In view of the present experimental data the energetically more favorable model proposed by Lin and Laidler,[5] *i.e.*, 1,4-H-atom migration, for the formation of butene-1 is not considered here.

Using the values of $l^{\ddagger} = 10$ and $E_0 = 61.4$ kcal/mol for the overall structural isomerization of MCP*, k_E's were calculated as a function of energy. The quantities $\Sigma P(E^{\ddagger})$ and $N(E_0 + E^{\ddagger})$ were evaluated by the method of Whitten and Rabinovitch[24] on an IBM 360/67 computer.

Thermochemistry. The energy content of the "hot" MCP molecule $E = E_{exo} + E_{ther}$, the exothermicity of the reaction plus the thermal contributions of the reactants. In the case of radical–radical combinations, the exothermicity is equal to the strength of the bond being formed, which, unfortunately, is unknown for MCP. Using an estimated value[25] of ΔH_f^{298}(MCP) = 8.1 kcal/mol and 34.0 and 61.0 kcal/mol for ΔH_f^{298} of methyl and cyclopropyl radicals, respectively,[26] D-(c-C_3H_5–CH_3) = 86.9 kcal/mol. At 57°, E_{ther} is estimated to be $\sim$2 kcal/mol, with the result that $E \simeq$ 89 kcal/mol.

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Chemiluminescence in Oxidation Reactions. The Oxidation Mechanism of Dimedone

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Abstract: The detailed mechanism whereby organic molecules chemiluminesce during autooxidation (oxyluminescence) has not been completely determined. Particularly, the reasons for the low luminescence quantum yield observed in such reactions have remained largely unexplained. In this paper the detailed mechanism of oxyluminescence is examined in the case of dimedone (1,1-dimethyl-3,5-cyclohexanedione) oxidation. This proceeds by formation of the 4-peroxydimedone radical which disproportionates with a rate constant of $(4.5 \pm 0.5) \times 10^8\ M^{-1}\ sec^{-1}$ and propagates with a rate constant of $(7 \pm 1) \times 10^2\ M^{-1}\ sec^{-1}$ at 22° and with an activation energy of 5 ± 1 kcal. The disproportionation reaction leads to two chemiluminescent products, one of which, a precursor, is believed to be either the first excited single state of 1,1-dimethyl-3,4,5-cyclohexanetrione (D=O) or a complex between triplet D=O and adjacently formed singlet oxygen. If the precursor is the complex then triplet D=O is initially formed by an adiabatic transition from the vibrationally excited triketone molecule in its electronic ground state. The other chemiluminescent species, shown to be a product of the first, is triplet D=O. The observed chemiluminescence efficiency is $(2.5 \pm 0.5) \times 10^{-10}$. The lifetime of the precursor is estimated to be 10^{-7} sec and its emission efficiency $(3.6 \pm 0.2) \times 10^{-3}$. The efficiency with which the precursor decomposes (or intersystem crosses) to give triplet D=O is >0.12, and the efficiency with which it is initially formed is $(4.5 \pm 0.5) \times 10^{-8}$. The low oxyluminescence quantum yield is attributed to the low excitation efficiency of the precursor which, whether its formation depends on an adiabatic transition from the ground state or directly on the efficiency of formation of the first excited singlet state, is a statistically unlikely process.

The oxidation mechanism of simple organic compounds has been extensively studied.[1] Detailed mechanisms of the oxidation of aromatic and aliphatic hydrocarbons such as tetralin,[2–4] cumene,[2,3] and ethylbenzene[1b,3,5] have been proposed by Ingold and coworkers; methyl oleate[6] and benzaldehyde oxidation[7] have also been extensively studied. This study presents an initial attempt to investigate the oxidation of compounds with reactive methylene groups, such as dimedone[8] which forms secondary 4-peroxydimedone radicals during oxidation. The disproportionation of such peroxy radicals is exothermic by 115–150 kcal,[9] and is assumed to proceed *via* the decomposition of a tetroxide intermediate as proposed by Russell.[10] The ketone produced in this reaction has been shown to chemiluminesce from its triplet state.[11,12] There is, however, much evidence[11,13] that some portion of this luminescence is oxygen insensitive. Kellogg[11] ascribes

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[1] (a) K. U. Ingold, *Accounts Chem. Res.*, **2**, 1 (1969); (b) R. F. Vassilév, "Progress in Reaction Kinetics," Vol. IV, G. Porter, Ed., Pergamon Press, London, 1967.

[2] J. A. Howard, W. J. Schwalin, and K. U. Ingold, *Advan. Chem. Ser.*, No. **75**, 6 (1968).

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[5] V. F. Tsepalov and V. Ya. Shlyapintokh, *Kinet. Katal.*, **3**, 870 (1962).

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[10] G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 3871 (1957).

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[13] (a) R. F. Vassilév, A. A. Vichutinsleii, O. N. Karpukhin, and V. Ya. Shlyapintokh, *Izv. Akad. Nauk SSSR*, **1**, 320 (1962); (b) V. Ya. Shlyapintokh, R. F. Vassilév, O. N. Karpukhin, L. M. Postnikov, and L. A. Kibalko, *J. Chim. Phys. Physicochim. Biol.*, **57**, 1113 (1960).

this to the possible rapid quenching of the triplet ketone by the adjacently formed oxygen; however, this implies that the excitation efficiency of formation of excited states prior to any quenching reaction is high and that the adjacently formed oxygen is in the ground state. The luminescence lifetime has been estimated as 10^{-6} to 10^{-7} sec,[14] which is longer than can be expected from the previously proposed mechanism.[11]

The detailed mechanism of the disproportionation reaction, as proposed in the literature, must then be based on the possibility, at least, that the excitation efficiency is low.

$$\text{DHOO}\cdot + \text{DHOO}\cdot \rightleftarrows [\text{DHO}_4\text{HD}] \qquad \text{(R1)}$$

$$[\text{DHO}_4\text{HD}] \longrightarrow \text{C}^* \qquad \text{(R2)}$$

$$[\text{DHO}_4\text{HD}] \longrightarrow [\text{D{=}O} + {}^1\text{O}_2 + \text{DHOH}] \qquad \text{(R3)}$$

$$\text{C}^* \longrightarrow \text{C} \qquad \text{(R4)}$$

$$\text{C}^* \longrightarrow \text{C}' + h\nu_1 \qquad \text{(R5)}$$

$$\text{C}^* \longrightarrow {}^3\text{D{=}O} + {}^3\text{O}_2 + \text{DHOH} \quad \text{or} \qquad \text{(R6)}$$

$$\text{C}^* \longrightarrow {}^3\text{D{=}O} + {}^1\text{O}_2 + \text{DHOH} \qquad \text{(R6')}$$

$$^3\text{D{=}O} \longrightarrow \text{D{=}O} \qquad \text{(R7)}$$

$$^3\text{D{=}O} + \text{O}_2 \longrightarrow \text{D{=}O} + {}^1\text{O}_2 \qquad \text{(R8)}$$

$$^3\text{D{=}O} \longrightarrow \text{D{=}O} + h\nu_2 \qquad \text{(R9)}$$

DHO_4HD is Russell's tetroxide intermediate. In cases where the excitation efficiency is high, then $k_2 > k_3$ and, to explain the low observed quantum yields, $k_4 \gg k_5$. Furthermore, $C^* = [{}^3D{=}O + {}^3O_2 + DHOH]$, $C = [{}^1D{=}O + {}^1O_2 + DHOH]$, and $C' = [{}^1D{=}O + {}^3O_2 + DHOH]$. k_6 may then reasonably be assumed to be very small, since most of the triplet ketone is quenched in the solvent cage and a very small portion of it escapes the cage while still in the electronically excited state. The emission from this small portion of freely solvated triplet ketone is quenched by oxygen.

If, on the other hand, the excitation efficiency is low then $k_2 \ll k_3$ and k_4 may be smaller than k_5. Furthermore, C* is then an unknown excited state precursor of $^3D{=}O$, which is not quenched by oxygen.

The total intensity of luminescence for the above scheme is given by

$$I = \phi_{ex}(\phi^{C^*} + \eta\phi_P{}^{D=O^*})(k_1/2)[\text{DHOO}\cdot]^2 = \phi_t(k_1/2)[\text{DHOO}\cdot]^2 \qquad (1)$$

where

$$\phi_{ex} = k_2/(k_2 + k_3) \qquad (2)$$

is the excitation quantum efficiency

$$\phi^{C^*} = k_5/(k_4 + k_5 + k_6) \qquad (3)$$

the phosphorescence efficiency of C*

$$\eta = \phi^{C^*}(k_6/k_5) \qquad (4)$$

the efficiency with which D=O* is released and

$$\phi_P{}^{D=O^*} = k_9/(k_7 + k_8[O_2] + k_9) \qquad (5)$$

the phosphorescence efficiency of D=O*.

It was possible, in this investigation, to determine the separate excitation and phosphorescence efficiencies of the luminescing species as well as the termination and propagation rate constants of the peroxy radical. From these the detailed model of the oxyluminescence process was verified and two possible sources of oxygen insensitive radiation are proposed.

Experimental Section

Chemicals. The solvent, used without further purification in all of the experiments, was anhydrous acetonitrile (Eastman No. X488). Dimedone (Eastman No. 1259) was twice recrystallized from absolute ethanol, then vacuum dried at 65°. Fluorescein (Aldrich No. F245-G) was recrystallized from acetonitrile until the extinction coefficient at 499 nm was 9.2×10^4.[15] All other chemicals were used without further purification.

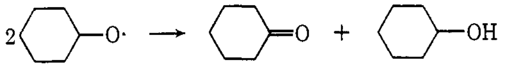
Chemiluminescence Apparatus. The chemiluminescence apparatus, similar to that of Lloyd,[16] had a collection angle of $0.00915 \times 4\pi$ steradians, as determined by observing the luminescence intensity of the reaction of oxygen with tetrakis(dimethylamino)-ethylene. The photomultiplier (EMI 9558Q) was cooled to $\sim -60°$ with cold N_2 gas. Signal amplification and discrimination was performed with the HP Models 5582A linear amplifier and 5583A single channel analyzer. The photon counter was an HP Model 5321B. Sample volume was 10 ml except for spectral determinations when it was increased to 30 ml. Sample cells (55 × 23 mm i.d.) were thermostated and fitted with a water-cooled reflux condenser housed in a light-tight box. Spectra were taken by interposing a Bausch and Lomb high-intensity grating monochromator (*f*/3.5) with a 350–700-nm grating between the sample and the photomultiplier.

Chemiluminescence Experiments. The thermal initiator used in the oxyluminescence experiments was dicyclohexyl peroxydicarbonate (DCPDC, Lucidol No. R229) which decomposes to cyclohexyloxy radicals and CO_2.

Cyclohexyloxy radicals abstract hydrogen from dimedone (DH_2) which then reacts with oxygen to form the 4-peroxydimedone radical.[1,14] The subsequent reaction of the peroxy radical consists primarily of the chain propagation step[1,14]

$$\text{DHOO} + \text{DH}_2 \longrightarrow \text{DHOOH} + \text{DH} \qquad \text{(R10)}$$

and the termination reaction, described by reaction steps R1–R9 of which steps R5 and R9 give the chemiluminescence. Further decomposition of the hydroperoxide plays a minor part in the early stages of the reaction. A weak contribution to the chemiluminescence (<5%) was found to come from the disproportionation reaction of the cyclohexyloxy radical.



(R11)

Oxygen Consumption Apparatus. The apparatus for measuring oxygen consumption rates is similar to that described by Shlyapintokh.[17] The light source was a Bausch and Lomb high-intensity xenon arc lamp. Collimation was achieved with quartz optics. The sample volume was 60 ml and was contained in a 34 × 34 × 50 mm quartz cell. Agitation was achieved with an immersible magnetic stirrer. The chopper (rotating sector) was a Brauer Model 312C with either one 90° or two 45° sectors.

Oxygen Consumption Rate Experiments. The rate constants k_{10} and k_1 are derived from measurements of oxygen consumption rates. In these experiments the initiator was bis(2,*o*-chlorophenyl-4,5-di-*m*-methoxyphenylimidazole) (L_2). The photochemical decomposition of this compound leads to the formation of two radicals,[18] which, in turn, abstract hydrogen from dimedone

$$\text{L}_2 \xrightarrow{h\nu} 2\text{L} \qquad \text{(R12)}$$

$$\text{L} + \text{DH}_2 \longrightarrow \text{LH} + \text{DH} \qquad \text{(R13)}$$

where LH is 2-*o*-chlorophenyl-4,5-di-*m*-methoxyphenylimidazole. The subsequent reaction of the dimedone radical is assumed to be identical with that previously described and the oxygen consumption

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[14] K. D. Gundermann, "Chemilumineszenz Organischer Verbindungen," Springer Verlag, Berlin, 1968, p 21.

[15] P. G. Seybolt, M. Gouterman, and J. Callis, *Photochem. Photobiol.*, **9**, 229 (1969).

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[17] O. N. Karpukhin, V. Ya. Shlyapintokh, and N. V. Zolotova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 10, 1722 (1963).

[18] (a) L. E. Cescon, *et al.*, *J. Org. Chem.*, in press; (b) H. Zimmerman, H. Baumgaertel, and F. Back, *Angew. Chem.*, **73**, 808 (1961).

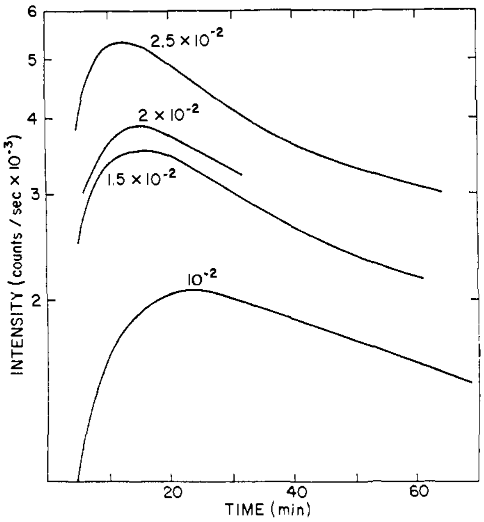

Figure 1. Chemiluminescence intensity *vs.* time for various initiator concentrations: temperature, 50°; dimedone concentration, 2.9×10^{-2} *M*.

rate is given by[19]

$$\frac{-\mathrm{d}[\mathrm{O}_2]}{\mathrm{d}t} = \sqrt{r_i}\frac{k_{10}}{\sqrt{k_1}}[\mathrm{DH}_2] + \frac{r_i}{2} \tag{6}$$

where r_i, the rate of initiation, is proportional to the absorbed light intensity

$$r_i = -2\frac{\mathrm{d}[\mathrm{L}_2]}{\mathrm{d}t} = \phi' I_a \tag{7}$$

where ϕ' is the quantum yield of L· production, and I_a is the absorbed light intensity. The value of k_1 was evaluated by measuring the oxygen consumption rate at 22.9° with a rotating sector. The ratio of average peroxide radical concentration at a given sector speed, over the peroxy radical concentration under continuous illumination, is given by[20]

$$\frac{[\mathrm{DHOO}\cdot]}{[\mathrm{DHOO}\cdot]_s} = \frac{-1 + \sqrt{1 + \frac{\gamma^2}{2}\frac{\bar{r}}{[\mathrm{DH}_2]^2}}}{-1 + \sqrt{1 + \frac{\gamma^2}{2}\frac{r_s}{[\mathrm{DH}_2]^2}}} \tag{8}$$

where $\bar{r}$ and r_s are the average rate of oxygen consumption at a given sector speed, and the rate of oxygen consumption with continuous illumination, respectively. The ratio calculated by eq 11 is related to sector speed and lifetime of the peroxy radical given by[21]

$$\frac{[\mathrm{DHOO}\cdot]}{[\mathrm{DHOO}\cdot]_s} = (q + 1)^{-1}\{1 + m^{-1}\ln[1 + qm/(1 + \alpha)]\} \tag{9}$$

where

$$\alpha = \frac{2(qm + \tanh m)}{qm \tanh m + [q^2m^2 \tanh^2 m + 4(qm + \tanh m)\tanh m]^{1/2}}$$

$$m = (r_i k_1)^{1/2}\lambda = k_1\lambda[\mathrm{DHOO}\cdot] = \lambda/\tau$$

where q = dark period/light period, λ = light period (seconds), and τ = lifetime of the peroxy radical (seconds). In the case of these experiments $q = 3$.

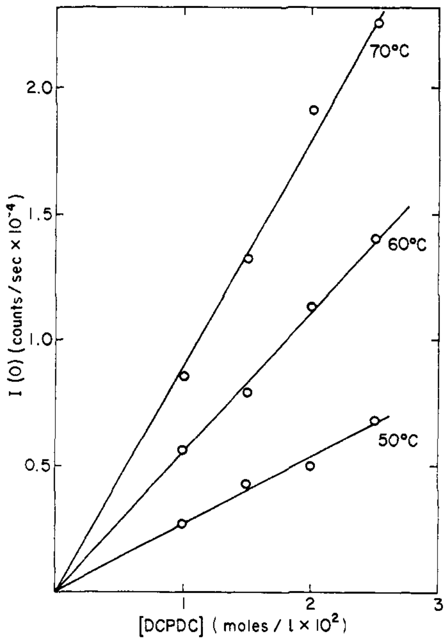

Figure 2. Chemiluminescence intensity (at $t = 0$) *vs.* initiator concentration at various temperatures: dimedone concentration, 2.9×10^{-2} *M*.

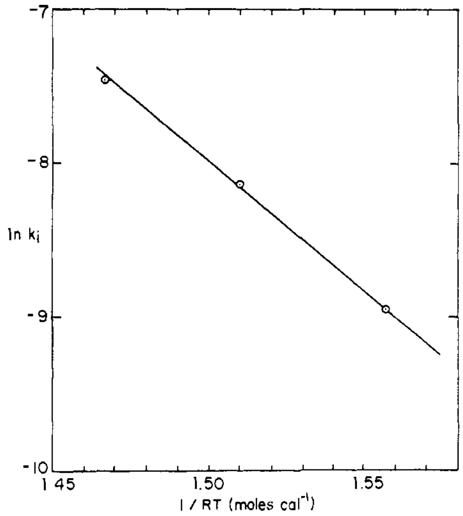

Figure 3. Arrhenius plot of the initiation rate constant.

Results

a. Initiation Rate Constant and Total Quantum Efficiency of Luminescence. Figure 1 shows the behavior of luminescence intensity *vs.* time of 2.9×10^{-2} *M* dimedone at various concentrations of DCPDC. Figure 2 shows the linear relationship between initial DCPDC concentration and luminescence intensity, extrapolated to $t = 0$, at three temperatures in accordance with the steady-state approximation

$$\frac{-\mathrm{d}[\mathrm{DCPDC}]}{\mathrm{d}t} = k_i[\mathrm{DCPDC}] = (k_1/2)[\mathrm{DHOO}\ ]^2 \tag{10}$$

where k_i is the initiation rate constant. Combining eq 10 and 1 and solving the differential equation gives

$$I_0 = \phi_t k_i[\mathrm{DCPDC}]_0 \tag{11}$$

$$\ln(I_0/I) = k_i t \tag{12}$$

where I_0 = luminescence intensity at $t = 0$ and k_i and ϕ_t are derived from eq 11 and 12. Figure 3 is an

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(19) Reference 12b, p 34.

(20) V. F. Tsepalov and V. Ya. Shlyapintokh, *Kinet. Katal.*, **3**, 870 (1962).

(21) H. W. Melville and G. M. Burnett, *Tech. Org. Chem.*, **8**, 133 (1953).

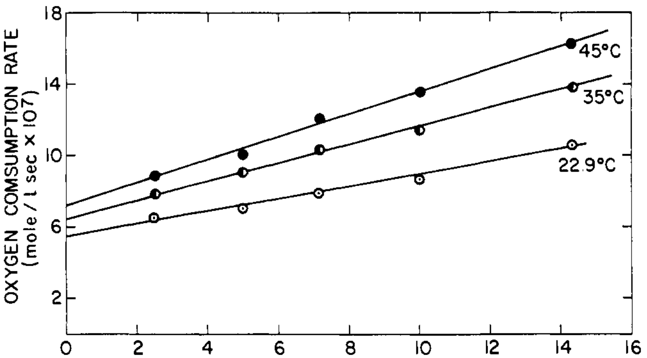

Figure 4. Oxygen consumption rate *vs.* dimedone concentration under steady illumination.

Arrhenius plot of k_i. The derived values are

$$k_i = (2 \pm 0.5) \times 10^8 \exp(-[(18 \pm 5) \times 10^3/RT]) \text{ sec}^{-1}$$

$$\phi_t = (2.3 \pm 0.5) \times 10^{-10}$$

b. Kinetic Chain Length, Propagation, and Termination Rate Constants. A plot of initial oxygen consumption rate (at reasonably high concentrations of dimedone) *vs.* dimedone concentration is linear, as shown in Figure 4, and is used to calculate the initiation rate, r_i, and the kinetic chain length of the oxidation reaction, $\gamma = k_{10}/\sqrt{k_1}$ (eq 6). The values are given in Table I. The results of the rotating sector experiments are summarized in Table II. From these data, the values of $k_1 = (4.5 \pm 0.5) \times 10^8\ M^{-1}\ \text{sec}^{-1}$ and $k_{10} = (7 \pm 1) \times 10^2\ M^{-1}\ \text{sec}^{-1}$, at 22.9°, are obtained. Using the values of the kinetic chain length at 35 and 45°, respectively, and assuming k_1 to be diffusion controlled gives $k_{10} = (6.3 \pm 0.6) \times 10^5 \exp[(4 \pm 1) \times 10^3/RT]\ M^{-1}\ \text{sec}^{-1}$.

Table I. Chain Lengths and Initiation Rates at Various Temperatures

Temp, °C	γ, l.$^{1/2}$/mol$^{1/2}$ sec$^{1/2}$	r_i, mol/l. sec
22.9	$(3.4 \pm 0.3) \times 10^{-2}$	1.1×10^{-6}
35.0	$(4.6 \pm 0.4) \times 10^{-2}$	1.3×10^{-6}
45.0	$(5.4 \pm 0.5) \times 10^{-2}$	1.4×10^{-6}

Table II. Determination of the Lifetime of the Peroxy Radical

λ, sec	$\bar{r}$, M sec^{-1} $\times 10^7$	[DHOO·]/[DHOO·]$_s$	m	τ, sec
0.462	1.57	0.302	15.0	0.036
0.397	1.79	0.333	7.5	0.053
0.315	1.83	0.339	6.75	0.047
0.270	1.90	0.348	5.75	0.047
0.165	2.16	0.383	3.45	0.048
0.120	2.27	0.397	2.80	0.043
0.110	2.31	0.402	2.65	0.041
0.0824	2.38	0.411	2.32	0.036
0.0567	2.64	0.442	1.50	0.038
0.0425	2.89	0.472	0.90	0.047
0.0306	3.00	0.485	0.60	0.051

c. Excitation Quantum Yield and Lifetime of the Precursor. The excitation quantum yield and the lifetime of the precursor were determined by energy transfer experiments. This was done by adding an energy acceptor (A) to the system which modified the basic mechanism and thus enabled determination of these constants. When the acceptor A is added to the system the kinetic scheme becomes

$$C^* + A \longrightarrow C + A^* \qquad (R14)$$

$$D{=}O^* + A \longrightarrow D{=}O + A^* \qquad (R15)$$

$$A^* \longrightarrow A + h\nu_3 \qquad (R16)$$

$$A^* \longrightarrow A \qquad (R17)$$

This process does not obey a simple Stern–Volmer relation because there are two donors; however, the intensity of the acceptor's radiation can now be shown to be

$$I = \phi_t' k_i[\text{DCPDC}] \qquad (13)$$

where

$$\phi_t' = \phi_{ex}\phi_A(\mu_{tr}{}^{C^*} + \eta'\mu_{tr}{}^{D=O^*})$$

$$\phi_A = k_{16}/(k_{16} + k_{17})$$

$$\mu_{tr}{}^{C^*} = k_{14}[A]/(k_{14}[A] + k_4 + k_6)$$

$$\mu_{tr}{}^{D=O^*} = k_{15}[A]/(k_{15}[A] + k_8[O_2] + k_7)$$

$$\eta' = k_6/(k_{14}[A] + k_4 + k_6)$$

Equation 13 can be transformed to the equivalent of the Stern–Volmer relation

$$\frac{\rho}{I} = 1 + \frac{k_4\left(1 + \dfrac{\beta}{[A]}\right)}{k_{14}[A] + \alpha} \qquad (14)$$

which for the limiting case of high concentration of A gives

$$\underset{[A] \to \infty}{\rho/I} = 1 \qquad (15)$$

where $\beta = (k_8[O_2] + k_7)/k_{19}$, $\alpha = (k_{14}/k_{15})(k_8[O_2] + k_7) + k_6$, $\rho = \phi_A\phi_{ex}k_i[\text{DCPDC}]$.

Equation 14 contains the assumption that $k_4 > k_6$. Figures 5 and 6 show plots of luminescence intensity *vs.* acceptor concentration, with erythrosin and eosin as acceptors. In the case of eosin the luminescence intensity approaches an asymptote which, with eq 14, immediately yields ρ.

For eosin the value of ρ thus derived is 2.3×10^5 einsteins l.$^{-1}$ sec^{-1}. No similar evaluation of ρ for erythrosin is possible because of its limited solubility. However, in this case, a number of approximations can be made which allows the evaluation of a number of the rate constant ratios in eq 14 in addition to ρ.

In the region where $[A] > [O_2]$, eq 14 reduces to

$$\frac{\rho}{I} = 1 + \frac{k_4}{k_{14}[A] + \alpha} \qquad (16)$$

Since, in this region, I can be expected to be $\leqslant 0.5\rho$, a plot of I *vs.* [A] will be nearly linear having a ratio of intercept to slope, $\sigma = \alpha/k_{14}$.

Similarly, when $[A] < [O_2]$, eq 14 reduces to

$$\rho/I = 1 + \frac{k_4\beta}{k_{14}[A]([A] + \sigma)} \qquad (17)$$

A plot of $1/I$ *vs.* $1/[A]([A] + \sigma)$ for this range of concentration of erythrosin gives an intercept of $1/\rho$ and

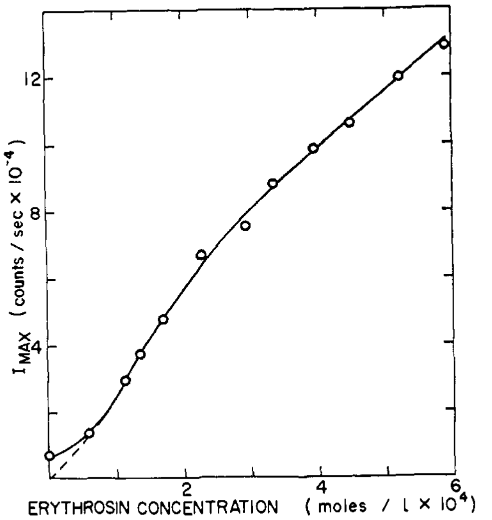

Figure 5. Maximum intensity *vs.* erythrosin concentration. Energy transfer from the oxidation product of dimedone: dimedone concentration, 2.9×10^{-2} *M;* initiator (DCPDC) concentration, 2×10^{-2} *M;* temperature, 60°.

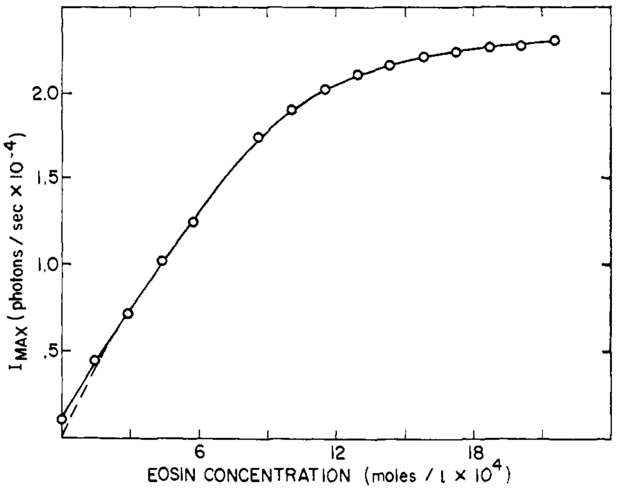

Figure 6. Maximum intensity *vs.* eosin concentration. Energy transfer from the oxidation product of dimedone: dimedone concentration, 2.9×10^{-2} *M;* initiator (DCPDC) concentration, 2×10^{-2} *M;* temperature, 60°.

a ratio of slope over intercept $k_4\beta/k_{14}$. This plot is shown in Figure 7. Finally, in the concentration range which fits eq 16, a plot of $1/I$ *vs.* $1/[A] + \sigma$ is linear (Figure 8) with a slope of $k_4/k_{14}\rho$. Using these limiting conditions, it is thus possible to calculate $\rho = (3.1 \pm 0.2) \times 10^5$ einsteins l.$^{-1}$ sec^{-1}, $k_4/k_{14} = (2.0 \pm 0.2) \times 10^{-3}$ *M*, $k_6/k_{14} = (5 \pm 0.5) \times 10^{-5}$ *M*, $\beta = (k_{14}[O_2] + k_{13})/k_{19} = 3.2 \times 10^{-6}$ *M*. From the above values the validity of the assumption required to derive eq 14 is verified ($k_6/k_4 = 2.5 \times 10^{-2}$) and from the value of k_6/k_{14} the maximum order of magnitude of k_6 can be estimated to be 10^7 sec^{-1}.[14] The lifetime of C* ($\tau_{C^*} \sim 1/k_6$) can therefore be no shorter than $\sim 10^{-7}$ sec.

In order to derive the value of the excitation efficiency it is still necessary to determine ϕ_A, the delayed luminescence efficiency of the acceptor. The emission spectra of the acceptor luminescence are shown in Figure 9, and can be seen to correspond to the fluorescence spectra of erythrosin and eosin shown in Figure 10. It is, therefore, assumed that ϕ_A is simply the fluorescence efficiency of the two acceptors. This was measured by comparing the integrated fluorescence spectra of the two acceptors to the integrated fluo-

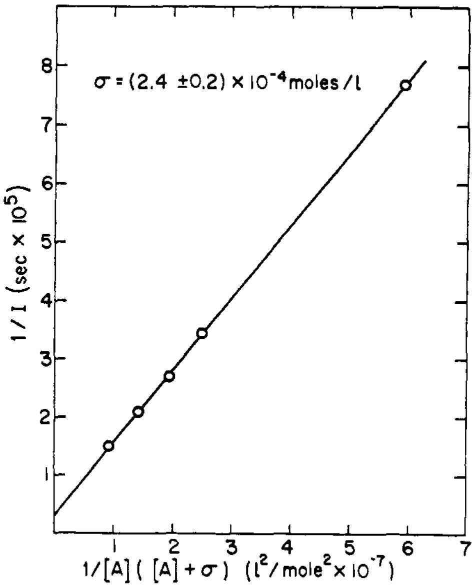

Figure 7. Reciprocal of chemiluminescence intensity *vs.* $1/[A] \cdot ([A] + \sigma)$ where [A] is the erythrosin concentration. See eq 17.

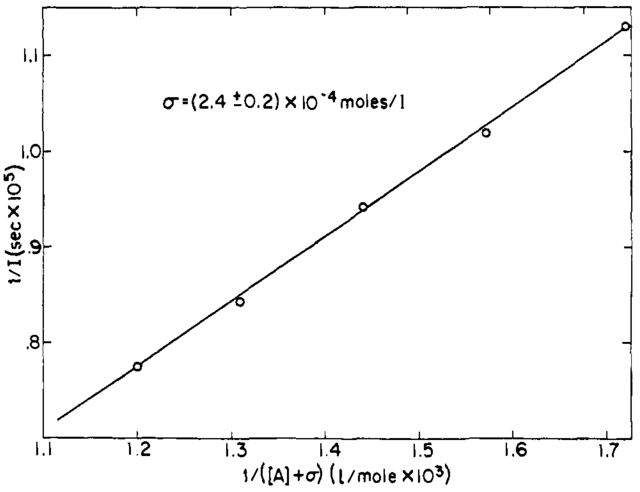

Figure 8. Reciprocal of chemiluminescence intensity *vs.* $1/[(A] + \sigma)$ where [A] is the erythrosin concentration. See eq 16.

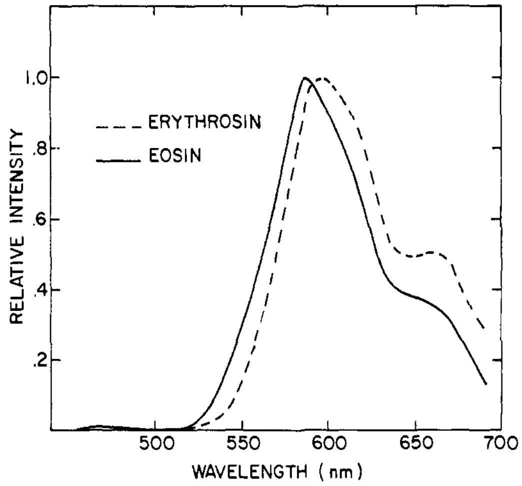

Figure 9. The luminescence spectra of the energy acceptors corrected for monochromator and photomultiplier response.

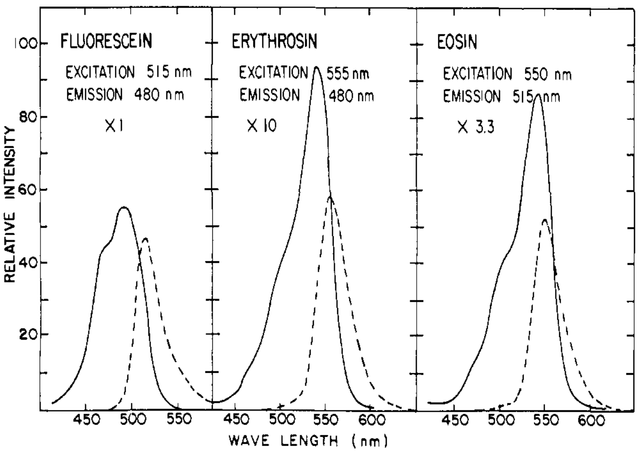

Figure 10. Emission and excitation spectra of the energy acceptors and of fluorescein.

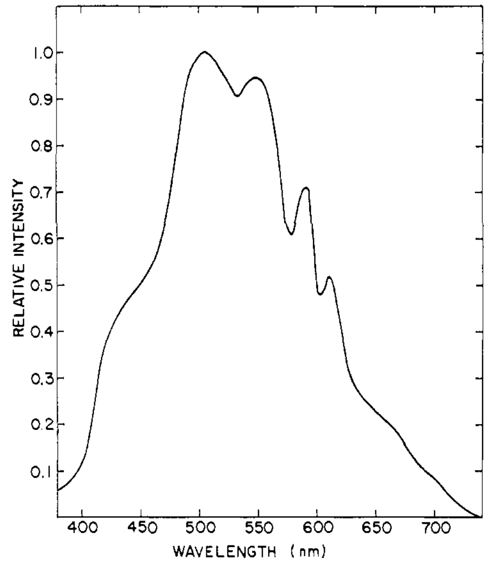

Figure 11. The chemiluminescence spectrum of dimedone oxidation products (100% oxygen bubbled into the luminescing solution).

rescence spectrum of fluorescein.[15] The concentration of the three compounds was adjusted to equal absorbances (0.7) at the corresponding absorption peaks. The values of ϕ_A thus obtained are 0.153 and 0.435, for erythrosin and eosin, respectively. ϕ_{ex} is now calculated from

$$\rho = \phi_{ex}\phi_A k_1[\mathrm{DCPDC}] \qquad (18)$$

giving a value

$$\phi_{ex} = (4.5 \pm 1.5) \times 10^{-8}$$

d. Spectra. The emission spectrum of the chemiluminescence when 100% oxygen is bubbled into the dimedone solution is shown in Figure 11.[22] When 10% oxygen in nitrogen is bubbled into the solution the spectrum changes to that shown in Figure 12. The sensitivity of the long wavelength emission to the oxygen concentration is obvious.[23] Using this effect and eq 1, the ratio of intensities gives

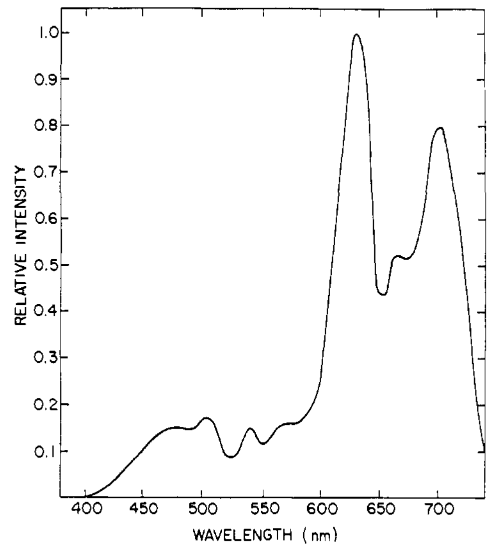

Figure 12. The chemiluminescence spectrum of dimedone oxidation products (10% oxygen in nitrogen bubbled into the luminescing solution).

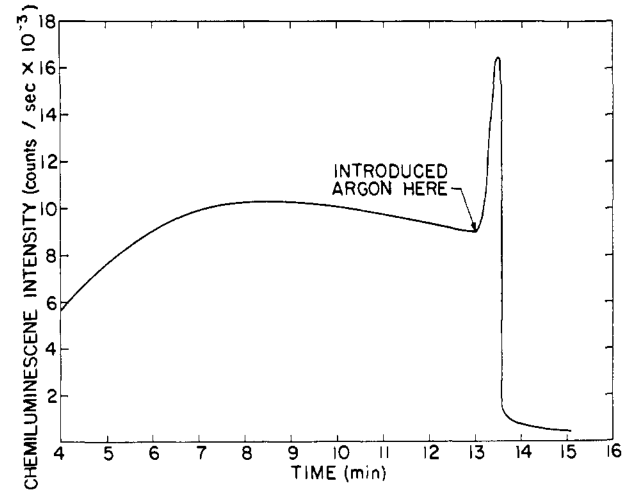

Figure 13. The characteristic burst of luminescence when argon displaces oxygen in a chemiluminescing solution: dimedone concentration, 2.9×10^{-2} *M*; initiator (DCPDC) concentration, 10^{-2} *M*; temperature, 70°.

$$I(615\ \mathrm{nm})/I(505\ \mathrm{nm}) = \eta\phi_P{}^{D=O^*}/\phi^{C^*} = 0.52 \qquad (19)$$

e. Efficiency of Formation of D=O* and Luminescence Efficiencies. When oxygen is depleted from the luminescing solution by replacing it with argon, the luminescence first increases to about twice the intensity prior to depletion of oxygen and then drops very rapidly to a low background value due to the chemiluminescence from reaction R11. The rise is due to the increase in $\phi_P{}^{D=O^*}$ at lower oxygen concentration.[12,13] The decay is characterized by

$$\frac{-\mathrm{d}I}{\mathrm{d}t} = (2I)^{3/2}(k_1/\phi_t)^{1/2} \qquad (20)$$

which was derived by differentiating eq 1 and substituting

$$[\mathrm{ROO}\cdot] = (2I/k_1\phi_t)^{1/2}$$

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[22] D=O is a thermally unstable species which was found to decompose to 3,3-dimethylglutaric acid. Its emission spectra could not be determined, but it was identified as the precursor of 3,3-dimethylglutaric acid by nmr and mass spectra of its stable complex with Cu(II) ion.

[23] The peaks at 575 and 665 nm ultimately grow to obscure most of the long-wavelength emission and are apparently due to further oxidation of the oxidation products of dimedone.

and

$$\frac{-\mathrm{d}[\mathrm{ROO}\cdot]}{\mathrm{d}t} \sim k_1[\mathrm{ROO}\cdot]^2$$

Equation 20 integrates to

$$\frac{1}{\sqrt{I}} - \frac{1}{\sqrt{I_0}} = 2t\sqrt{2k_1/\phi_t} \qquad (21)$$

During the decay, however, $\phi_P{}^{D=O*} \rightarrow 1$, so that

$$\phi_t = \phi_{ex}(\phi^{C*} + \eta) \sim \phi_{ex}\eta \qquad (22)$$

Figure 13 shows a characteristic decay curve. Using eq 21 and 22 and the previously determined values of ϕ_{ex} and k_1, a lower limit for the efficiency, η, of the formation of D=O* from the precursor is calculated to be $\eta \geqslant 0.12$. Having determined ϕ_t, ϕ_{ex}, $\eta\phi_P{}^{D=O*}/\phi^{C*}$, and the lower limit value of η, it is now possible to calculate $\phi^{C*} = (3.6 \pm 1.2) \times 10^{-3}$ and $\phi_P{}^{D=O*} \geqslant 8 \times 10^{-4}$ (solvent saturated with oxygen).

Discussion

Since the value of ϕ_{ex} is low and the value of ϕ^{C*} high, the mechanism suggested by Kellogg[11] cannot be applied in the case of dimedone; *i.e.*, it is not possible that triplet triketone be efficiently quenched by a ground state oxygen molecule which is formed adjacent to it by the decomposition of the tetroxide.

Two possible explanations for the observed phenomenon are as follows. The triketone is produced in a vibrationally excited state of the electronic ground state from which it may undergo an inefficient adiabatic transition to the triplet manifold. The adiabatic transition competes with vibrational decay of the triketone molecule ($\sim 10^{-13}$ sec) and thus the observed low efficiency for the formation of the triplet triketone ($\phi_{ex} \sim 10^{-8}$) is not unreasonable. The oxygen molecule, formed adjacent to the triketone, is, by spin selection rules, formed in a singlet state. In those few instances where an adiabatic transition occurs the triplet triketone molecule forms a triplet charge transfer complex[24] with the adjacent singlet oxygen. This complex is not quenched by oxygen and emits at 505 nm with an efficiency of $\sim 4 \times 10^{-3}$. It also decomposes to make triplet triketone and singlet oxygen in solution. The free triplet molecule phosphoresces at ~615 nm with an efficiency 8×10^{-4} at maximum oxygen concentration. This emission is very susceptible to oxygen quenching.

In the above model energy transfer from both the complex and the free triplet triketone must take place by the "trivial" radiative process.

Another equally consistent mechanism requires the occasional formation (one in 10^8 events) of the triketone in an excited singlet (S_1) state, while the usual event is the formation of a vibrationally excited ground state triketone. The excited singlet either fluoresces or intersystem crosses with a rate constant of $\sim 10^7$ sec^{-1}. The fluorescence at 505 nm is not quenched by dissolved oxygen and its efficiency is 4×10^{-3}. The triplet formed by the intersystem crossing step is readily quenched by oxygen and emits at 615 nm with an efficiency of 8×10^{-4} at maximum oxygen concentration. In this model, energy transfer from the S_1 state of the triketone takes place by a dipole–dipole interaction, while energy transfer from the triplet is again the "trivial" radiative process.

The kinetic chain length of dimedone oxidation is very low. This is primarily due to a termination rate constant which is higher than normally found for the oxidation of a methylene group; but this is not unexpected in view of its position between carbonyl groups.

Acknowledgment. I wish to thank R. E. Kellogg and P. Walker for many helpful discussions, and R. P. Schwenker for his help in constructing the photon counting apparatus.

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[24] H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).