

Figure 1. A plot of bonding charge vs. bond length: TP, tetraphenylbutatriene;^{4c} AD, allenedicarboxylic acid-acetamide;^{6a} PN, *p*-nitropyridine oxide;^{6d} D, diamond;^{6d} TCB, tetracyanocyclobutane;^{4b} P, perylene;^{6c} BCB, a bicyclobutane derivative, *exo,exo*-1,3-diethylbicyclobutane-2,4-dicarboxylic acid.^{6b}

chemical structure. (c) The number of bonding electrons in various C-C bonds falls off almost linearly with increasing bond length. Assuming the points to lie on a straight line ($y = 0.686x + 1.152$ where y is the charge and x is the bond length) yields a scatter, $(\sum \Delta^2 / (n - 1))^{1/2}$, $n = 16$, of 0.026e which compares favorably with the estimated standard deviation computed for tetraphenylbutatriene.

A similar correlation between the charge in the bond and its length is suggested by a simple electrostatic model of the chemical bond, which supposes that a chemical bond is a result of accumulation of negative charge in the region between bonded atoms to an extent sufficient to balance the nuclear forces of repulsion.¹⁴

References and Notes

- (1) See, for example, L. S. Bartell, *Tetrahedron*, **17**, 177 (1962).
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- (3) Difference density maps obtained by subtracting the density obtained from overlap of undistorted atomic densities from the molecular charge distribution provide a detailed picture of the net reorganization of charge density accompanying the formation of a molecule. Positive areas in these maps indicate accumulation of charge between bonded atoms and "lone-pair" peaks at the expense of depletion of charge from diffuse regions around the atomic centers.
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- (5) All the difference density maps used for the calculations were deformation maps calculated from a least-squares fitted model using a method developed by F. L. Hirshfeld (*Acta Crystallogr., Sect. B*, **27**, 769 (1971), and ref 4b) and not from the experimental Fourier maps.
- (6) (a) Z. Berkovitch-Yellin and L. Leiserowitz, *Acta Crystallogr.*, in press. (b) M. Eisenstein and F. L. Hirshfeld, unpublished results. (c) D. Rabinovich, unpublished results. (d) F. L. Hirshfeld, unpublished results.
- (7) Bond merging was encountered for only two of the 16 bonds reported. For these bonds the bounding surfaces were chosen to pass through contours of low density compared with the peak height so that small variations in defining the integration volume did not change the net bonding charge significantly.
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- (10) (a) The integrations were carried out numerically. Several grid sizes were

checked till convergence of the bond charge was achieved. For all bonds the grid step was 0.02 Å. (b) The standard deviation in charge was estimated for the two cumulenenic bonds in tetraphenylbutatriene of lengths 1.260 and 1.345 Å, by summation of the individual errors in the deformation density map over the appropriate integration volume.

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- (12) An extrapolation of the curve to a bond length of 1.20 Å would lead to a bonding charge of 0.4 e for the C≡C triple bond. This excess charge may be correlated with the relatively strong acidic properties of the acetylenic C-H bond.¹³
- (13) J. C. Calabrese, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. B*, 1235 (1966).
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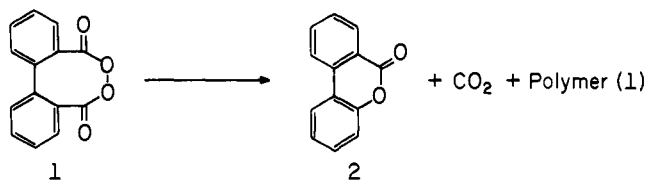
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Chemically Initiated Electron Exchange Luminescence. A New Chemiluminescent Reaction Path for Organic Peroxides

Sir:

We would like to report an efficient new chemiluminescent reaction that delineates an apparently important class of chemiluminescent processes and provides insight into several previously reported light-producing reactions. In general, the exothermic decomposition of peroxides to generate directly electronically excited-state carbonyl compounds has formed the basis for nearly all of organic chemiluminescence.¹ In this communication we will outline a reaction sequence in which diphenoyl peroxide (**1**) undergoes chemically initiated electron exchange with an aromatic hydrocarbon to form directly the electronically excited singlet state of the hydrocarbon which, in turn, emits a photon of visible light.

Thermolysis of a dilute solution of diphenoyl peroxide² in CH₂Cl₂ at ~24 °C for 24 h resulted in the formation of benzocoumarin (**2**) in 75% yield³ and polymeric peroxide (eq 1).



Under these conditions there was virtually no chemiluminescence from this reaction. However, addition of certain aromatic hydrocarbons (see Figure 2) to the reaction mixture resulted in efficient light formation. The spectrum of the emission corresponds in all of the cases studied to the fluorescence of the added hydrocarbon.

Such an observation is not unique among chemiluminescent systems and has been attributed to electronic energy transfer to the added hydrocarbon from a product molecule formed in an excited state. However, in this case, the unusual observation was made that, while 9,10-diphenylanthracene (DPA) was quite effective at promoting light formation, 9,10-dibromoanthracene and biacetyl were essentially completely ineffective.⁴ Moreover, incorporation of the aromatic hydrocarbon in the reaction solution increased the rate of consumption of the diphenoyl peroxide. These observations indicate a special interaction of the aromatic hydrocarbon with the peroxide rather than simple energy transfer as the light-forming step.

The chemiluminescence observed from peroxide **1** and aromatic hydrocarbons is strictly first order in peroxide con-

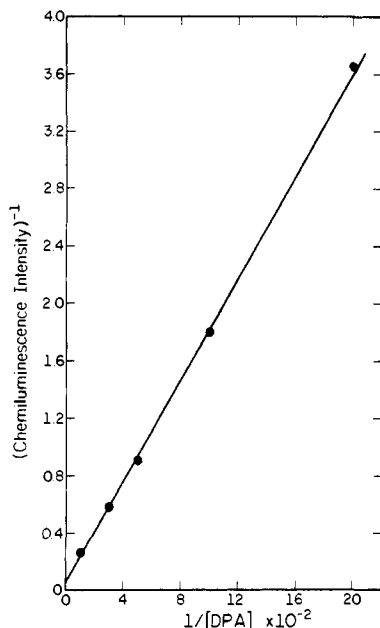


Figure 1. Reciprocal plot of chemiluminescence intensity against DPA concentration in CH_2Cl_2 at 32.5°C ; $[1] = 5 \times 10^{-5}\text{ M}$.

centration for more than 5 half-lives. This observation limits the possible excitation steps to those that involve only one peroxide molecule and, for example, precludes triplet-triplet annihilation of the aromatic hydrocarbon as a precursor to light emission. The effect of added aromatic hydrocarbon on the observed rate constant is first order in hydrocarbon and can be represented by a simple kinetic expression (eq 2), where k_1 is the rate constant for the unimolecular reaction and k_2 for the hydrocarbon dependent reaction.

$$k_{\text{obsd}} = k_1 + k_2 (\text{aromatic hydrocarbon}) \quad (2)$$

Additional evidence that the chemiluminescence is a result of the bimolecular reaction is revealed by the effect of aromatic hydrocarbon concentration on the emitted light intensity. If the unimolecular reaction is responsible for light generation, then at high hydrocarbon concentration, where nearly all of the peroxide reacts by the bimolecular path, the hydrocarbon should act as a quencher of the chemiluminescence. Figure 1, a reciprocal plot of intensity against concentration, shows that the chemiluminescent intensity is a linearly increasing function of the aromatic hydrocarbon concentration even when >90% of the reaction of **1** proceeds through the bimolecular path. Thus, for the cases studied, the formation of light must be a consequence of the reaction of aromatic hydrocarbon with ground-state peroxide.

The nature of this interaction was probed by examining the effect of hydrocarbon structure on the rate constant for the bimolecular reaction. Figure 2 shows a plot of the observed first-order rate of chemiluminescence decay against hydrocarbon concentration according to eq 2 for a series of hydrocarbons. As predicted by eq 2, all of the hydrocarbons pass through the same intercept (k_1); however, the slopes (k_2) are strongly dependent on the structure of the hydrocarbon. Figure 3 shows a plot of the natural log of k_2 against the one-electron oxidation potential of the aromatic hydrocarbons. The excellent correlation between the observed rate and the oxidation potential indicates that the initiating step in the chemiluminescent process is an electron transfer from the hydrocarbon to the peroxide.⁵ In Scheme I, we suggest a mechanism for this chemiluminescent reaction consistent with our observations.

Induced decomposition of peroxidic compounds by nucleophiles⁶ and redox metals⁷ is well known. Studies of the electrochemical reduction of diacyl peroxides indicate that the

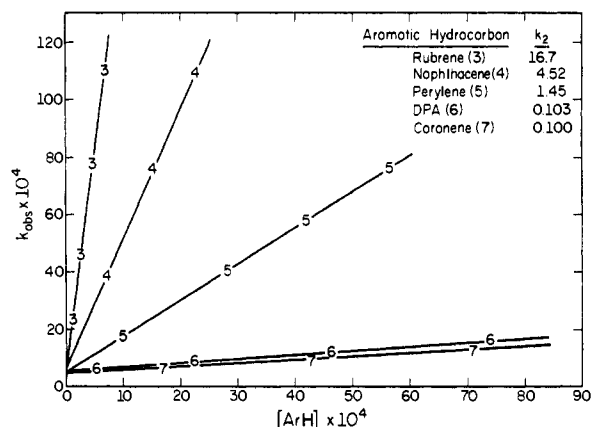


Figure 2. Effect of added aromatic hydrocarbon concentration on the reaction rate for peroxide **1** in CH_2Cl_2 at 32.5°C ; $[1] = 5 \times 10^{-5}\text{ M}$.

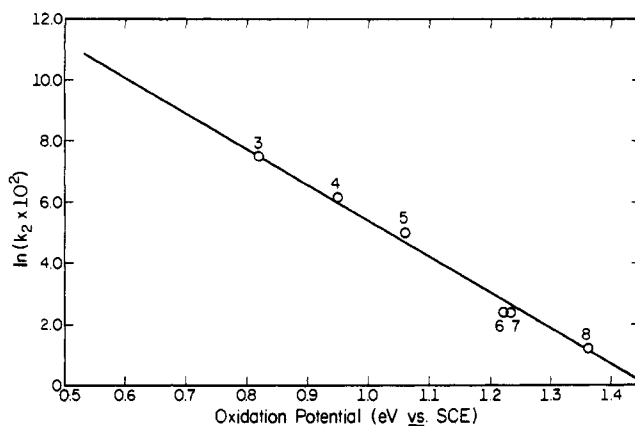
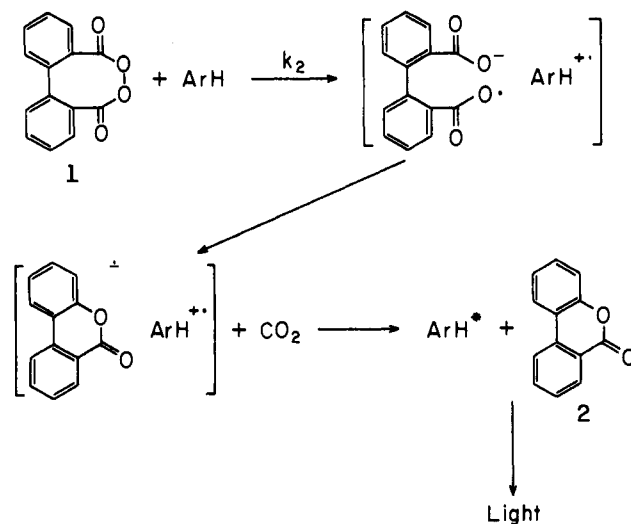


Figure 3. Correlation of $\log k_2$ and oxidation potential¹⁷ (in electron volts) for the chemically initiated electron exchange luminescence of peroxide **1**. Note that the point numbers correspond to those in Figure 2 and that **8** is pyrene.

Scheme I



electron transfer is irreversible.⁸ In the case under study the cage radical ion pair formed by the initial electron transfer from the hydrocarbon to the peroxide has a facile reaction path available. Decarboxylation followed by carbon oxygen bond formation results in the radical anion of benzocoumarin. We have determined that the reduction potential of benzocoumarin is -1.92 eV (vs. SCE).⁹ Thus, back-electron transfer from the radical anion of **2** to the radical cation of the aromatic hydrocarbon is sufficiently exothermic to generate the electronically excited singlet state of the hydrocarbon. Such reactions have

been observed to generate light during electrogenerated chemiluminescence.¹⁰ An important key feature of this new chemiluminescent mechanism is the rapid chemical reaction of what was a very easily reduced compound to form a strongly reducing species within the solvent cage. Return of an electron to the radical-cation form of the initial electron donor then results in excited-state generation. Preliminary evidence that the path leading to light generation occurs within the solvent cage comes from the observation of the effect of added trap molecules. Thus, saturating the chemiluminescing solution with O₂ results in only a small decrease in light emission due to quenching of the singlet state of the aromatic hydrocarbon. Also, the addition of tetramethylethylene does not divert the radical-ion intermediates leading to light generation.

The total yield of electronically excited states for this reaction should be sensitive to a number of factors such as the nature of the hydrocarbon, the rate of decarboxylation, the cage lifetime, the solvent polarity, and the excited-state yield on back-electron transfer. We have compared the chemiluminescence of **1** with perylene to tetramethyldioxetane.¹¹ Preliminary results indicate that for this system the yield of photons is $\sim 10 \pm 5\%$. Thus, even though the reaction has not been optimized, the light yield is remarkably high.

Several previously reported chemiluminescent reactions appear to be proceeding by the proposed electron exchange mechanism. The well-known oxalate ester system is reported to be "catalyzed" by aromatic hydrocarbons.¹³ Chemiluminescence from α -peroxylactones appears to be strongly dependent upon the nature of the aromatic hydrocarbon.¹⁴ The reaction of phthaloyl peroxide almost certainly proceeds by a similar mechanism.¹⁵ Our recent report of chemiluminescence from a suspected cyclic diacyl peroxide fits this interpretation.¹⁶ Chemically initiated electron-exchange luminescence may be a general phenomenon responsible for many chemi- and bioluminescent reactions. Further efforts to unravel the details of these chemiluminescent processes and probe the generality of this mechanism are underway.

Acknowledgment. We wish to thank Professor Faulkner of this department for the determination of the reduction potential of benzocoumarin and for many helpful discussions. This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

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- (18) Fellow of the Alfred P. Sloan Foundation, 1977-1979.

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Novel Cyclization of Allyldiazomethane to 3-Methyl-3H-pyrazole¹

Sir:

Among the large number of intramolecular cyclizations of diazoalkenes which afford formal 1,3-dipolar cycloaddition products such as pyrazoles or pyrazolines, those of allyldiazomethanes are apparently unknown. Allyldiazomethanes generally decompose thermally² or photochemically³ to form carbene-type reaction products, or in some case cyclize intermolecularly⁴ rather than intramolecularly. Herein we wish to report a novel example of the cyclization of an allyldiazomethane derivative through an unprecedented process which represents a notable exception to the generally observed reaction modes.

When the sodium salt of α -(1,3,5-cycloheptatrien-3-yl)-acetophenone tosylhydrazone (**1**, mp 129°C)⁵ was decomposed in dry diglyme at 145°C , the reaction mixture immediately turned red as sodium toluenesulfinate was liberated, and 10-phenyl-1,11-diazatricyclo[6.3.0.0^{4,6}]undeca-2,8,10-triene (**2**, mp 57°C) was isolated (Scheme I) in 66% yield ($\nu_{\text{max}}^{\text{KBr}}$ 3050, 1650, 1554 cm^{-1} ; λ_{max} 277 nm (log ϵ 4.33) in cyclohexane; m/e 222 (M^+ , 100%), 221, 207, 194, 157, 128, 104). The ¹H NMR spin decoupling and the observance of a 5% NOE between the exo-C(7)-H and C(9)-H proton provide an unequivocal assignment for all the hydrogens of **2**. This assignment was further supported by the close similarity of its ¹³C NMR spectrum⁶ to that of 1,10-diazatricyclo[5.3.0.0^{4,6}]deca-2,7,9-triene⁷ recently reported by Dreiding and coworkers (¹³C NMR spectrum of **2** (δ units in CDCl₃), C(2), 128.0 (d); C(3), 120.1 (d); C(4), 13.0 (d); C(5), 9.6 (t); C(6), 22.1 (d); C(7), 26.7 (t); C(8), 135.4 (s); C(9), 104.5 (d); C(10), 144.9 (s)).

Scheme I

