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(12) The ^{15}N NMR spectra of the Ph$_4$P$^+$ salts (^{15}N 97%) in acetone-d_6 at room temperature show resonances at −184.0 ppm ($W_{1/2}$ = 44 Hz) for the cobalt compound and the central five lines of a septet at −272.6 ppm ($W_{1/2}$ = 1.0 Hz) with respect to external CD$_3$^{15}NO$_2$, ^1J(Rh^{15}N) = 6.1 Hz, for the rhodium compound. Corresponding resonances are observed in the ^{14}N spectra, although the resonance of the rhodium compound shows only three poorly resolved lines of the expected septet, ^1J(Rh^{14}N) $\simeq$ 4 Hz, due to unfavorable relaxation effects.
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Secondo Martinengo*
Centro del C.N.R. sui bassi stati di ossidazione
Via G. Venezian 21, 20133 Milan, Italy

Gianfranco Ciani,* Angelo Sironi
Istituto di Chimica Generale dell'Università
Via G. Venezian 21, 20133 Milan, Italy

Brian T. Heaton
University Chemical Laboratory
Canterbury, Kent, CT2 7NH, England

Joan Mason
Open University, Milton Keynes
Buckinghamshire, England
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Chemiluminescence of Diphenoyl Peroxide. Pulsed Laser Spectrophotometric Detection of Radical Ion Intermediates on the CIEEL Path

Sir:

Our investigation of the chemiluminescence of diphenoyl peroxide (DPP) led us to postulate the chemically initiated electron-exchange luminescence (CIEEL) mechanism for that[1] and, later, for numerous other peroxides.[2] The key feature of the CIEEL mechanism is the rate-limiting single-electron transfer from the chemiluminescent activator to the peroxide to generate radical-ion intermediates from the neutral, ground-state, closed-shell reactants. These ions undergo further chemical transformations before they finally annihilate to form electronically excited states. The primary evidence for the intermediacy of the radical ions in this sequence has been the correlation of reaction kinetics with the redox properties of the reactants. We report herein the results of our pulsed laser spectrophotometric[3] study of the reaction of DPP with several electronically excited electron donors (activators). Pulse excitation enables us to identify the intermediate reaction products by their characteristic absorption spectra and also to measure the rate of the reaction. These experiments show quite clearly that radical ions are formed in the reaction of DPP with the chemiluminescence activators and that generation of caged ions precedes the formation of electronically excited products in the chemiluminescence process.

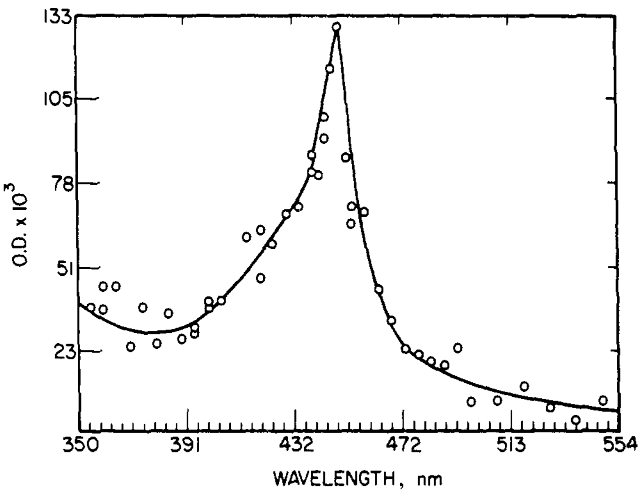

Figure 1. Absorption spectrum of pyrene radical cation recorded 200 ns after excitation. The solvent is acetonitrile, the pyrene concentration is 3.04 × 10^{-5} M, and the DPP concentration is 2.4 × 10^{-3} M.

The fluorescence of excited singlet pyrene (Py*^{1}), in acetonitrile solvent, is quenched by DPP. The yield of benzocoumarin (BC), the only volatile product of the reaction, is 60%. When Py*^{1} is generated by irradiation with the nitrogen laser, it is possible to record the absorption spectra of the transient intermediates that result from its reaction with the peroxide. The spectrum that we observed 200 ns after the excitation of the pyrene, shown in Figure 1, is identical with that which has been attributed previously to pyrene radical cation (Py$^{+}\cdot$).[4] The yield of cage escaped Py$^{+}\cdot$ can be estimated by measuring the optical density of its characteristic absorption 150 ns after the excitation when essentially all of the Py*^{1} has reacted, but well before there is any significant reaction of Py$^{+}\cdot$. The yield of cage escaped Py$^{+}\cdot$ under these conditions in acetonitrile was determined to be 5%.

We have also investigated the electron-transfer reactions of Py*^{1} with several other electron acceptors including *p*-dicyanobenzene (DCB) and phthaloyl peroxide (PP). Comparison of the yield of Py$^{+}\cdot$ from these systems with that from the Py*^{1}-DPP system is particularly revealing. Weller has shown that Py*^{1} is quenched by DCB in acetonitrile by electron transfer to generate Py$^{+}\cdot$.[5] We have determined that the yield of cage escaped Py$^{+}\cdot$ in this system is 67% of the Py*^{1} that reacts with DCB. The remaining 33% of the Py*^{1} is evidently converted into ground- or triplet-state pyrene, apparently by in cage-ion annihilation. When phthaloyl peroxide[6] reacts with Py*^{1}, we have determined that the yield of escaped Py$^{+}\cdot$ is 48%. It should be noted also, that in comparison with DPP, phthaloyl peroxide is not chemiluminescent.[7] The CIEEL mechanism provides a convincing explanation for the different behavior of phthaloyl and diphenoyl peroxides.

One-electron reduction of DPP by Py*^{1}, followed by oxygen-oxygen bond cleavage, generates diphenate radical anion. Rapid decarboxylation and ring closure of this species produces a powerful reducing agent, benzocoumarin radical anion (BC$^{-}\cdot$), presumably within the same solvent cage as Py$^{+}\cdot$. The radical-ion pair, Py$^{+}\cdot$BC$^{-}\cdot$, has several energetically possible reaction channels. Annihilation within the cage can generate singlet or triplet excited pyrene, or pyrene ground state.[8] In competition with annihilation, diffusion into bulk solution generates the low yield of escaped Py$^{+}\cdot$ that we observe. On the other hand, one-electron reduction of PP generates phthalate radical anion. The structure of this species precludes its efficient rearrangement to a powerful reducing agent. The cage annihilation reactions that consume the BC$^{-}\cdot$Py$^{+}\cdot$ pair

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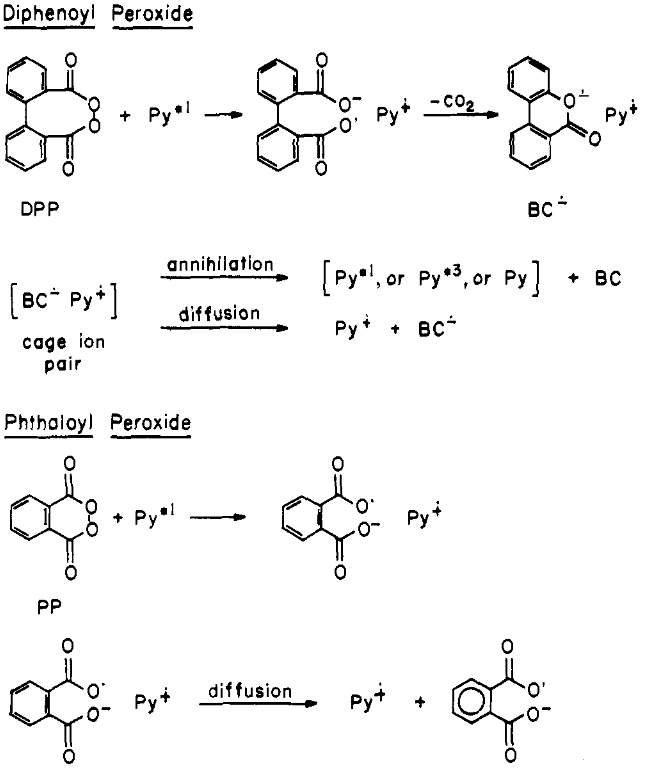
Scheme I



from DPP do not occur with PP because simple electron transfer from phthalate radical anion to $Py^{+\cdot}$ is endergonic (based upon the estimated value of the oxidation potential of simple carboxylates[9]) even for generation of ground-state pyrene. Thus, diffusion competes effectively with the in-cage reactions of the PP system, and we observe a relatively high yield of escaped $Py^{+\cdot}$.[10] These reactions are summarized in Scheme I.

Confirmation of the notion that reaction of Py^{*1} with DPP can eventually regenerate Py^{*1} comes from an analysis of the reaction kinetics. Both DPP and PP are sufficiently easy to reduce that electron transfer from Py^{*1} should occur at a diffusion-limited rate.[11] Indeed, we have determined that PP reacts with Py^{*1} with the diffusion-limited rate constant of $1.67 \pm (0.01) \times 10^{10}\ M^{-1}\ s^{-1}$ in acetonitrile. In contrast, DPP reacts with Py^{*1} with an apparent rate constant of only $1.02 \pm (0.007) \times 10^{10}\ M^{-1}\ s^{-1}$. These observations can be reconciled if, as we suggest in Scheme I, Py^{*1} is, to some extent, regenerated from the cage-radical ion pair resulting from its reaction with DPP, but not from its reaction with PP. In fact, the extent of Py^{*1} regeneration estimated from the pyrene quenching results is in agreement with the efficiency of Py^{*1} production that we have determined for the chemiluminescent reaction of ground-state pyrene with DPP. Of course, the $Py^{+\cdot}BC^{-\cdot}$ radical ion pair should be the same regardless of whether it is formed from ground- or excited-state pyrene.

Finally, we have established a kinetic link between the chemiluminescence of DPP and its reactions with electronically excited states. According to the CIEEL mechanism, the predictor of the rate constant for reaction between the peroxide and an activator is the one-electron oxidation potential of the activator. If this is correct, then the rate constant for reaction of electronically excited, as well as ground-state, activators should be predicted equally well by their oxidation potentials. The oxidation potential of Py^{*1} is −2.00 V (vs. SCE). Extrapolation of the ground-state chemiluminescence data to the oxidation potential of Py^{*1} (Figure 2) predicts a bimolecular rate constant of $1.2 \times 10^{16}\ M^{-1}\ s^{-1}$. Of course, this is much greater than the diffusion limit, and the rate we observe indicates, essentially, a diffusion-controlled reaction. We also investigated triplet anthracene as an excited-state activator. The oxidation potential of triplet anthracene is calculated to be −0.47 V. This excited-state activator is expected, therefore, to react with DPP with a rate constant slower than the diffusion limit. We have measured the rate of reaction of triplet anthracene with DPP by monitoring the triplet-triplet absorption spectrum following laser excitation of anthracene. The rate constant for this reaction was found to be $1.44\ (\pm 0.03) \times 10^{8}\ M^{-1}\ s^{-1}$. The excellent correlation of this rate constant with the previously determined ground state activator rate data is shown in Figure 2. This correlation demands that the rate-determining step for the ground- and excited-state reactions of DPP with the various activators is the same, namely, electron transfer from the activator to the peroxide.

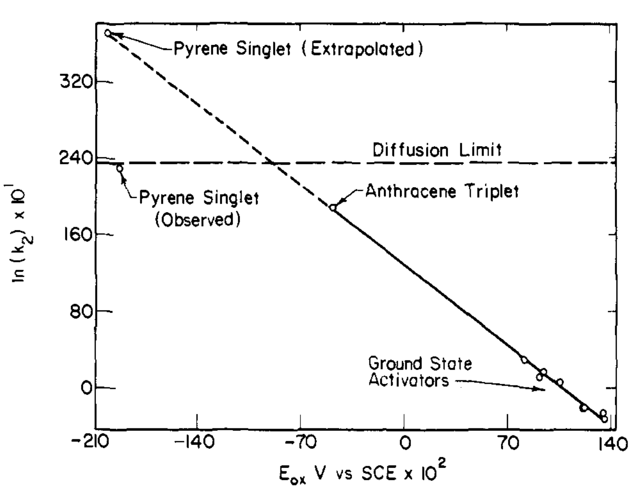


Figure 2. Correlation of reaction kinetics for reaction of DPP with ground and excited-state activators. The data for the ground-state activators come from ref 1b. In order of increasing oxidation potential these points are rubrene, tetracene, triphenylamine, perylene, diphenylanthracene, coronene, anthracene, and pyrene.

In conclusion, this investigation and our other studies of the CIEEL mechanism permit a fairly detailed sketch of the reaction coordinate. Electron transfer from the activator (which may be in its ground, or an electronically excited state) occurs, with a rate constant determined by the activator oxidation potential, to generate a pair of oppositely charged radical ions. These ions may diffuse from the solvent cage or may undergo further rapid chemical transformation. Annihilation of those ion pairs which are sufficiently energetic forms electronically excited product. We have investigated this sequence of reactions primarily for reagents capable of giving excited-state products. We suspect, however, that rate-limiting electron transfer may underlie the mechanism of many strictly ground-state reactions as well. We are continuing to investigate this and other aspects of these reactions.

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(3) The pulsed laser apparatus consists of a Molectron 900-kW nitrogen laser (337.1 nm, ~20-ns pulse duration) focused to a 3 × 10 mm rectangle in a 1-cm cell for excitation and a PRA 450 W xenon lamp pulsed with a 60-μf capacitor to probe the reaction. The probe beam intensity was monitored

with a Hamamatsu 938 photomultiplier tube. The data were recorded and analyzed with a Tektronix R7912 transient digitizer.

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Keith A. Horn, Gary B. Schuster*[12]
Department of Chemistry, Roger Adams Laboratory
University of Illinois, Urbana, Illinois 61801

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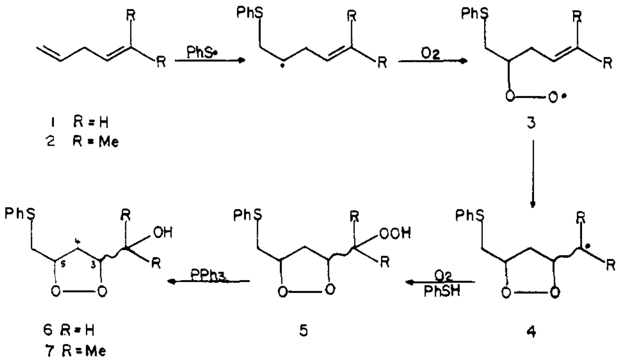
Formation of Cyclic Peroxides by Oxygenation of Thiophenol-Diene Mixtures

Sir:

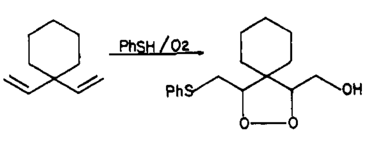
Since the biosynthetic pathway to prostanoids is believed to involve the intermediacy of 1,2-dioxolanes formed by cyclization of appropriately constituted alkylperoxy radicals,[1] there is considerable interest in accomplishing mechanistically similar transformation in vitro.[2] We now report that oxygenation of mixtures of thiophenol with suitable dienes[3] affords moderate yields of disubstituted cyclic peroxides, mainly with cis orientation, by a mechanism involving alkenylperoxy radical cyclization.

When 5-methylhexa-1,4-diene, **2** (8.8 mmol), thiophenol (8.8 mmol), and di-*tert*-butyl peroxyoxalate (0.88 mmol) in ethyl acetate–hexane (600 mL, 1:5) were stirred under oxygen at ambient temperature for 45 h, and the cooled (5 °C) solution was then treated with triphenylphosphine (8.8 mmol), the products isolated by LC were *cis*-**7** (20%) and *trans*-**7** (5%) (Scheme I). *cis*-**7**: *m/e* 254.09766 (M^+, $C_{13}H_{18}O_3S$, 254.09773); IR (CCl_4) 3600 cm^{-1}; NMR ($CDCl_3$) δ 7.23 (5 H, m, ArH), 4.3 (1 H, m, H-5), 4.07 (1 H, t, H-3), 3.47–2.83 (2 H, m, SCH_2), 2.83–2.23 (2 H, m, H-4), 2.1 (1 H, s, OH), 1.23 (3 H, s, CH_3), 1.13 (3 H, s, CH_3). *trans*-**7**: *m/e* 254.09773 (M^+, $C_{13}H_{18}O_3S$, 254.09773); IR (CCl_4) 3600 cm^{-1}; NMR δ 7.23 (5 H, m, ArH), 4.3 (1 H, q, H-3), 4.1 (1 H, dd, $J = 5$, 8 Hz, H-5), 3.47–2.87 (2 H, m, SCH_2), 2.87–2.23 (2 H, m, H-4), 2.0 (1 H, s, OH), 1.23 (3 H, s, CH_3), 1.12 (3 H, s, CH_3).

Scheme I



Similar treatment of **8** afforded *cis*-**9** (38%) and its trans isomer (4%), while **1** gave the alcohol **10** (23%), the diol **11** (12%), and the cis and trans isomers of the cyclic peroxide **6** (32 and 8%, respectively). 1,5-Hexadiene gave a mixture of four compounds, two of which have been tentatively identified as 1,2-dioxanes.



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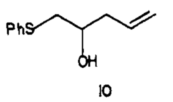

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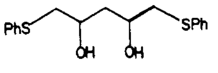

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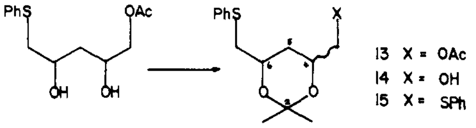
Having considered the previously known features of the thiol–oxygen co-oxidation reaction[3] and the catalysis of our reactions by free-radical initiators, we believe that the cyclic peroxides are formed from dienes by the mechanisms shown in Scheme I. The observed exclusive exo mode of ring closure of **3** and similar peroxy radicals is consistent with the behavior of related oxygen- and carbon-centered radicals,[4] while the nature of the products from **2** indicates that initial attack of PhS• occurs regiospecifically at the terminus of the least substituted double bond.

Assignments of structure and stereochemistry to the various cyclic peroxides rest on chemical and spectral evidence. Thus the mixture of *cis*-**6** and *trans*-**6** obtained from the thiol co-oxidation of **1** readily formed a mixture of monoacetates, which, when treated with cobalt chloride and $NaBH_4$, gave a mixture of the stereoisomers of the acetoxy diol **12.** Treatment of **12** with dimethoxypropane in acetone afforded a mixture of 1,3-dioxanes which were separated by TLC. The minor fraction was identified as *trans*-**13**: NMR (CCl_4) δ 7.17 (5 H, m, ArH), 4.9–4.3 and 4.1–3.7 (2 H, 2 m, H-4 and H-6), 3.7–3.4 (2 H, m, OCH_2), 3.1–2.8 (2 H, m, SCH_2), 1.9 (3 H, s, $COCH_3$), 2.4–1.9 and 1.8–1.2 (2 H, 2 m, H-5), 1.2 (6 H, s, 2 CH_3). The major fraction was *cis*-**13**: NMR (CCl_4) δ 7.16 (5 H, m, ArH) 4,2–3.7 (2 H, m, H-4 and H-6), 3.9 (2 H, d, OCH_2), 3.2–2.6 (2 H, m, SCH_2), 2.0 (3 H, s, $COCH_3$), 2.0–1.5 (2 H, 2 overlapping m, H-5), 1.43 and 1.40 (6 H, 2 s, 2 CH_3). The assignment of stereochemistry, which accords with the observation that the NMR spectrum of the trans isomer shows the two acetonide methyls as coincident whereas those in the cis isomer are not, was confirmed by conversion of the major product into *cis*-**15.**



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Reduction of *cis*-**13** with $LiAlH_4$ and conversion of the resultant alcohol, *cis*-**14,** into the phenylthio ether by treatment of the mesylate with lithium thiophenoxide afforded *cis*-**15:** NMR (CCl_4) δ 7.3 (10 H, m, ArH), 4.2–3.6 (2 H, m, H-4 and H-6), 3.3–2.7 (4 H, m, SCH_2), 2.1–1.8 and 1.6–1.2 (2 H, 2 m, H-5 and H-5′), 1.38 and 1.35 (6 H, 2 s, 2 CH_3). When the sample was irradiated at the H-4 frequency, the signal attributed to the protons at C-5 collapsed to a doublet pair ($J =$ 12.2 Hz), while on irradiation at the H-5′ frequency the signal for H-4 and H-6 became a simple triplet. When the SCH_2 protons were irradiated, H-4 and H-6 were seen as a doublet pair ($J = 9.8$ and 1.4 Hz). The ^{13}C NMR spectrum of *cis*-**15** shows two methyl resonances at 30.18 and 19.98 ppm, whereas the spectrum for *trans*-**15** contains only one such signal at 25.08 ppm. This spectral evidence confirms the structure of the compound as *cis*-**15,** which, since it possesses a plane of

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