

other bands could also be assigned to the skeletal or hydrogen motions of a stereoisomer of I.

The failure to observe the formation of I during the photolysis of IV and its appearance only after warm-up indicates that the reported formation of I during the solution photolysis of IV⁶ involves the primary photochemical formation of V followed by thermal ring closure to produce I.

Failure to observe any evidence of II or III during the matrix photolysis of I, taken together with the flash photolysis results,⁷ strongly suggests that the efficiency of the formation of these products is at least an order of magnitude lower than that of the photopathways which lead to V and to benzene and ethylene. Although the volatility of ethylene could easily explain how it escaped detection, it is more difficult to understand why benzene, which appears to be a major photoproduct, was not reported by any of the previous workers.⁴⁻⁶ The possibility that I is converted first to IV and then to benzene is ruled out by failure to observe any evidence for the formation of IV despite the fact that IV does not photolyze appreciably faster than I. It is possible, although rather unlikely, that the low-temperature matrix environment might greatly favor benzene and ethylene production as compared to the room-temperature solution conditions.

The flash photolysis work on solutions of I in hydrocarbon solvents⁶ showed that four or five times as much ring opening to V results from decomposition of the short-lived cyclic intermediate than from direct opening

of I. However, the relative absorption peak heights indicate that in the matrix experiments the concentration of V is at least twice that of the other unstable product. Preliminary flash photolysis experiments on I in the gas phase result in the formation of V only, with no evidence of the other transient.¹⁸ A mechanism suggested by these results involves photoexcitation of I to an excited singlet state followed by a transition to an excited vibrational level of the ground electronic state of the cyclic stereoisomer. If this excited vibrational state is only metastable with respect to ring opening, the rapid formation of V would compete successfully with vibrational deactivation in the gas phase, whereas in the condensed phase, collisional deactivation would result in the stabilization of the stereoisomer. In an argon matrix vibrational deactivation would be intermediate between gas and liquid resulting in the observed intermediate ratio of V to the strained stereoisomer.

Little can be inferred from the experiments about the mechanism of benzene and ethylene formation from I other than that it does not involve the secondary photolysis of either of the other products. On the basis of energy requirements (breaking of two bonds), it almost certainly must occur from an electronically excited state. The increased efficiency of benzene and ethylene formation relative to the yield of V is not surprising since a Franck-Condon transition from IV would result in an electronic state that had a more appropriate geometry for this process than in the case of I.

(18) Unpublished results recently obtained in our laboratories.

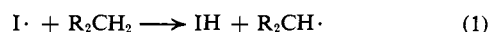
Mechanism of Chemiluminescence from Peroxy Radicals

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Abstract: Chemiluminescence accompanying disproportionation of peroxy radicals is studied. This reaction produces triplet states specifically ($T/S > 10^4$) and with high efficiency. The low emission yield, $\Phi_c \cong 10^{-8}$ – 10^{-10} , is ascribed to quenching in the cage by the eliminated O_2 .

Chemiluminescence accompanying air oxidation of saturated hydrocarbons has been studied extensively.¹ The chain-step oxidation is usually summarized by initiation



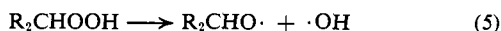
propagation



termination



and branching



(1) R. F. Vassilev, *Progr. Reaction Kinetics*, **4**, 305 (1967), and references therein.

By identifying the weak chemiluminescence with the termination step, it has been possible to devise experiments to measure the rate constants for each of the above reactions.²⁻⁶

There is much evidence that the disproportionation is concerted: (1) since the reaction exothermicity is ~ 115 – 150 kcal⁷ and the luminescence state of the carbonyl is commonly 75–80 kcal, a concerted reaction is virtually required to concentrate the energy in the ketone fragment, at least for those events leading to luminescence; (2) the termination rate constant for second-

(2) R. F. Vassilev, *Kinetica i Kataliz*, **6**, 990 (1965).

(3) R. F. Vassilev, *Dokl. Akad. Nauk SSSR*, **114**, 143 (1962).

(4) O. N. Karpukhim, V. Ya. Shliapintokh, N. V. Zolotova, Z. G. Kozlova, and I. F. Rusina, *Zh. Fiz. Khim.*, **37**, 1636 (1963).

(5) A. A. Vichutinskii, *Dokl. Akad. Nauk SSSR*, **157**, 150 (1964).

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(7) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 34.

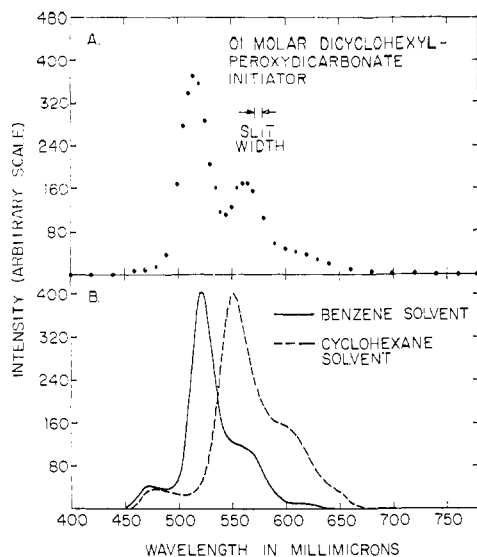


Figure 1. (A) Oxyluminescence spectrum of 2-butanone at 70° taken point by point with steady air flow. Correction was made for initiator depletion but not for photomultiplier or grating response. (B) Emission of biacetyl in degassed solutions by photoexcitation. The lack of resolution was due to the need for wider slit widths.

dary peroxy radicals is 10^3 times faster than for tertiary peroxy radicals where there is no α hydrogen;¹ (3) the termination rate constant decreases by 1.9 with α deuteration.⁸⁻¹⁰

Some oxyluminescence spectra reported by Vassilev appear to be due to triplet carbonyl.¹ Howard and Ingold reported detection of singlet oxygen in the oxidizing system.¹¹ Our contribution is a detailed rationalization of the sequence of events that produces and deactivates the excited carbonyl, consistent with previous findings and with the additional supporting data reported here.

Experimental Section

Apparatus. The apparatus used was similar to that described by Lloyd¹² with an estimated collection solid angle of $0.0102 \times 4\pi$ steradians. The normal sample volume was 10 ml. The photomultiplier was an EMI 9558Q cooled to -80° with cold N_2 gas. A Hamner Electronics Model N301 Non-Overload Amplifier, which includes a discriminator, was used for photon counting. The counter was a Hewlett-Packard Model 5532A; 10^5 cps could be recorded without significant statistical error.

For taking spectra, a larger sample cell (150 mm \times 22 mm i.d.) containing a 50-ml sample was placed end on to the slit of a Bausch and Lomb high intensity grating monochromator ($f/3.5$) with a visible grating. The monochromator was coupled to the cell compartment and the photomultiplier housing, and also enclosed with a black box to cover light leaks. Spectra were taken point by point.

Chemicals. The initiator used was dicyclohexyl peroxydicarbonate which has a half-life of about 1 hr at 70°. It was supplied by Lucidol and used without further purification. The 10^{-2} M solutions normally used showed no evidence of autodecomposition.

All other chemicals were obtained commercially and vacuum distilled, except benzyl phenyl ketone which was purified by recrystallization from hexane.

(8) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

(9) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **43**, 2737 (1965).

(10) J. A. Howard and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 1058 (1968).

(11) J. A. Howard and K. U. Ingold, *ibid.*, **90**, 1056 (1968).

(12) R. A. Lloyd, *Trans. Faraday Soc.*, **61**, 2173 (1965).

Results

Spectrum of 2-Butanone Oxidation. The spectrum from 2-butanone is shown in Figure 1A. No corrections for the relative response of the grating or photomultiplier were made. Additional resolution has been obtained over that reported by Vassilev.¹³ The peaks and shoulder are virtually identical in intensity and wavelength with that reported¹⁴ for photoexcited biacetal phosphorescence in a degassed benzene solution at 20°. The photoexcitation spectra in Figure 1B, which show less resolution, were obtained in our laboratory. The most interesting aspect of the chemiluminescence spectrum is that the dominant emission is phosphorescence, even though the solution is air saturated at 70° ($[O_2] \sim 10^{-3}$ M). If the chemiluminescence reaction produced excited singlet states, the O_2 quenching of phosphorescence would leave a total emission dominant in fluorescence.¹⁴ Assuming some typical numbers, $k_F = 10^7$ for singlet decay, $k_P = 10^3$ for triplet decay, $k_R = 10^{11}$ for oxygen quenching, and $[O_2] = 10^{-3}$ M, the phosphorescence should be quenched by four orders of magnitude ($10^7/10^3$), relative to fluorescence. Even if we assume the shoulder on the high-energy side is fluorescence, we can conservatively estimate that the ratio of triplets to singlets initially produced in the chemical reaction is $>10^4$.

O_2 Quenching. The observation of phosphorescence in an air-saturated solution led us to determine the extent of O_2 quenching of the oxyluminescence using cyclohexanone oxidation with dicyclohexyl peroxydicarbonate as the initiator.

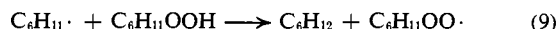
The chemistry is summarized.



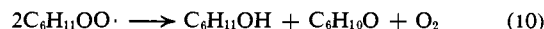
In the case of air oxidation



while in anaerobic solution containing cyclohexyl hydroperoxide



These two systems allow us to make peroxy radicals at the same rate in the presence and absence of O_2 . The results are compared in Figure 2. Although the disproportionation produces O_2



this should be chewed up by the initiation and propagation reactions



As an additional measure against the possibility that the chemistry is insufficient to remove the O_2 , a system using an argon flush is included. The spread of luminescence intensity from the three systems barely spans a factor of 2, confirming the absence of dominant quenching by adventitious O_2 .

An additional run is shown in Figure 3, where oxygen is added to a hydroperoxide system. Quenching by a factor of 2 is explicit here. This is roughly equivalent in magnitude to that observed by Vassilev¹⁵ using the

(13) R. F. Vassilev and I. F. Rusina, *Dokl. Akad. Nauk SSSR*, **156**, 1402 (1964).

(14) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

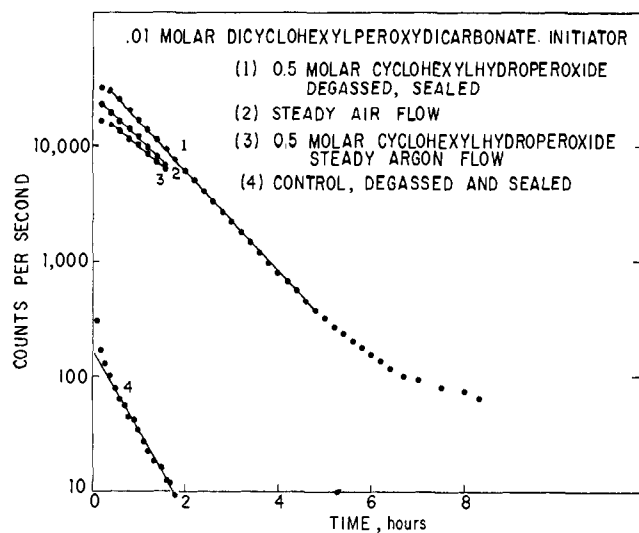


Figure 2. Cyclohexane oxidation at 70°.

“oxygen drop” method. The fact that the $10^{-3} M O_2$ can only quench by a factor of 2 indicates that the triplets are already being quenched in 10^{-8} sec ($10^3 \times 10^{-11}$).

Quantum Yields. Quantum yields were measured by dividing the number of photon counts by the number of initiator molecules. (One initiator molecule gives two radicals; two peroxy radicals disproportionate to one ketone.) Corrections were made for the collection solid angle and for the relative photomultiplier response. The emission wavelengths were taken from measured spectra.¹⁶

The results are shown in Table I. All measurements were made in neat solution except for benzyl phenyl ke-

Table I. Chemiluminescence Yields^a

Molecule	ϕ_{cl}
<i>n</i> -Heptane	0.8×10^{-9}
<i>n</i> -Octane	0.16
<i>n</i> -Dodecane	0.15
Cyclohexane	2.4
Cyclododecane	1.1
Ethylbenzene	0.9
2-Butanone	7
2-Heptanone	2.4
Benzyl phenyl ketone ^b	8
Cyclopentanone	40

^a Yields are computed by comparing the number of photon counts with the number of initiator molecules. They are corrected for the collection solid angle and for the photocathode efficiency (using manufacturer's chart). ^b All numbers are measured in neat materials except for benzyl phenyl ketone which is in chlorobenzene solution.

tone which was in chlorobenzene solution. The cyclopentanone purity was improved from 98.6 to 99.9% by preparative gas chromatography raising the quantum yield by a factor of 5–10. Ideally, this degree of purification should have been used for the other compounds also.

(15) R. F. Vassilev and I. F. Rusina, *Dokl. Akad. Nauk SSSR*, 153, 1101 (1963).

(16) Unpublished results.

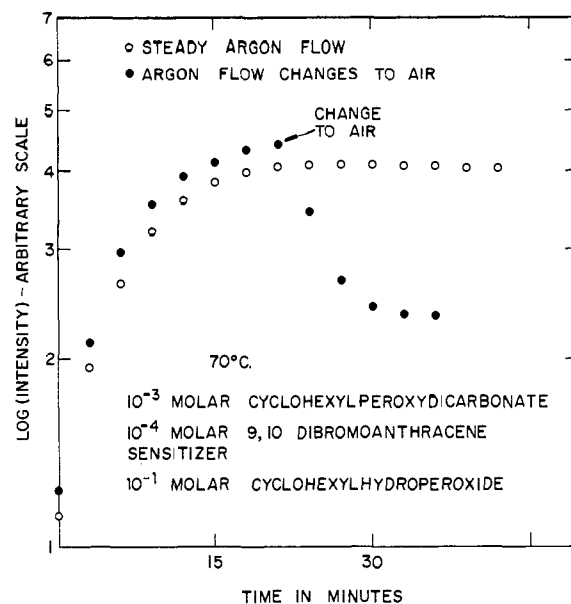


Figure 3. The introduction of air to cyclohexane oxidation at 70°. 9,10-Dibromoanthracene was used as a sensitizer in this case.

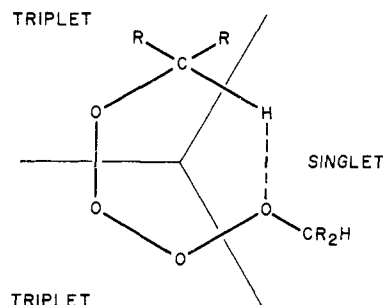


Figure 4. “Russell diagram” showing the probable geometry of the transition state.

Singlet Oxygen. The singlet O_2 states are $^1\Sigma$ at 7619 Å and $^1\Delta$ at 12,683 Å. Our photomultiplier can detect emission from $^1\Sigma$ but not from $^1\Delta$.

Using a Corning 7-69 filter (0.73–1 μ), we detected a weak emission from cyclohexane oxidation with a photon yield of 0.9×10^{-11} . We could not differentiate between $^1\Sigma O_2$ emission and the tail of the cyclohexanone phosphorescence.

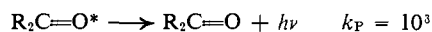
Conclusions

These results can be explained with a somewhat novel rationalization of the sequence of events, using the Russell diagram⁸ in Figure 4. To obtain an excited state, the reaction exothermicity must be concentrated in the carbonyl fragment. The concerted fragmentation then gives singlet ground-state alcohol and triplet ground-state O_2 . To satisfy spin selection rules, the excited carbonyl must be triplet.

Further, the poor efficiency of quenching by adventitious O_2 can be attributed to more efficient quenching by the O_2 eliminated in the reaction and retained in the solvent cage. The rate of triplet-triplet transfer quenching in the solvent cage by an exchange interaction has been estimated by Wagner¹⁷ to be $\sim 10^{11}$ sec⁻¹.

(17) P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, 90, 2232 (1968).

If we assume the rate constant for O₂ quenching is roughly the same, we can imagine the following scheme.



$$k_Q' = k_{\text{diffusion}} \times [O_2] = 10^{11} \times 10^{-3} = 10^8$$

These rate constants indicate that only one excited carbonyl in 10⁸ emits due to competition with quenching in the cage. Assuming a high efficiency of excited state production, the predicted maximum emission yield is 10⁻⁸. The largest experimental yield is 4 × 10⁻⁸. This means that excited carbonyl are indeed being produced with efficiencies of the order of unity. The adventitious O₂ quenching by 50% is probably due to a few excited carbonyls that escape from the cage before the dominant cage quenching occurs.

The ¹Σ O₂ can be produced by energy transfer or perhaps directly in the disproportionation reaction. Ogryzlo¹⁸ has recently estimated the lifetime of the ¹Σ state

in solution to be 10⁻⁹ sec. Since the radiative lifetime is 7 sec, the maximum observable photon yield is 1.4 × 10⁻¹⁰. If we assume the observed count to be ¹Σ emission, the experimental yield is 0.9 × 10⁻¹¹, which is probably within experimental error of the maximum.

The apparent high selectivity of the disproportionation for the excited ketone triplet (rather than ground-state ketone and singlet O₂) should be predictable by a theoretical study of potential energy surfaces. The molecular framework involved in the concerted fragmentation is small enough so that this might be a feasible study.

Acknowledgment. The photon counting apparatus was designed and built by Mr. R. P. Schwenker. The cyclohexyl hydroperoxide was a gift from Dr. M. Rappaport. The author has also benefited from innumerable discussions with other workers in the field.

(18) S. J. Arnold, M. Kubo, and E. A. Ogryzlo, *Advances in Chemistry Series*, No. 77, American Chemical Society, Washington, D. C., 1968, p 133.

Dynamic Nuclear Polarization in Phosponitrilic Ring Compounds

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Contribution from the Physical Chemistry Laboratory, University of Oxford, Oxford, England, Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada, School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903, and Institute for Exploratory Research, U. S. Army Electronics Command, Fort Monmouth, New Jersey 07703. Received April 18, 1969

Abstract: A series of chlorinated phosponitrilic ring compounds, ranging from (PNCl₂)₃ to (PNCl₂)₇, was examined by dynamic nuclear polarization with four different free radicals. A definite radical order was observed which suggests that enhancement details are related to the chemical properties of the ring compounds. The cyclochlorine atoms appear to be primarily responsible for the over-all magnitude of the intermolecular hyperfine coupling, while the detailed order of polarization within the series may be interpreted in terms of differing amounts of electron delocalization within the rings.

In recent years, numerous dynamic nuclear polarization (dnp) measurements have been reported for solutions containing free radicals in hydrocarbon² and fluorocarbon³⁻⁵ solutions. For protons, only dipolar radical-solvent interactions are generally present, while for fluorine both dipolar and scalar hyperfine coupling are important. Furthermore, the chemical environment⁶ of F considerably affects the degree of scalar coupling. This is conspicuously apparent when aromatic and aliphatic fluorocarbons are compared: aromatic

fluorocarbons always show greater scalar coupling. In view of this, the degree of aromaticity in phosponitrilic ring compounds, of concern for several years,⁷⁻⁹ appeared to be an apt subject for study by dnp. Here, we report preliminary measurements for a graded sequence of phosponitrilic ring compounds with only small differences between adjacent members. This approach should enable controlled isolation of factors related to the size and shape of the molecules. Because dnp is extremely sensitive to such variations, a better understanding of the nature of these compounds and their collisional interactions in solution should be obtained.

Theory

Dynamic enhancement of an nmr signal is effected by stimulating the resonance of a paramagnetic species

(1) (a) Physical Chemistry Laboratory; (b) University of British Columbia; (c) Rutgers; (d) Institute for Exploratory Research.

(2) (a) R. A. Dwek, O. W. Howarth, D. F. S. Natusch, and R. E. Richards, *Mol. Phys.*, **13**, 457 (1967); (b) K. D. Kramer, W. Müller-Warmuth, and J. Schindler, *J. Chem. Phys.*, **43**, 31 (1965).

(3) R. A. Dwek, H. D. W. Hill, J. G. Kenworthy, D. F. S. Natusch, and R. E. Richards, *Mol. Phys.*, **13**, 27 (1967).

(4) W. Müller-Warmuth, R. Van Steenwinkel, and F. Noack, *Z. Naturforsch.*, **23a**, 506 (1968).

(5) E. H. Poindexter, J. R. Stewart, and P. J. Caplan, *J. Chem. Phys.*, **47**, 2862 (1967).

(6) J. R. Stewart, E. H. Poindexter, and J. A. Potenza, *J. Am. Chem. Soc.*, **89**, 6017 (1967).

(7) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

(8) D. P. Craig and K. A. R. Mitchell, *ibid.*, 4682 (1965).

(9) C. E. Brion, D. J. Oldfield, and N. L. Paddock, *Chem. Commun.*, 226 (1966).