

should readily hydrogen bond to these functions, making intramolecular hydrogen bonding unfavorable. Furthermore, specific solvent interaction may be expected to alter the potential energy for rotation about backbone C'-N, N-C $\alpha$ , and C $\alpha$ -C' bonds.

One clear case of specific solvent binding and a rotational potential function which is sensitive to solvent is that of poly-L-proline. The compact *cis* helix (form I) is stable in poor solvents, but is converted to the extended *trans* helix (form II) in good solvents, such as water. From the transition kinetics in glacial acetic acid and acetic acid-propanol, the barrier to rotation about the C-N bond in this polymer has been estimated to be in excess of 20 kcal/mol.<sup>16</sup> However, this barrier must be significantly lowered in aqueous solution, since the I-II transition takes place readily.

(16) I. Z. Steinberg, W. F. Harrington, A. Berger, M. Sela, and E. Katchalski, *J. Amer. Chem. Soc.*, **82**, 5263 (1960).

Upon heating an aqueous solution of poly-L-proline II to 55°, complete precipitation takes place to give solid form II.<sup>17</sup> Swenson and Formanek<sup>18</sup> have shown that hydrogen bonding of water to the proline carbonyl function is disrupted at temperatures prior to precipitation. Their infrared measurements indicated the appearance of a free and a bonded poly-L-prolinamide I band, the former increasing in proportion as the temperature is raised. Clearly, solvation of the carbonyl function is intimately related to the stability of the solution phase in water.

**Acknowledgments.** C. F. N. is grateful for the financial assistance of a NDEA Title IV Fellowship (No. 65-0684) and a Public Health Service grant (No. 5-SO1-FR-05370-08).

(17) L. Mandelkern in ref 9, p 675.

(18) C. A. Swenson and R. Formanek, *J. Phys. Chem.*, **71**, 4073 (1967).

## Chemiluminescence of Decomposition of 1,4-Peroxy-1,4-dimethoxy-9,10-diphenylanthracene

G. W. Lundeen and A. H. Adelman

*Contribution from the Battelle Memorial Institute, Columbus Laboratories, Columbus, Ohio. Received November 29, 1969*

**Abstract:** A kinetic study is presented of the chemiluminescent decomposition of 1,4-dimethoxy-9,10-diphenylanthracene peroxide in 1,4-dioxane containing a carboxylic acid and a fluorescent hydrocarbon. It is shown that a nonreversible reaction, induced by the acid, is responsible for the generation of an excited product which in turn excites the fluorescent hydrocarbon by energy transfer.

In the course of their very extensive (and continuing) study of the photoperoxides of aromatic hydrocarbons Dufraisse and coworkers<sup>1</sup> noted that several of the *meso*-aryl substituted hydrocarbons formed peroxides which, on heating, regenerated the hydrocarbon and oxygen nearly quantitatively (in solid state) and at the same time produced chemiluminescence. Chemiluminescence was also observed when these peroxides were decomposed in solution.

Notable among the peroxides which they studied were the 1,4-dialkoxy-substituted anthracenes<sup>1b,c</sup> which decompose at relatively low temperatures as compared with the others, and produced a brighter light emission. Dufraisse and Velluz<sup>1b</sup> noted that the oxygen generated in this reaction was not in its normal state. It has recently been shown<sup>2</sup> that it is generated in an excited singlet state.

Because of the low energy of this reversible reaction<sup>3</sup> the singlet oxygen is probably in the <sup>1</sup> $\Delta_g$  state. The dimer of this species would not have sufficient energy to excite the emission. We were not able to detect

any emission from the hydrocarbon solution when singlet oxygen was generated photochemically (with Eosin as sensitizer). The reaction kinetics also argue against the participation of singlet oxygen in the excitation process, as shown below.

Since the energy released<sup>3</sup> per molecule in this reversible decomposition is much less than needed to excite the fluorescence of the hydrocarbon (which is the emission observed) the mechanism by which this excitation is produced has been an intriguing question. Since the chemiluminescence efficiencies seemed to vary symbatically with the extent of the reversible reaction, it has been thought that an irreversible side reaction was not likely to be the source of excitation.<sup>4</sup> This is contrary to our results as discussed below.

Recently Dufraisse and coworkers<sup>1d</sup> have shown that the structure of the 1,4-dialkoxy peroxides contain the oxygen bridge across the 1,4 positions rather than across the 9,10 positions as previously supposed. Further, Rigaudy<sup>1e</sup> has shown that in some solvents (*e.g.*, benzene) the peroxide decomposes to a very large extent *via* a nonreversible path. He found that only 20% of the hydrocarbon is regenerated when the peroxide of 1,4-dimethoxy-9,10-diphenylanthracene is decomposed in benzene at room temperature.

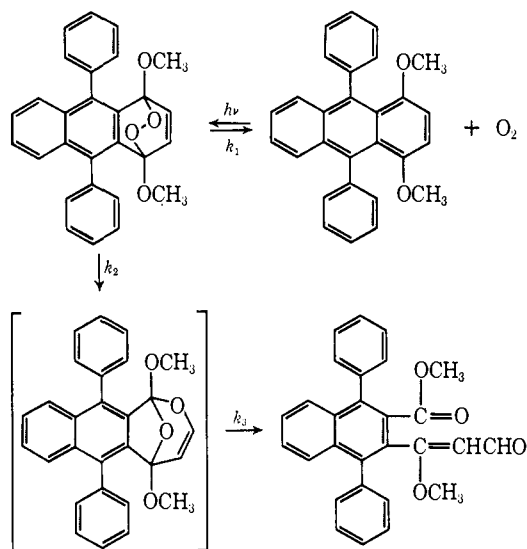
The reaction scheme proposed by Rigaudy<sup>1e</sup> is

(1) (a) C. Moreu, C. Dufraisse, and C.-L. Butler, *C. R. Acad. Sci.*, **183**, 101 (1926); (b) C. Dufraisse and L. Velluz, *Bull. Soc. Chim. Fr.*, **9**, 171 (1942); (c) Y. Lepage, *Ann. Chim. (Paris)*, **4**, 1137 (1959); (d) C. Dufraisse, J. Rigaudy, J. J. Basselier, and N. K. Cuong, *C. R. Acad. Sci.*, **260**, 5031 (1965); (e) J. Rigaudy, *Pure Appl. Chem.*, **16**, 169 (1968).

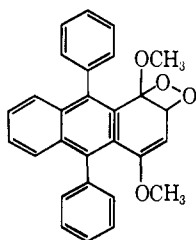
(2) H. H. Wasserman and H. R. Scheffer, *J. Amer. Chem. Soc.*, **89**, 3073 (1967).

(3) P. Bender and J. Farber, *ibid.*, **74**, 1450 (1952).

(4) E. J. Bowen, *Pure Appl. Chem.*, **9**, 473 (1964).



In tetrahydrofuran, on the other hand, Rigaudy observed nearly quantitative regeneration of hydrocarbon. A different structure for the intermediate has been



suggested by Baldwin, Basson, and Krauss,<sup>5</sup> which involves formation of a dioxetane structure similar to those found by McCapra<sup>6</sup> to be important in many bioluminescent systems. Baldwin, *et al.*,<sup>5</sup> have shown that acids do induce ring cleavage of the peroxide, resulting in the final product shown above.

We have studied the chemiluminescence of the decomposition of the peroxide of 1,4-dimethyl-9,10-diphenylanthracene. We find significant emission in solvents in which a nonreversible decomposition is found to occur. Benzene solutions produce emission, whereas solutions in pure tetrahydrofuran, dioxane, or dimethoxyethane do not. We found, however, that solutions of the peroxide in these latter solvents can be made chemiluminescent by the addition of a carboxylic acid such as acetic or benzoic acid. The addition of such acids also causes a significant part of the peroxide to decompose *via* a nonreversible path. Mineral acids (HCl or H<sub>2</sub>SO<sub>4</sub>) do not produce chemiluminescence.

Using standard bond energy values, it is seen that more than 70 kcal/mol would be released in the nonreversible reaction proposed by Rigaudy. This is more than sufficient to excite the fluorescence state of the hydrocarbon.

Our kinetic study of peroxide in dioxane is consistent with a mechanism in which an acid induced nonreversible reaction is responsible for excitation of chemiluminescence.

(5) J. E. Baldwin, H. H. Basson, and H. Krauss, Jr., *Chem. Commun.*, 984 (1968).

(6) F. McCapra and R. Wrigglesworth, *ibid.*, 1256 (1968).

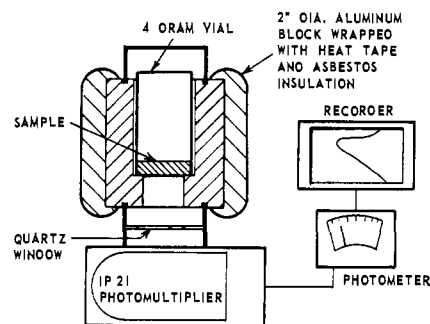


Figure 1. Apparatus used for chemiluminescence measurements.

## Experimental Section

1,4-Dimethoxy-9,10-diphenylanthracene was synthesized according to the method of Dufrasse and Velluz<sup>1b</sup> and purified by basic alumina chromatography (Baker Analyzed reagent, powder for chromatography) using benzene as eluent. Dioxane was distilled over NaOH, the beginning and end fractions being discarded.

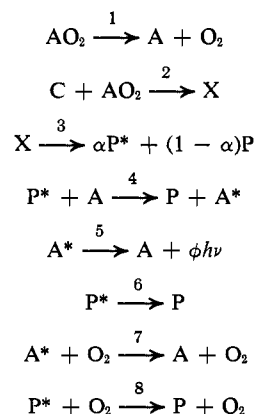
The apparatus used for measurement of light consisted of a 2-in. diameter aluminum block wrapped with heating tape and covered with a layer of asbestos insulation. Temperature was varied by adjusting the voltage to the heating tape by means of a Variac. A hole through the center of the block held a 4-dram glass vial. A light-tight cover was fitted on top and a photomultiplier housing was connected to the bottom so that the photomultiplier (1P21) viewed the bottom of the vial which held the sample (Figure 1). The signal from the photomultiplier was fed to an Aminco microphotometer and the output was recorded on a strip chart recorder.

Samples were irradiated with a tungsten lamp (300- or 500-W projector) filtered with a Corning 3-74 filter. Samples of peroxide and hydrocarbon in dioxane were normally prepared immediately before use by irradiating a solution of the hydrocarbon for a short time (usually 1 min) so as to convert a small fraction (<10%) to peroxide. This reaction is very clean. Irradiating a solution until the hydrocarbon fluorescence was gone and adding aliquots of this to solution of hydrocarbon gave the same results as directly converting a fraction of the hydrocarbon.

## Results and Discussion

When the peroxide of 1,4-dimethoxy-9,10-diphenylanthracene is decomposed in dioxane containing a carboxylic acid and a fluorescent hydrocarbon the intensity increases to a maximum and then falls off. If the acid concentration is large compared to the peroxide concentration the decay of chemiluminescence is first order (Figure 2).

The following mechanism is consistent with our kinetic results.



where A = the hydrocarbon, AO<sub>2</sub> = peroxide, X = the intermediate, P = the product, α = the fraction of P formed in the excited state, C = the carboxylic acid, and φ = the fluorescence efficiency of the hydrocarbon.

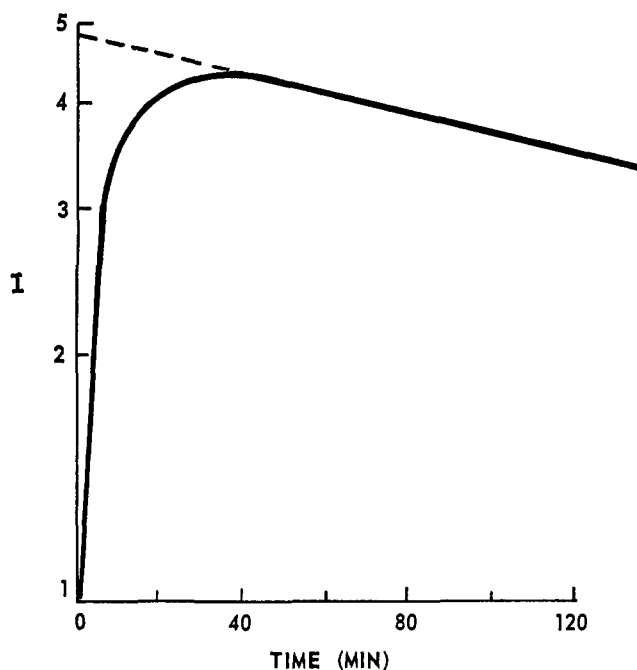


Figure 2. Typical intensity vs. time curve with first-order decay line extrapolated to  $I_0$  at zero time; temperature 25°, 0.02 M dimethoxydiphenylanthracene, 0.002 M peroxide, 0.05 M acetic acid in dioxane.

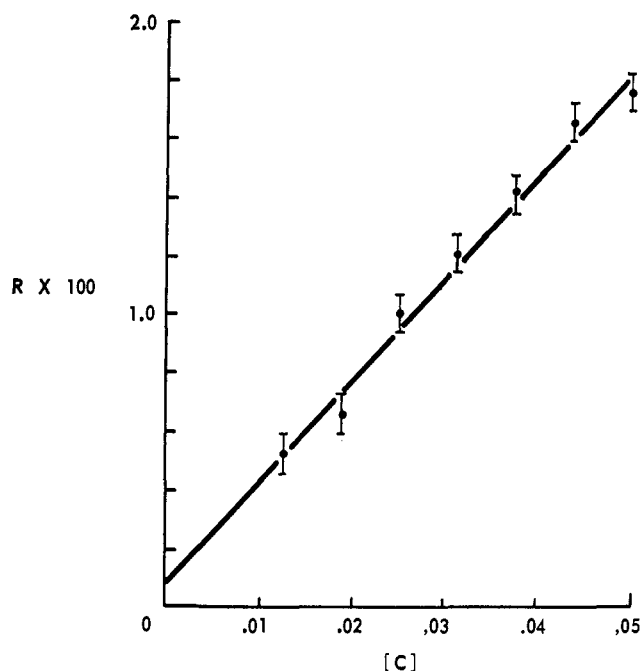


Figure 3. Rate of chemiluminescence decay ( $\text{min}^{-1}$ ) vs. acetic acid concentration (mol/l.); temperature 42.5°, slope =  $k_2$ , intercept =  $k_1$ .

From this mechanism we have

$$I = \phi k_3 [A^*] = \frac{\alpha \phi k_3 k_4 k_5 [A][X]}{(k_6 + k_4[A] + k_8[O_2])(k_5 + k_7[O_2])} \quad (1)$$

We find that  $k_6$  and  $k_5$  are the dominant terms in the denominator so we have

$$I \cong \frac{\alpha \phi k_3 k_4 [A][X]}{k_6} = B[A][X]$$

$$[X]_t = K e^{-(k_1 + k_2[C])t} - K e^{-k_3 t}$$

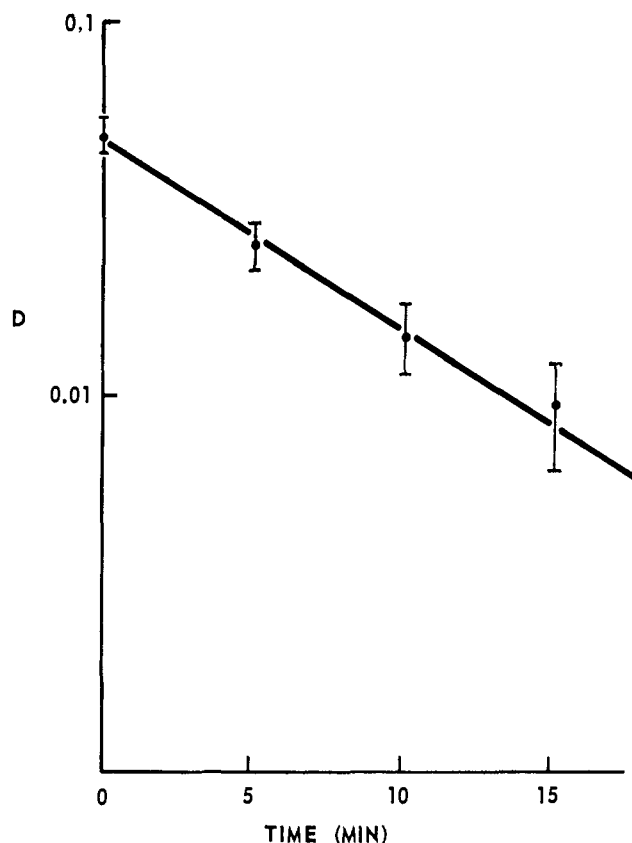


Figure 4. Log  $D$  vs. time; temperature 25°, 0.02 M dimethoxydiphenylanthracene, 0.002 M peroxide, 0.05 M acetic acid in dioxane.

where

$$K = -\frac{k_2[C][AO_2]_0}{k_3 - (k_1 + k_2[C])} \cong \frac{k_2[C][AO_2]_0}{k_3}$$

For the range of acid concentration used  $k_3 \geq 50(k_1 + k_2[C])$ . Then

$$I_t \cong B[A]K(e^{-(k_1 + k_2[C])t} - e^{-k_3 t}) \quad (2)$$

Since  $k_3 \gg k_1 + k_2[C]$  the second term goes to zero much more rapidly than the first, and after the maximum intensity is passed we have

$$I_t \cong B[A]K e^{-(k_1 + k_2[C])t}$$

and

$$\ln I_t = \ln B[A]K - (k_1 + k_2[C])t \quad (3)$$

Thus, from a plot of  $\ln I$  vs.  $t$  (Figure 2) we obtain a straight line for the latter part of the plot, with slope =  $-(k_1 + k_2[C])$ . Thus we have an apparent first-order rate constant  $R = k_1 + k_2[C]$  for the decay of luminescence. A plot of  $R$  vs.  $[C]$  then yields a straight line with slope =  $k_2$  and intercept =  $k_1$ , as seen in Figure 3.

Subtracting the rising part of the curve from the extrapolated line of the  $\ln I$  vs.  $t$  plot (Figure 2) yields the second term in eq 2.

Plotting  $\ln D$  vs.  $t$  yields a straight line with slope =  $-k_3$  and intercept  $B[A]K$  (Figure 4) ( $D_t = I_t(\text{extrapolated}) - I_t$ ).

A computer program was written to resolve the intensity vs. time data into the two straight lines above

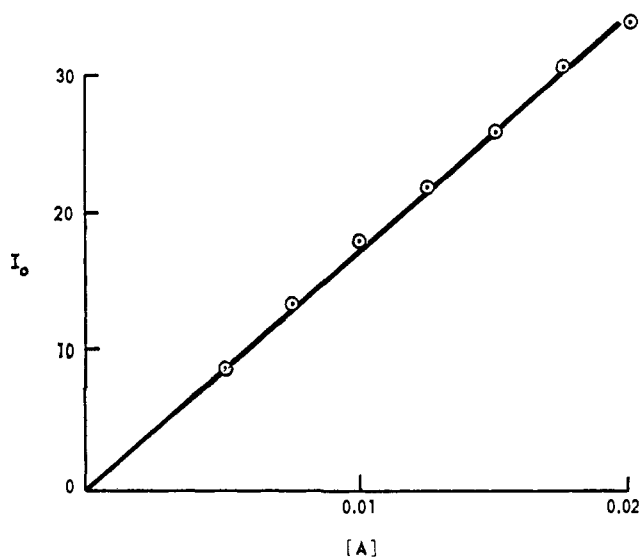


Figure 5.  $I_0$  (in arbitrary units) vs. concentration (mol/l.) of dimethoxydiphenylanthracene, temperature 42°.

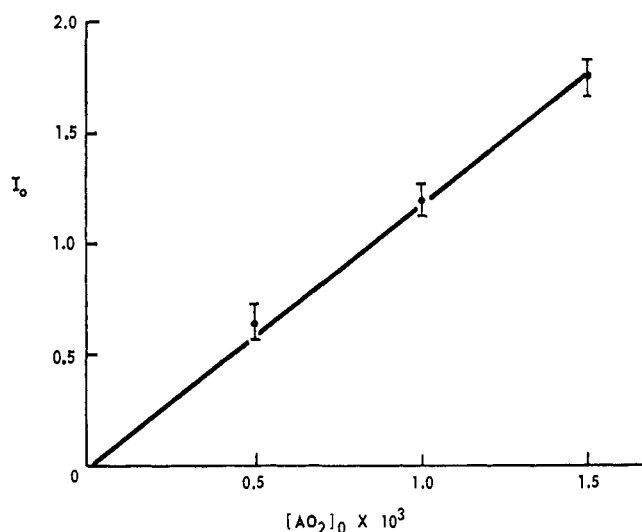


Figure 6.  $I_0$  (in arbitrary units) vs. initial peroxide concentration (mol/l.); temperature 36°, 0.02 *M* dimethoxydiphenylanthracene, 0.05 *M* acetic acid.

and at the same time obtain least-squares values for the slopes and intercepts along with error estimates.

The intercept of Figures 2 and 4 is

$$\ln I_0 = \ln B[A]K \cong \ln \frac{\alpha\phi k_4 k_2 [AO_2]_0 [A][C]}{k_6}$$

Then  $I_0$  should be proportional to  $[A]$ ,  $[AO_2]_0$ , and  $[C]$ . That this is the case can be seen in Figures 5, 6, and 7.

Further evidence that the hydrocarbon is excited by energy transfer is found in the fact that when peroxide is heated in a dioxane solution containing rubrene and a carboxylic acid the characteristic fluorescence emission of rubrene is observed. 9,10-Dimethylantracene, on the other hand, does not emit under these conditions, and when 9,10-dimethylantracene is added to an acidified solution containing 1,4-dimethoxy-9,10-diphenylanthracene and its peroxide the chemiluminescence is very slightly quenched. This suggests that the energy level of  $P^*$  is below the first excited state of

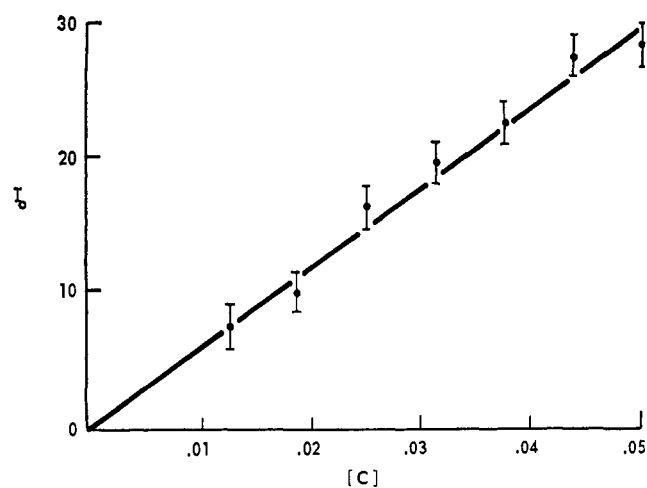


Figure 7.  $I_0$  (in arbitrary units) vs. acetic acid concentration (mol/l.); temperature 42.5°, 0.02 *M* dimethoxydiphenylanthracene, 0.002 *M* peroxide.

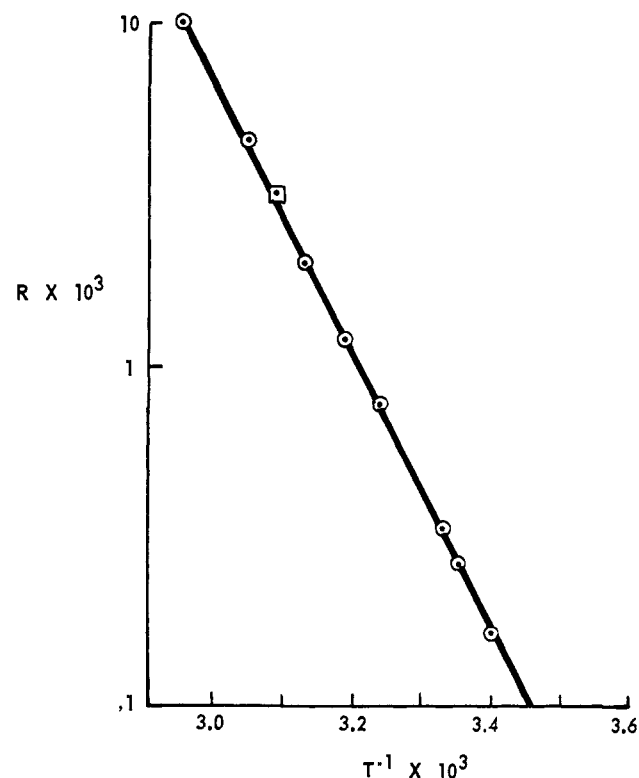
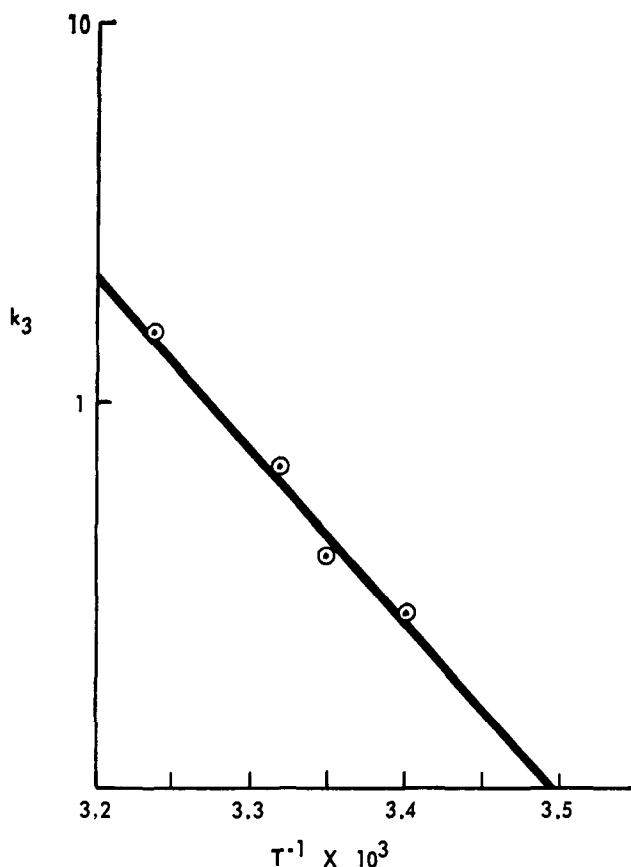
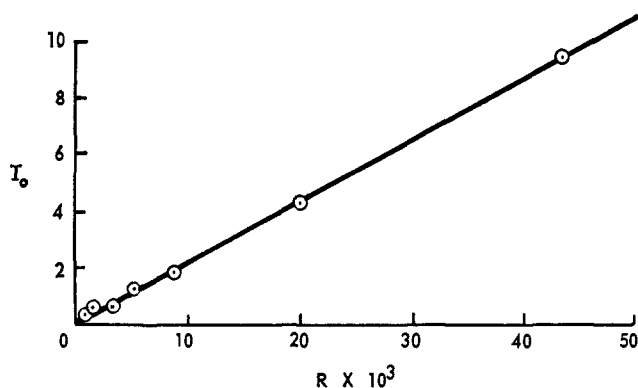


Figure 8. Log  $R$  vs. reciprocal of the temperature; circles from chemiluminescence measurements, square from spectrophotometric measurement.

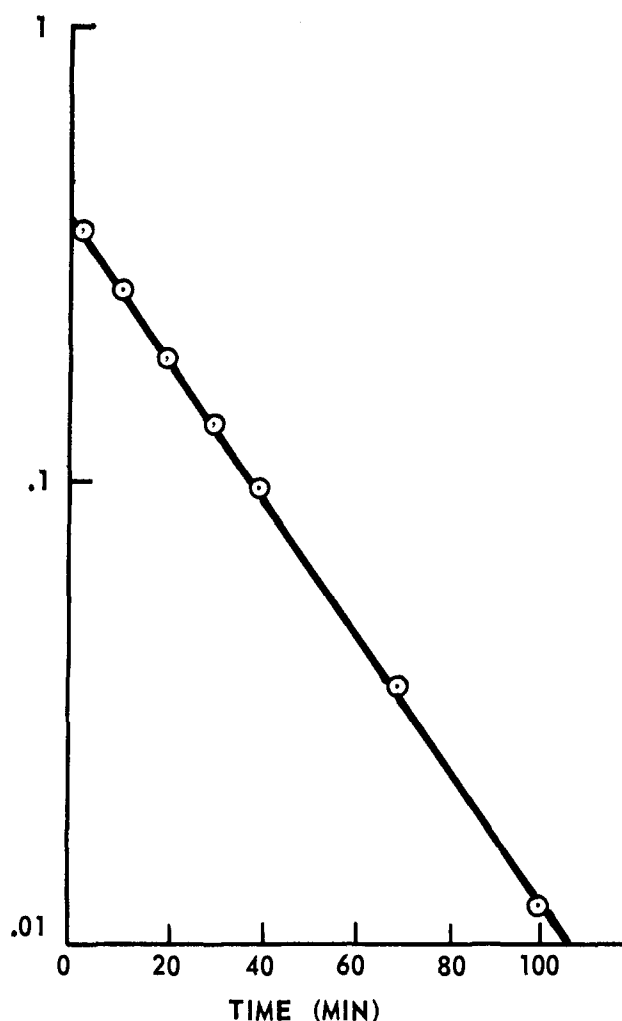
9,10-dimethylantracene but above that of 1,4-dimethoxy-9,10-diphenylanthracene. The slight quenching might be due to triplet excitation of the dimethylantracene.

Measurements were normally made with air-saturated solutions. In order to check the importance of oxygen quenching, solutions were flushed with argon, air, and oxygen during the course of the reaction. The quenching observed was, within experimental error, that expected for oxygen quenching of the hydrocarbon fluorescence. Fluorescence quenching by oxygen was determined with a Turner Model 210 spectrofluorimeter. At room temperature air-saturated solutions of the

Figure 9.  $k_3$  vs. reciprocal of the temperature.Figure 10.  $I_0$  (in arbitrary units) vs.  $R$ , the first-order rate of chemiluminescence decay.

dimethoxydiphenylanthracene were quenched by about 25% for emission of both fluorescence and chemiluminescence. At elevated temperatures quenching of chemiluminescence was less, presumably owing, at least in part, to the lower solubility of oxygen. We see then that reaction 8 can be neglected and, to a fair degree of approximation, reaction 7 also. Since we find that the intensity is proportional to  $[A]$ , then  $k_6$  must be the dominant term in eq 1. Thus in this system most of the excited product formed decays without producing emission.

A very approximate calibration of the photometer was made using a solution of benzoyl peroxide in dichlorobenzene containing 0.02 M diphenylanthracene as a standard. (This system had previously been com-

Figure 11. Spectrophotometric measure of peroxide decay rate:  $\log([A]_{\infty} - [A]_t)$  vs. time, temperature 50°.

pared<sup>7</sup> with a standard emitting solution provided by Professor J. W. Hastings.<sup>8</sup>) The quantum efficiency calculated in this way was found to be approximately  $3 \times 10^{-5}$  einstein/mol of peroxide decomposed in the presence of 0.02 M dimethoxydiphenylanthracene.

Arrhenius plots for  $k_2$  and  $k_3$  yield  $E_2 = 18.4$  kcal/mol and  $E_3 = 19 \pm 3$  kcal/mol (Figures 8 and 9).

As the temperature is changed,  $I_0$  is proportional to  $k_2$  (Figure 10). This indicates that the quantity  $\alpha\phi k_4/k_6$  is relatively independent of temperature. This is not surprising since none of these quantities by itself is expected to be strongly dependent on temperature.

The generation of hydrocarbon was observed spectrophotometrically for a solution of  $10^{-4}$  M peroxide in dioxane containing 0.3% acetic acid. The solution was maintained at 50° and the absorption of the hydrocarbon measured periodically until no further change was observed. In this example about 30% of the peroxide decomposed *via* the reversible reaction.

From the above mechanism we have

$$\frac{d[A]}{dt} = k_1[AO_2] = k_1[AO_2]_0 e^{-(k_1 + k_2[C])t}$$

(7) G. Lundeen and R. Livingston, *Photochem. Photobiol.*, **4**, 1085 (1965).

(8) J. W. Hastings and G. J. Weber, *J. Opt. Amer.*, **53**, 1410 (1963).

from which we obtain

$$[A]_{\infty} - [A]_t = \frac{k_1[AO_2]_0}{k_1 + k_2[C]} e^{-(k_1 + k_2[C])t}$$

and

$$\ln([A]_{\infty} - [A]_t) = \ln \frac{k_1[AO_2]_0}{k_1 + k_2[C]} - (k_1 + k_2[C])t$$

The values of  $k_1 + k_2[C]$  obtained in this way (Figure 11)

were found to agree with values derived from the decay of chemiluminescence (squared point in Figure 8).

A high-resolution mass spectrum of the product obtained in acidified dioxane is in agreement with the structure proposed by Rigaudy<sup>1e</sup> and Baldwin, *et al.*<sup>5</sup>

We are also investigating the decomposition of 1,4-dialkoxy-9,10-diphenylanthracene peroxides in benzene, where a nonreversible reaction occurs apparently without the action of acid or other reactants. This nonreversible reaction appears to be responsible for the generation of light.

## Electron Spin Resonance Studies of Nitroxide Radicals and Biradicals in Nematic Solvents<sup>1a</sup>

Carlo Corvaja, Giovanni Giacometti, Kenneth D. Kopple,<sup>1b</sup> and Ziauddin

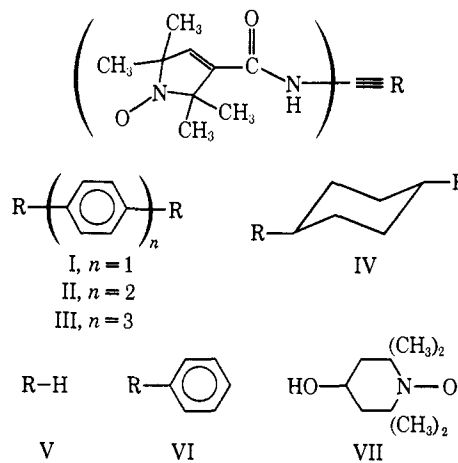
Contribution from the Institute of Physical Chemistry, University of Padua, Padua, Italy, and the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. Received September 20, 1969

**Abstract:** Electron spin resonance spectra of a series of nitroxide radicals and biradicals in the nematogenic solvents *p*-azoxyanisole and *p*-butyloxybenzoic acid have been examined. Three of the biradicals constitute a series of rigid molecules of graduated length between nitroxide groups. The observed nitrogen hyperfine splittings were used to determine the orientation of the solutes in the liquid crystal. The degree of orientation increases with increasing molecular length and is consistent with the observed electron-electron dipolar splittings where these were observed.

Use of liquid crystal solvents for electron spin resonance studies of organic radicals and biradicals has recently received much attention.<sup>2-7</sup> In this paper we report the spectra in both isotropic and nematic solvents of the series of nitroxide biradicals I-IV, which are molecules with graduated, approximately fixed spacings between radical sites. The isotropic spin exchange coupling between the radical sites in these molecules is small, but they also provide a series of rigid radicals of graduated lengths that can be used for an investigation of the effect of chain length on the orientation of molecules in liquid crystal phases. A quantitative study of this kind of orientation has recently been reported by Ferruti, *et al.*,<sup>7</sup> using one nitroxyl radical with a long flexible tail. For comparison we have also examined the behavior of analogous monoradicals, V and VI, in nematic solvents.

Numerous bis(nitroxide) radicals have already been prepared. Most extensively studied have been esters of the alcohol VII with dibasic acids. ESR spectra of such molecules in isotropic solvents indicate that flexibility that permits the radical sites to approach each other is

necessary if there is to be strong ( $J \gg a_N$ ) spin exchange coupling between sites.<sup>8-11</sup> For example there is strong coupling in the succinate ester<sup>9</sup> but none in the tere-



phthalate.<sup>8,10</sup> Spectra of the carbonate,<sup>6,9</sup> glutarate,<sup>3</sup> and terephthalate<sup>3</sup> have also been examined in nematic solvents. The biradicals we now report on are more rigid than these, in that the potentially flexible six-membered ring is replaced by a rigid five-membered

(1) (a) Supported by the National Research Council of Italy (Chemistry Committee) and the National Science Foundation, Grant No. GP 6779; (b) address correspondence to this author at Illinois Institute of Technology.

(2) A. Carrington and G. R. Luckhurst, *Mol. Phys.*, **8**, 401 (1964).

(3) H. R. Falle, G. R. Luckhurst, H. Lemaire, Y. Marechal, A. Rassat, and P. Rey, *ibid.*, **11**, 49 (1966).

(4) G. R. Luckhurst, *ibid.*, **11**, 205 (1966).

(5) H. C. Longuet-Higgins and G. R. Luckhurst, *ibid.*, **8**, 613 (1964).

(6) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **44**, 2884 (1966).

(7) P. Ferruti, D. Gill, M. A. Harpold, and M. P. Klein, *ibid.*, **50**, 4545 (1969).

(8) R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 3290 (1965).

(9) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **47**, 1374 (1967).

(10) E. G. Rozantsev, V. A. Golubev, M. B. Nieman, and Yu. V. Kokhanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 572 (1965).

(11) E. G. Rozantsev, G. F. Pavelko, A. L. Buchachenko, and M. B. Nieman, *ibid.*, 2306 (1967).