reversion of **6** to **5** (vs. the 1,3 shift of **6** to **7**), than the E_{act} for the 1,3 shift is *at most* ~0.7 kcal/mol higher than that for reversion. A comparison of the bond and strain energies involved in the two steps makes clear that this small difference is unrealistically low.[13]

Acknowledgment. We are grateful to Professors John Brauman and Andrew Kende for helpful discussions, and the Army Research Office for partial support of this research.

References and Notes

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(6) Prepared from optically active 3-phenylbutanoic acid[7] using the method of Meurling.[8] The substrate so prepared has $[\alpha]^{27}_D$ +109° (*c* 1.7, benzene) (lit.[8] $[\alpha]^{25}_D$ +115° (*c* 2.0, benzene)).
(7) A.-M. Wieder and G. Bergson, *Acta Chem. Scand.*, **18**, 1484 (1964).
(8) L. Meurling, *Acta Chem. Scand., Ser. B*, **28**, 399 (1974).
(9) Clean inversion of the methane carbon in di-π-methane rearrangements has been demonstrated; cf. H. E. Zimmerman, T. P. Gannett, and G. E. Keck, *J. Am. Chem. Soc.*, **100**, 323 (1978); H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *ibid.*, **96**, 4630 (1974).
(10) G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **99**, 4853 (1977), and references therein.
(11) Reference 10, footnote 11.
(12) Determined by monitoring **9** and using the 0.93 ratio determined from the deuteriomethyl series.
(13) There is evidence for the 1,3 shift mechanism in certain heterocycle photorearrangements; cf. ref 2c and 2e.

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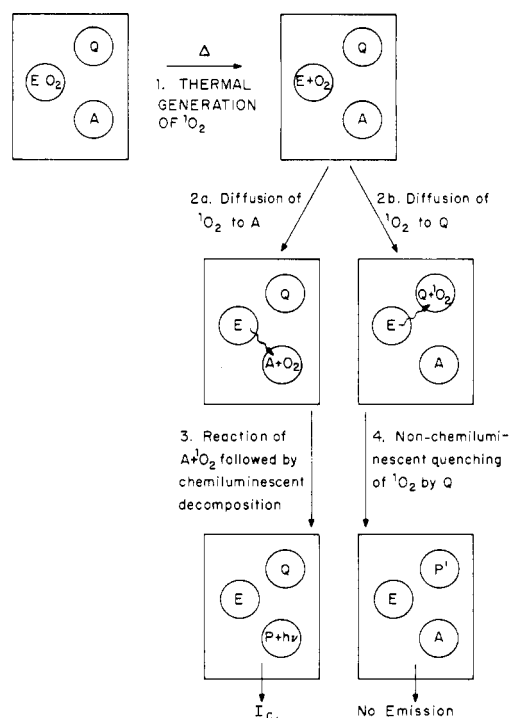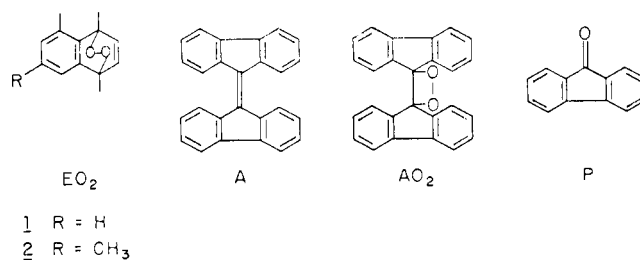*West Lafayette, Indiana 47907*
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Figure 1. Schematic representation of the chemiluminescent system designed to measure $^1O_2$ diffusivity and reactivity in polymers. Step 1 is thermal decomposition of a naphthalene endoperoxide (EO_2) to generate $^1O_2$ at a polymer site distinct from that of $^1O_2$ acceptor (A) and $^1O_2$ quencher (Q). Step 2 involves either diffusion to the site of A (step 2a) or to the site of Q (step 2b). Step 3 is the reaction of $^1O_2$ with A to yield detectable chemiluminescence. Step 4 is the nonchemiluminescent quenching of $^1O_2$ which is competitive with step 3 and therefore is competitive with chemiluminescence.

chemical pathways leading to polymer disintegration are known with certainty. We report a simple, nonphotochemical method for generation and quantitative investigation of the physical and chemical properties of $^1O_2$ in polymer films. Conceptually, our method (Figure 1) employs (1) an endoperoxide (EO_2) which may be solubilized in polymer films and which is capable of generating $^1O_2$ thermally at convenient temperatures; (2) a singlet oxygen acceptor, A, which forms an adduct AO_2 upon reaction with $^1O_2$; (3) selection of adducts (AO_2) which are capable of decomposing in the polymer with the production of a chemiluminescent product P. Quantitative measurement of the chemiluminescence intensity I_{CL} as a function of the concentration of A, C_A, at constant temperature provides information concerning physical properties (diffusivity) of $^1O_2$ in the polymer film. Measurement of I_{CL} as a function of the addition of singlet oxygen quenchers (Q) at fixed C_A and temperature provides information concerning the chemical properties (reactivity) of $^1O_2$ toward these quenchers in the polymer systems.[2]

The compounds employed in this study are given in Chart I. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) films were used as test matrices to explore the feasibility of the

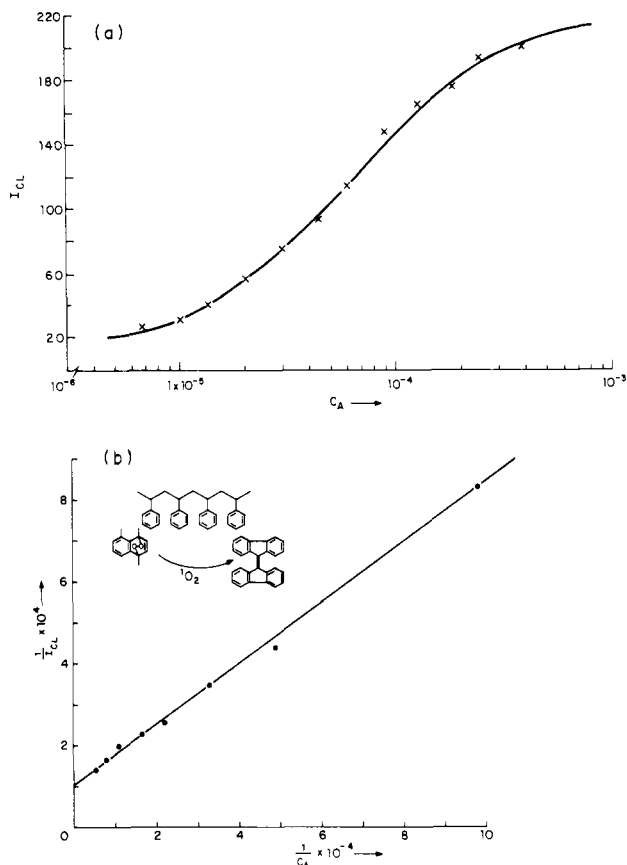## Generation, Diffusivity, and Reactivity of Singlet Oxygen in Polymer Matrices. A Convenient and Sensitive Chemiluminescent Technique

Sir:

Singlet oxygen $^1O_2$ has been suggested as an important contributor to thermal and photochemical degradation of polymers.[1] In spite of a vast and ever expanding literature, neither the method of generation of $^1O_2$ nor the details of the

Chart I

1 R = H
2 R = CH$_3$

Figure 2. (a) Graph of the measured chemiluminescence intensity (I_{CL}) as a function of acceptor concentration C_A in polystyrene films. The units of concentration are mole of A per mole of monomer of polystyrene. (b) Graph of experimental data of (a) plotted according to eq 5.
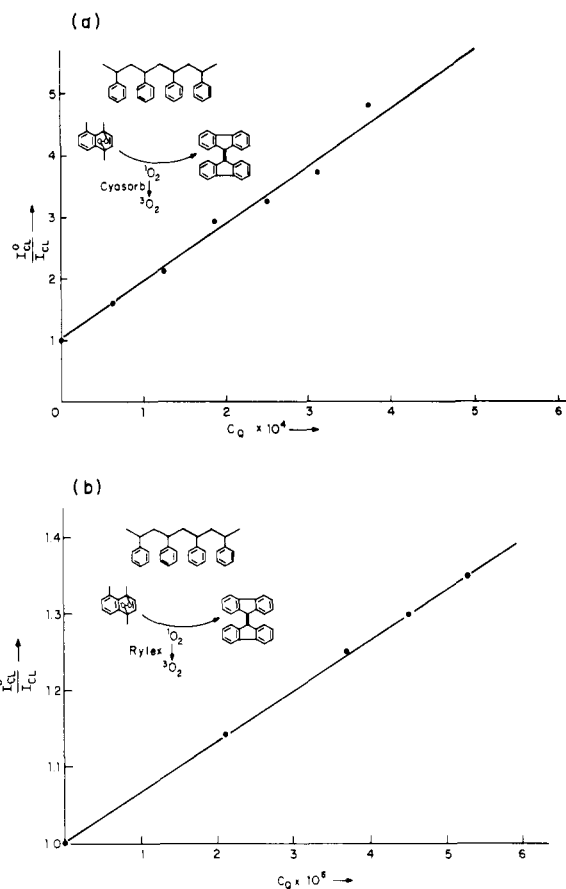

Figure 3. Graph of $I_{CL}{}^0/I_{CL}$ vs. C_Q in units of mole of Q per mole of monomer of polystyrene (Stern–Volmer quenching plot). According to eq 6, the slope of this plot equals $P_Q/(C_P + PC_A)$. (a) Cyasorb as quencher. (b) Rylex as quencher.

method. Polymer films containing EO_2 and A were found to be chemiluminescent, with the emission being experimentally indistinguishable from that of fluorenone fluorescence. Fluorenone was detected as a reaction product by IR and TLC analysis. We conclude that the reaction sequence given in eq 1–3 is involved in the chemiluminescent reaction.[3] Increasing the concentration of A resulted in an initial increase followed by a leveling off in I_{CL} (Figure 2a).

$$EO_2 \xrightarrow{\Delta} E + {}^1O_2 \qquad (1)$$

$$A + {}^1O_2 \rightarrow AO_2 \qquad (2)$$

$$AO_2 \rightarrow 2P + h\nu \qquad (3)$$

A model analogous to the hopping model employed for exciton migration[4] can be employed to handle the data and derive quantitative parameters relating to ${}^1O_2$ diffusivity. From this model, the relationship between the measured chemiluminescence intensity I_{CL} and the concentration of A is given by

$$I_{CL} = \alpha_{CL} k_r C_A / (k_q C_A + k_d C_P) \qquad (4)$$

where α_{CL} is a constant that is characteristic of the rate of generation of ${}^1O_2$ from EO_2, k_r is the rate constant for *reaction* of ${}^1O_2$ and A to yield AO_2, k_q is the rate constant for total quenching of ${}^1O_2$ by A, and k_d is the rate characteristic decay constant of ${}^1O_2$ in the polymer in the absence of A. C_P is the hypothetical concentration of intrinsic polymer quencher that leads to unit quenching efficiency of ${}^1O_2$. *The unit of concentration is mole of substance per mole of monomer.*

At high concentrations of A (i.e., $C_A \rightarrow \infty$), I_{CL} approaches a limiting value ($I_{CL}{}^{max}$). Experimentally, $I_{CL}{}^{max}$ is readily measurable so that eq 4 is reformulated as eq 5, where $P \equiv k_q/k_d$.

$$(I_{CL})^{-1} = (I_{CL}{}^{max})^{-1}[1 + (C_P/PC_A)] \qquad (5)$$

Equation 5 predicts a linear relationship between $(I_{CL})^{-1}$ and $(C_A)^{-1}$ and identifies the slope of such plots with $C_P/I_{max}P$, i.e., slope/intercept is identified as equal to C_P/P. Indeed, experimental plots of $(I_{CL})^{-1}$ vs. $(C_A)^{-1}$ are linear (Figure 2b) and a value of C_P/P of 7×10^{-5} for PS is evaluated from the data. Since a limiting value of I_{CL} is obtained, we may assume[4b] that $P \sim 1$. Under this assumption, the ratio of slope to intercept of Figure 2b is identified as C_P. From the exciton migration model,[4] the "number of hops", n, made by an exciton through a polymer during its lifetime is given by $n = (C_P)^{-1}$. We now associate "the hop" of an exciton between polymer units with the translational displacement of ${}^1O_2$ between two pendant monomers of a given (average) separation. From the data of Figure 2b, $n = 1.43 \times 10^4$ for ${}^1O_2$ in PS. Thus, the "range", l, of diffusion[5] of ${}^1O_2$ in PS is evaluated as 660 Å. Similar treatment of data for PMMA yields a value of 420 Å.

It is proposed that ${}^1O_2$ is responsible for polymer degradation.[1] Therefore, known quenchers of ${}^1O_2$ may be effective polymer stabilizers. Data relevant to the efficiency of quenchers of ${}^1O_2$ in polymers are therefore of substantial importance. Such data are available by use of our chemiluminescent method. Consider the influence of an additional, nonchemiluminescent quencher that quenches ${}^1O_2$ with rate constant k_Q. A simple Stern–Volmer relation (eq 6) should obtain if our conclusion concerning the range of diffusivity is correct; i.e., "statistical mixing" of ${}^1O_2$ should occur during its lifetime.[6] Equation 6 (where $P_Q = k_Q/k_d$) predicts a straight-line plot of $I_{CL}{}^0/I_{CL}$ vs. C_Q, as is found experimentally for Cyasorb and Rylex as quenchers (Figure 3).[7] Control ex-

periments demonstrated that these quenchers do not quench fluorescence from photoexcited fluorenone under the reaction conditions. Thus, the observed chemiluminescence quenching in polymers must be due to interception of $^1O_2$.

$$I_{CL}^0/I_{CL} = 1 + [P_Q/(C_P + PC_A)]C_Q \qquad (6)$$

Since our experimental method is novel and potentially subject to unsuspected artifacts, we seek independent confirmation that our conclusions are tenable. With the assumption that the diffusivities of $^1O_2$ and $^3O_2$ are similar, we may evaluate the lifetime, τ, of singlet oxygen from the equation[4] $l = \sqrt{3D\tau}$, where D is the diffusion coefficient of $^3O_2$. Taking our experimental values of l and literature values of D, we calculate $\tau(^1O_2)$ is 135×10^{-6} and 430×10^{-6} s in PS and PMMA, respectively. These values fall in the range of literature values[8] reported for the lifetime of $^1O_2$ in fluid solutions: 10×10^{-6} to 1000×10^{-6} s. Furthermore, our values of ($\sim$500–600 Å) are comparable with those found[9] for the average diffusional distance of $^1O_2$ in stearate monomolecular films ($\sim$500 Å). The ratio of quenching constants for Rylex and Cyasorb derived from the ratio of slopes in Figure 3 is $\sim$7 (6.7×10^4 vs. 9.4×10^3). The ratio of rate constants for these quenchers in fluid solution is $\sim$30 (5×10^9 vs. 1.6×10^8).[7] This difference is attributable to a "leveling" effect of the polymer medium on relative quenching rates.[10]

The conformity of our data and conclusions with those derived from three completely independent sources of measurement is substantial support for the validity of the proposed mechanism. The measurement of relative quenching constants for $^1O_2$ in polymers now is relatively straightforward matter. It will be of interest to study quenching effectiveness of "physical" and "chemical" quenchers of $^1O_2$ in polymers and to compare these results with those obtained from liquid-phase experiments. Such investigations are now in progress and will be reported in due course.

References and Notes

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(5) The l is the value of the end to end distances of random walks in *n* hops, according to $l = a \times n^{1/2}$, when *a* is the average separation distance between nearest neighbor monomers and is taken to be 5.5 Å for PS.
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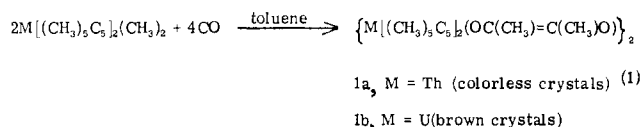*New York, New York 10027*
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Bis(pentamethylcyclopentadienyl)actinide Alkyls: Facile Activation of Carbon Monoxide, Carbon–Carbon Double Bond Formation, and the Production of Unusual Oxygen-Bonded Migratory Insertion Products

Sir:

As part of our investigation of the relationship of organoactinide[1] electronic configuration and ligation pattern to chemical reactivity,[2] we recently reported thermally stable bis(pentamethylcyclopentadienyl)thorium and -uranium dialkyls[3] and their rapid hydrogenolysis to give bis(pentamethylcyclopentadienyl)actinide dihydrides.[3,4] The enhanced reactivity of the organoactinides over analogous titanium and zirconium compounds was noted.

Recently, there has been considerable interest in the reactions of early transition metal organometallics with carbon monoxide since the products,[5,6] which are frequently not classical[7] metal acyls, may be representations of intermediates in the catalytic reduction of CO.[5b,8,9] Carbonylation chemistry of organoactinides would clearly be of interest, and we report here the very facile activation of CO by bis(pentamethylcyclopentadienyl)thorium and -uranium alkyls (the first example of migratory insertion involving actinide–carbon σ bonds), the unusual molecular structure of the $Th[(CH_3)_5C_5]_2(CH_3)_2$ dicarbonylation product, and some structure-sensitivity observations on the CO incorporation process.

In toluene solution at -80 °C, $Th[(CH_3)_5C_5]_2(CH_3)_2$[3] and $U[(CH_3)_5C_5]_2(CH_3)_2$[3] take up 2.0 equiv of carbon monoxide ($<$1 atm) within 1 h (eq 1). Warming to room temperature

$$2M[(CH_3)_5C_5]_2(CH_3)_2 + 4CO \xrightarrow{\text{toluene}} \{M[(CH_3)_5C_5]_2(OC(CH_3)=C(CH_3)O)\}_2$$

1a, M = Th (colorless crystals) (1)

1b, M = U (brown crystals)

produces **1** in quantitative yield. The insertion products were recrystallized from toluene and characterized by standard analytical techniques;[10] cryoscopic molecular measurements reveal them to be dimeric.[10] Infrared transitions at 1655 ($\nu_{C=C}$), 1252 and 1220 (ν_{CO}) cm^{-1} as well as a single nonring methyl signal in the ^1H NMR spectrum are suggestive of a 2-butene-2,3-diolate fragment (A). This ligand was proposed
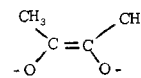
A

for the monomeric product of the slower (requiring 24 h at 75 °C) dicarbonylation of $Zr[(CH_3)_5C_5]_2(CH_3)_2$.[5a]

Single crystals of **1a**, obtained by cooling of a hot toluene solution, are monoclinic, space group $P2_1/n$ (an alternate