Hydrogen–Deuterium Exchange between Triethylammonium Chloride and Methanol-*d* in Benzene. Triethylammonium chloride (1.5 g, 11 mmoles; prepared by passing dry hydrogen chloride through an ethereal solution of triethylamine; recrystallized from a chloroform–ether mixture; mp 255–256°), triethylamine (1.1 g, 11 mmoles), and methanol-*d* (0.3 g, 11 mmoles) were added to 30 ml of benzene and allowed to stir for 1 hr under nitrogen. The triethylammonium chloride was collected by filtration and dried *in vacuo*. The infrared spectrum of this salt indicated no deuterium incorporation.

Check on Hydrogen–Deuterium Exchange between Triethylammonium Chloride and Methanol-*d* under the Exact Reaction Conditions. Methanesulfonyl chloride (11.4 g, 0.10 mole) was added to methanol (3.8 g, 0.12 mole) and triethylamine (13.1 g, 0.13 mole) in the usual manner. After stirring for 1 hr, methanol-*d* (2.0 g, 0.06 mole) was added and the reaction mixture was stirred for an additional 30 min. The triethylammonium chloride was isolated by filtration, washed with benzene, and dried *in vacuo*. The infrared spectrum showed no exchange.

Acknowledgments. This investigation was supported by the Purdue Research Foundation and by Public Health Service Research Grant No. CA-04536-07 from the National Cancer Institute.

A Study of Chemiluminescence from Reactions of Oxalyl Chloride, Hydrogen Peroxide, and Fluorescent Compounds[1]

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Abstract: The chemiluminescent reaction between oxalyl chloride and hydrogen peroxide in the presence of a fluorescer was investigated with respect to the emitting species, the reaction products, the effects of reactant concentrations on absolute quantum yields and reaction rates, and the effects of free-radical chain inhibitors. Water was found to be a critical reactant in the chemiluminescent process. The system was found to be the most efficient nonbiological chemiluminescent system yet reported, providing quantum yields on the order of 5%. A mechanism involving the decomposition of monoperoxyoxalic acid in a key step is proposed.

Although the direct conversion of chemical energy to light has been observed in a wide variety of chemical reactions,[2] only a few reactions are known which provide moderately high chemiluminescent light intensities indicative of quantum yields above 10^{-3}. Prominent examples of such "bright" chemiluminescence include the reactions of hydrogen peroxide or oxygen with certain phthalhydrazide derivatives,[3,4] imidazole derivatives,[5,6] and acridinium salts.[7-9] Investigation of the mechanisms by which light is produced in such reactions has proved to be difficult because of the complex multistep processes involved and because of low quantum yields of emission. Thus, the identity of the key reaction step that produces the emitting singlet excited state in these reactions tends to be obscured by earlier reaction steps, subsequent reaction steps, and by competing nonluminescent side reactions. Even the identification of the emitting species in these reactions is subject to uncertainty[10] since the available assignments rest entirely on comparisons of chemiluminescence and fluorescence spectral distributions in systems which lack well-defined and uniquely characteristic emission bands.[4,6,8,9]

With these difficulties in mind, we have sought a model chemiluminescent reaction more suitable for mechanistic studies. The chemiluminescent reaction between oxalyl chloride, hydrogen peroxide, and various fluorescent compounds, discovered by Chandross,[11] appeared particularly attractive in this regard. Using aqueous hydrogen peroxide and a fluorescent aromatic hydrocarbon such as anthracene in an organic solvent, Chandross reported the emission as a bright flash having a color matching the fluorescence of the fluorescent additive. Thus, the emitting species, as

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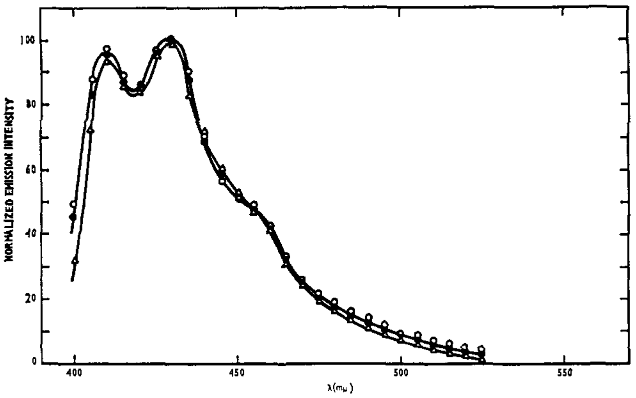

Figure 1. 9,10-Diphenylanthracene chemiluminescence and fluorescence spectra: △, chemiluminescence emission from 1 × 10^{-4} M 9,10-diphenylanthracene, 1.93 × 10^{-3} M oxalyl chloride, and 1.17 M hydrogen peroxide in ether solution; ●, fluorescence from 1 × 10^{-4} M 9,10-diphenylanthracene in ether containing 1.17 M hydrogen peroxide; ○, fluorescence from reaction mixture following chemiluminescent reaction.

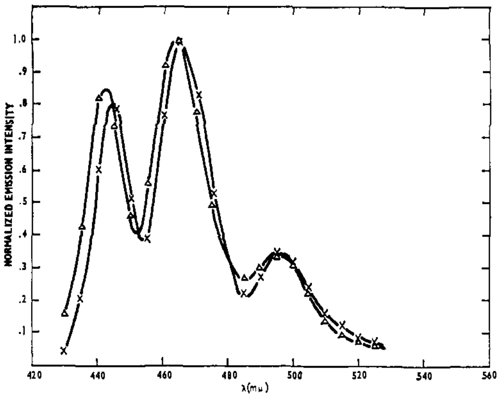

Figure 2. Perylene chemiluminescence and fluorescence spectra: ×, chemiluminescence emission from 1 × 10^{-4} M perylene, 1.93 × 10^{-3} M oxalyl chloride, and 2.60 × 10^{-2} M hydrogen peroxide in ether; △, fluorescence emission from 1 × 10^{-4} M perylene in ether.

Chandross suggested, appeared likely to be the singlet excited state of the fluorescer.

An adequate description of the over-all mechanism of the oxalyl chloride–hydrogen peroxide–fluorescent compound system requires answering fundamental questions dealing with (1) the mechanisms of the chemical process involved, (2) the identity of the key reaction step where chemical energy is converted to electronic excitation energy, and (3) the mechanism of the process by which the excitation energy appears as the singlet excited state of the emitter. The present paper deals primarily with the first two of these questions, which must be answered to permit access to the energy conversion mechanism.

Results

The Emitting Species. Chemiluminescence spectra were determined for ethereal oxalyl chloride–hydrogen peroxide reactions containing the fluorescers 9,10-diphenylanthracene (DPA) and perylene, and were compared with the fluorescence spectra of these fluorescers, determined under comparable conditions. As seen in Figures 1 and 2, good correspondence was obtained for the chemiluminescence and fluorescence spectral distributions for the two fluorescers, demonstrating that the singlet excited state[12] of the fluorescent additive is formed in the reaction and is the emitting species.

A number of oxalyl chloride–hydrogen peroxide experiments were carried out in ether or benzene solutions in the absence of any fluorescent additive. Under these conditions a very weak chemiluminescent emission was only occasionally seen. Since this very weak emission was not reproducible under the conditions studied, it may result from a trace fluorescent impurity. Indeed the reaction is a remarkably sensitive detector of fluorescent materials; concentrations of DPA below 10^{-6} M produce easily visible emission.

No indication of ultraviolet emission was observed from reactions without added fluorescer using an ultraviolet-sensitive photomultiplier tube. Moreover, DPA emission was not seen when an oxalyl chloride–hydrogen peroxide reaction in ether was separated from ethereal DPA solution by a thin quartz plate. Radiative energy transfer[13] was thus shown to be absent in the system.

The fate of DPA (6.7 × 10^{-5} M) in a reaction with 1.5 × 10^{-2} M oxalyl chloride and 2.0 × 10^{-1} M hydrogen peroxide in ether containing 1.2 × 10^{-2} M water was determined by ultraviolet absorption analysis of its concentration before and after reaction. Within a probable error of 1%, the DPA concentration was found to be unchanged. The radiation output from the reaction was found to be 2.1 × 10^{-5} einsteins l.^{-1} and since less than 6.7 × 10^{-7} mole l.^{-1} of DPA was consumed, it is clear that light emission does not require fluorescer consumption. Related experiments, summarized in Table XIII, confirm this result but show that DPA consumption can occur as a side reaction under other conditions.

To examine the possibility that ground-state complexes of the fluorescer with either oxalyl chloride or hydrogen peroxide were involved in the chemiluminescent process, the visible absorption spectrum of rubrene in ether was compared with the absorption spectra of a similar solution containing 2 × 10^{-1} M oxalyl chloride or 1 M hydrogen peroxide. The three spectra were superimposable, and no evidence of such complexes was seen.

Since the over-all chemiluminescence quantum yield is dependent on the emission efficiency of the fluorescer, the effects of oxalyl chloride and hydrogen peroxide on the fluorescence quantum yields of DPA, perylene, and rubrene were determined. The results summarized in Table I show that oxalyl chloride is a powerful fluorescence quencher. (It is also shown in Table I that oxalyl chloride was rapidly photolyzed[14] by the ultraviolet exciting light so that the quenching decreased with the irradiation time.) To minimize the effect of oxalyl chloride quenching in subsequent quantitative chemiluminescence experiments, oxalyl chloride concentrations below 2 × 10^{-2} M were used with a large excess of hydrogen peroxide. It was shown (see below) that in ether solutions, oxalyl chloride is essentially consumed prior to the bulk of light emission under these

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(14) K. B. Krauskopf and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 443 (1936).

Table I. Fluorescence Quenching by Oxalyl Chloride in Ether[a]

Fluorescer (concn, M)	$OxCl_2$ concn, M	Wavelength, mμ	Initial emission intensity (arbitrary units)	Intensity after addition of $OxCl_2$	Time required to reach final intensity	Final emission intensity (arbitrary units)
9,10-Diphenylanthracene (0.7×10^{-4})	6×10^{-3}	430	74	18.0	5 min	74
Perylene (1.0×10^{-4})	3×10^{-3}	465	70	53	<30 sec	70
Rubrene (9×10^{-4})	2×10^{-3}	550	47.0	37.6	2 sec	46.5
Rubrene (9×10^{-4})	1×10^{-2}	550	40.0	19.2	1 hr	36.0

[a] H_2O_2 up to 1 M had no effect on the emission intensity of either rubrene, DPA, or perylene.

Table II. Gaseous Products from Oxalyl Peroxide Decomposition Reactions

Oxalyl chloride, mmoles	Hydrogen peroxide, mmoles	Solvent	Soln vol, ml	Conversions based on oxalyl chloride,[a] % — Mass spectrum				Conversions based on oxalyl chloride,[a] % — Vpc	
				CO[a]	CO_2[a]	O_2[b]	$COCl_2$[a]	CO[a]	O_2[b]
4.93	4.90	Ether	15	38.2	47.0	1.8	0	...	...
5.00[c]	5.00	Ether	15	46.5	46.8	7.0	0	...	...
10.00	10.00	Ether	20	35.2	41.7	0	0	...	0
5.35	4.90	DMP	15	25.0	71.2	0.13	11.8	...	...
5.35	9.80	DMP	20	30.7	69.3	0.05	12.9	...	...
9.36	7.66	DMP	20	29.7	73.0	0.68	7.2	...	...
9.36	15.43	DMP	20	26.0	71.6	2.2	13.7	...	...
10.00	10.00	DMP	15	31.6	64.4	0.78	9.1	28.8	0
10.00	50.00	DMP	35	29.0	59.8	0.60	12.4	25.7	0.24
Phosgene[d]	Hydrogen peroxide	Benzene	10	0	42.8[d]	5.2[d]	1.61[d]	0.06[d]	5.6[d]
9.98	10.00	DMP	5						

[a] Per cent conversion of oxalate carbon. [b] Millimoles of oxygen per millimole of initial oxalyl chloride times 100. [c] This reaction was allowed to age 36 min following the end of light emission before sampling the evolved gases. All other experiments were sampled within 2 min after chemiluminescence had ceased. [d] Relative yields. Absolute yields were not determined.

conditions and does not appreciably influence the emission process. No fluorescence quenching by 1 M hydrogen peroxide was observed for the three fluorescers.

The possibility that 9,10-diphenylanthracene peroxide, a known chemiluminescent material,[15] might be involved in the chemiluminescent reaction was eliminated by showing that the peroxide does not provide chemiluminescent emission when added to oxalyl chloride–hydrogen peroxide reactions.

The Reaction Products. The stoichiometry of the reaction was determined by titration of standard oxalyl chloride solutions in ether with standardized ethereal hydrogen peroxide solution in the presence of DPA, using the disappearance of chemiluminescence to indicate the end point. Both titration of oxalyl chloride with hydrogen peroxide and the reverse titration indicated a stoichiometry of almost 1:1. However, in most chemiluminescence experiments (see below) where hydrogen peroxide was used in large excess, the stoichiometry would be expected to be closer to 2:1 hydrogen peroxide/oxalyl chloride.

Yields of gaseous products from reactions of oxalyl chloride with hydrogen peroxide in the presence of DPA under varying conditions were estimated by measuring the volume, pressure, and temperature of gas generated in a closed system, and analyzing the composition of the gas by mass spectrometry. The results are summarized in Table II. Reasonable account (generally within ±10%) of the oxalyl chloride carbon was obtained as carbon monoxide, carbon dioxide, and (in dimethyl phthalate experiments) as phosgene. Ratios of CO and CO_2 were somewhat variable even within a set of experimental conditions, but higher CO_2:CO ratios were found in dimethyl phthalate than in ether.

Phosgene was found in dimethyl phthalate experiments but not in experiments carried out in ether. Evidently the rapid gas evolution in these experiments is able to remove phosgene from the liquid phase in spite of its reactivity toward hydrogen peroxide. It is likely, however, that a portion of the higher CO_2 yield found under these conditions results from a phosgene–hydrogen peroxide reaction. Phosgene reacts with hydrogen peroxide to give CO_2 exclusive of CO as indicated in Table II. The phosgene–hydrogen peroxide–fluorescer reaction is not appreciably chemiluminescent.

Only insignificant amounts of oxygen were found in the experiments. Removal of liberated oxygen by autoxidation might occur in ether, but would not be expected in dimethyl phthalate.[16] Therefore, we conclude that oxygen is not a product of the chemiluminescent reaction.

Infrared Spectroscopic Examination of Oxalyl Chloride–Hydrogen Peroxide Reactions. Several reactions in ether solution were analyzed spectrophotometrically for the rate of O=CCl disappearance and for the rate of total carbonyl disappearance using absorption bands at 750 and 1790 cm^{-1}, respectively. Results obtained with oxalyl chloride and hydrogen peroxide concentrations of 7.50×10^{-2} M are indicated in Figure 3. It was found that the rate of O=CCl disappearance is

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[15] C. Dufraisse, L. Velluz, and L. Velluz, *Compt. Rend.*, **209**, 516 (1939).

[16] M. W. Rigg and H. Gisser, *J. Am. Chem. Soc.*, **75**, 1415 (1953).

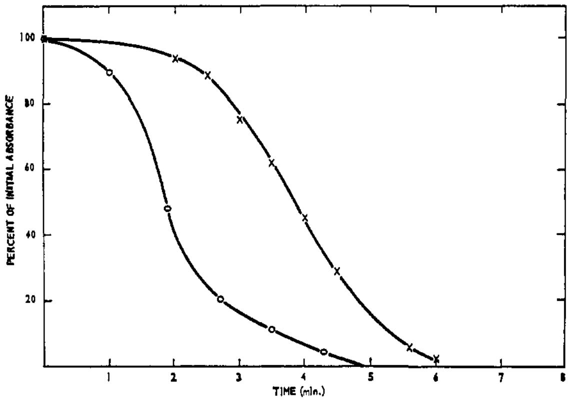

Figure 3. Disappearence of chlorocarbonyl and total carbonyl absorption bands in the reaction of 0.075 *M* oxalyl chloride with 0.075 *M* hydrogen peroxide in ether at 25°: o, absorbance at 750 cm^{-1} (COCl); ×, absorbance at 1790 cm^{-1} (COCO).

substantially more rapid than the rate of total carbonyl disappearance. Thus, while only 20% of the initial O═CCl absorption remains after 2.7 min, 89% of the initial carbonyl absorption remains. Similar results were obtained in a second experiment where the concentrations were 5.0×10^{-2} *M* oxalyl chloride and 1.0×10^{-1} *M* hydrogen peroxide. It is clear from the results that oxalyl chloride disappears from the system far more rapidly than the over-all reaction rate and that a carbonyl-containing intermediate is formed.

Effect of Oxalyl Chloride Concentration on Quantum Yield and Reaction Rate. Absolute quantum yields based on starting oxalyl chloride were determined as a function of oxalyl chloride concentration over a 40-fold concentration range in experiments with constant hydrogen peroxide, water, and DPA concentrations in ether solution. The results are summarized in Table III. While there is some scatter in the values obtained, it is evident that the quantum yield is essentially constant over the range studied. Since oxalyl chloride is a powerful quencher of DPA emission, the quantum yield would necessarily decrease with increasing oxalyl chloride concentration if oxalyl chloride remained during the emission process. This result thus indicates that oxalyl chloride is essentially consumed prior to the bulk of light emission under these conditions. At oxalyl chloride concentrations above 2×10^{-2} *M*, however, an apparent induction period appeared in the emission process, and quantum yields were seriously reduced. These results suggest the presence of oxalyl chloride during the early part of the emission at high oxalyl chloride concentrations.

The experiments in Table III were carried out with a large excess of hydrogen peroxide relative to oxalyl chloride. Under these conditions, only an intermediate derived from oxalyl chloride would be expected to change significantly in concentration during a run, and pseudo-first-order kinetics should result. This pseudo-first-order kinetic design permits the first-order rate eq I to be used in the form of eq II provided only that the intensity of emission (*I*) is directly proportional to the concentration of a chemiluminescent intermediate [A] derived from oxalyl chloride.[17] That this latter condition is met under the conditions studied is shown by the constancy of quantum yield with changing oxalyl chloride concentration. Plots of log

$$\ln \frac{[A]^0}{[A]} = k'T \qquad \text{(I)}$$

$$\ln \frac{I^0}{I} = k'T \qquad \text{(II)}$$

I vs. time were, in fact, linear up to at least 90% reaction at oxalyl chloride concentrations of 2×10^{-2} and below.

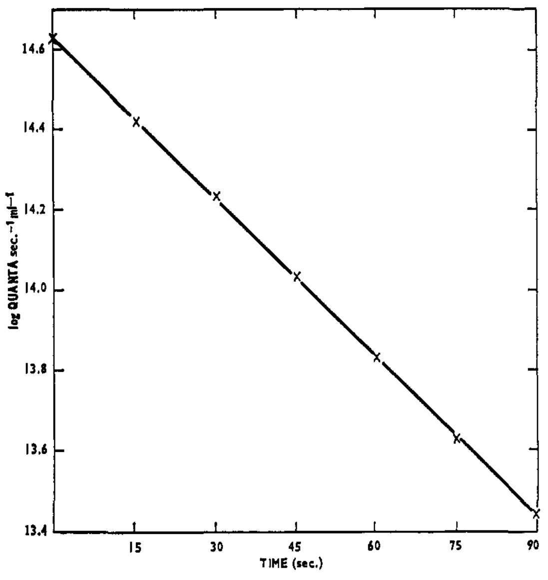

Figure 4. First-order plot of spectrally integrated intensity decay from reaction of 5.0×10^{-3} *M* oxalyl chloride, 0.10 *M* hydrogen peroxide, ~0.028 *M* water, and 1.5×10^{-3} *M* 9,10-diphenylanthracene in ether at 25°.

Table III. Variation of Reaction Rate and Chemiluminescence Quantum Yield with Oxalyl Chloride Concentration in Ether[a]

Oxalyl chloride concn, moles/l. $\times 10^3$	Pseudo-first-order rate constant, $sec^{-1} \times 10^2$	Chemiluminescence quantum yield,[b] $\times 10^2$ einstein $mole^{-1}$
0.5	3.48[c]	0.60[c]
1.0	3.49 ± 0.03	0.51 ± 0.02
2.0	3.24 ± 0.00	0.49 ± 0.01
5.0	3.05 ± 0.01	0.49 ± 0.03
10.0	2.40 ± 0.10	0.42 ± 0.00
20.0	1.59 ± 0.05[d]	0.59 ± 0.01

[a] Experiments with 1.0×10^{-1} *M* H_2O_2, ~2.8 × 10^{-2} *M* H_2O, and 1.5×10^{-3} *M* DPA at 25°. Results are the average of two experiments, except where noted. [b] Based on oxalyl chloride. [c] Single experiment. [d] A small "induction period" was noted in the first-order luminescence decay plot (see text).

Data from a typical experiment is summarized in Table IV and a typical plot is shown in Figure 4.

The pseudo-first-order rate constants summarized in Table III decrease moderately with increasing oxalyl chloride concentration. It is shown in the following section that the reaction rate is also dependent on the water concentration. The decreasing rate constants are probably a consequence of water consumption by oxalyl chloride in a minor side reaction.

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(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 28.

Table IV. Typical Experimental Data for Oxalyl Chloride + Hydrogen Peroxide + DPA Reaction in Ether[a]

Time, sec	Intensity,[b] quanta sec^{-1} ml^{-1} $\times 10^{-13}$	k^1, sec^{-1} $\times 10^2$
(0)	42.8[c]	...
15	26.8	3.12
30	17.3	3.02
45	10.8	3.06
60	6.8	3.07
75	4.3	3.06
90	2.8	3.03
105	1.9	2.98

[a] Initial concentrations: oxalyl chloride, 5.0×10^{-3} *M;* H_2O_2, 1.0×10^{-1} *M;* DPA, 1.5×10^{-3} *M;* H_2O, $\backsim 2.8 \times 10^{-2}$ *M;* temperature 25°. [b] Measured at 430 mμ and converted to total quanta sec^{-1} ml^{-1} by multiplication by instrument calibration and unit spectral area factors. [c] Extrapolated value.

Table V. Effect of Water on Oxalyl Chloride–Hydrogen Peroxide Chemiluminescence in Ether Solutions[a]

$[H_2O]$ $\times 10^2$ *M*	Initial intensity, quanta sec^{-1} ml^{-1} $\times 10^{-12}$	K^1, sec^{-1} $\times 10^2$	Quantum yield $\times 10^4$
<0.4[b]	0.80	1.93(1.13[d])[c]	0.41 (0.14)[d]
2.46	8.4	3.53	1.59
3.69	16.6	4.75	2.33
4.92	29.3	6.82 (6.58[d])	2.85 (2.65)[d]
6.15	46.6	9.04	3.43
7.38	67.2	12.50	3.57

[a] The reactions were carried out with 2.54×10^{-3} *M* oxalyl chloride, 2.13×10^{-2} *M* H_2O_2, and 2.3×10^{-4} *M* DPA, at 25° where the amount of water specified was added prior to injection of oxalyl chloride. [b] Lower limit of analysis by Karl Fischer method. [c] Log *I vs. T* plot was linear only after 30 sec of reaction. Earlier intensities were below the extrapolated linear plots. [d] Result from separately dried ether.

Table VI. Effect of Water on Quantum Yield and Reaction Rate in Dimethyl Phthalate Solution[a]

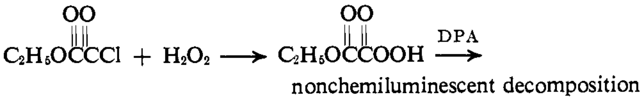
$[H_2O]$, moles $l.^{-1}$ $\times 10^2$	Time of water addition, sec	Time to reach maximum intensity, sec	Time to decay to 1/2 intensity, sec	Maximum intensity, quanta sec^{-1} ml^{-1} $\times 10^{-14}$	Quantum yield, einsteins $mole^{-1}$ $\times 10^2$
0.67[b]	...	15	56	8.6	4.69
1.18	0	12	45	10.1	4.64
3.21	0	10	26	12.9	3.91
4.22	0	8	26	14.5	3.97
4.22	30	...	...	...	4.10[c]
4.22	60	...	...	...	4.47[c]

[a] Reactant concentrations were: oxalyl chloride, 2.42×10^{-3} *M;* H_2O_2, 0.15 *M;* DPA, 1×10^{-3} *M;* temperature, 25°. [b] Water concentration in solvent. [c] Quantum yields were calculated by multiplying the measured quanta after 30 or 60 sec by the corresponding ratio obtained from the first experiment (total quanta/quanta after 30 sec).

The Effect of Water on Quantum Yield and Reaction Rate. Results from a series of experiments in ether solution where the initial water concentration was varied under otherwise constant homogeneous conditions are summarized in Table V. Both the initial intensity and the rate of intensity decay with time increased substantially with increasing water concentration. The intensity increase more than compensated for the lifetime decrease so that the quantum yield also increased with increasing water up to a concentration of about 6.15×10^{-2} *M.* Excellent linear log intensity *vs.* time plots were obtained for all experiments except at the lowest water concentration where water was not in substantial excess relative to oxalyl chloride.

Results showing the effect of water on reactions in dimethyl phthalate solutions are summarized in Table VI. As in the ether experiments, the initial intensity and the rate of intensity decay increased with increasing water concentration. Linear pseudo-first-order plots were not obtained until a substantial excess of water was present. It is clear, however, from the times required to reach one-half intensity, that the reaction is appreciably less rapid in dimethyl phthalate than in ether. Moreover, quantum yields in dimethyl phthalate are substantially higher than in ether. As indicated in Table VI, added water reduced the time required for the intensity to reach the maximum value. In spite of the increase in maximum intensity with increasing water, the quantum yield decreased somewhat as a consequence of the shorter lifetime. When water addition was delayed 30 sec, the quantum yield of the aqueous portion of the reaction increased only slightly from the quantum yield of the corresponding experiment with water present initially. A 60-sec delay in water addition, however, increased the quantum yield significantly.

The Effect of Ethanol on Quantum Yield and Reaction Rate. As indicated in Table VII, added ethanol increases the reaction rate of experiments in ether solution, but decreases the intensity and quantum yield. Ethanol would be expected to compete with water in reactions leading to chemiluminescence; the decrease in quantum yield suggests that in contrast to water, ethanol-derived intermediates do not lead to chemiluminescence. This is consistent with the observation that the reaction of ethyl oxalyl chloride with hydrogen peroxide in the presence of DPA does not provide chemiluminescence.[18]



$$C_2H_5O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl + H_2O_2 \longrightarrow C_2H_5O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH \xrightarrow{DPA}$$

nonchemiluminescent decomposition

The Effect of Hydrogen Peroxide on Quantum Yield and Reaction Rate. Reaction rate and quantum yield results from experiments where the hydrogen peroxide concentration was varied independently of oxalyl chloride, water, and DPA are summarized in Table

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[18] M. M. Rauhut, D. Sheehan, R. A. Clarke, and A. M. Semsel, *Photochem. Photobiol.*, 4, 1097 (1965).

Table VII. The Effect of Ethanol on the Reaction Rate and Chemiluminescence Quantum Yield for the Oxalyl Chloride-Hydrogen Peroxide-Fluorescer Reaction in Ether Solution[a]

Ethyl alcohol, moles l.$^{-1}$ × 10^2	Initial intensity, quanta sec^{-1} ml^{-1} × 10^{-12}	k^1, sec^{-1} × 10^2	Chemiluminescence yield, einsteins mole^{-1} × 10^4
None	9.5	2.11	3.18
3.3	9.0	2.81	2.30
5.0	7.9	3.04	1.85
6.67	7.5	3.36	1.60

[a] Reactant concentrations were: oxalyl chloride, 2.35 × 10^{-3} *M*; H_2O_2, 8.2 × 10^{-2} *M*; DPA, 7.5 × 10^{-5} *M*; temperature, 25°. [b] Based on oxalyl chloride concentration.

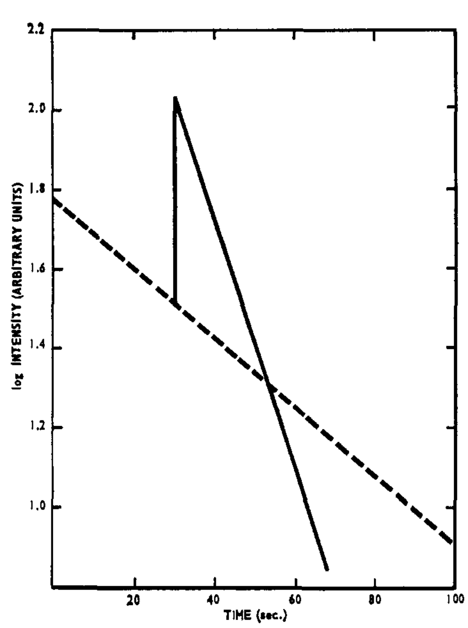

Figure 5. Effect of water injection on first-order intensity decay in the reaction of 2.42 × 10^{-3} *M* oxalyl chloride, 0.10 *M* H_2O_2, and 2.0 × 10^{-4} *M* DPA in ether at 25°: - - -, [H_2O] = ~0.01 *M*; —— water injected to give a total concentration of 0.044 *M*.

VIII. It is evident that the quantum yield increased approximately linearly with the hydrogen peroxide concentration in the range studied, but that the reaction rate was essentially independent of hydrogen peroxide concentration. Thus, in contrast to water, hydrogen peroxide is evidently not involved in a rate-determining step, but like water, is required for steps leading to chemiluminescence. Hydrogen peroxide was varied in a second series of experiments where a constant water concentration was introduced 30 sec following the onset of reaction (Table IX). This procedure was adopted to minimize direct reaction of water with oxalyl chloride. The marked effect of water injection is shown in Figure 5. Since, under the conditions used, water injection followed completion of 45 to 41% of the "standard" chemiluminescent reaction, the fraction (F_W) of active intermediate remaining for reaction in the presence of water varied from 55 to 59% as indicated in Table IX. The true quantum yield (Q_W^T) for the hypothetical system where direct reaction between oxalyl chloride and water is absent was estimated by dividing the fractional quantum yield observed after water addition (Q_W^F) by F_W. Substantially higher quantum yields were obtained when water addition was delayed than when the same amount of water was present initially. In agreement with the previous series, the hydrogen peroxide concentration has at most a minor effect on the reaction rate, and the quantum yield increases substantially as the hydrogen peroxide concentration increases. A comparison of the pseudo-first-order rate constants k^1 and Q_W^T values in Table IX with the quantum yield and rate values for the low water system in Table VIII reemphasizes the effect of water on the reaction rate and quantum yield. However, it is clear from the ratios of Q_W^T/Q^T that the influence of added water on the quantum yield decreases at higher hydrogen peroxide concentrations.

Table VIII. Effect of Hydrogen Peroxide Concentration on Oxalyl Chloride-Hydrogen Peroxide Chemiluminescence[a]

[H_2O_2] × 10^2 *M*	k^1, sec^{-1} × 10^{2b}	Quantum yield × 10^4
1.0	1.8	0.85
2.0	1.8	1.5
5.0	1.9	4.3
10.0	2.1	8.6

[a] Reactions were carried out with 2.42 × 10^{-3} *M* oxalyl chloride, and 2.0 × 10^{-4} *M* DPA in alumina-dried ether at 25°. The water concentration was approximately 1 × 10^{-2} *M*. [b] Pseudo-first-order plots were linear after 15 sec. Earlier points fell somewhat below the extrapolated line.

Table IX. Effect of Hydrogen Peroxide on Reaction Rate and Quantum Yield in Systems Containing Added Water[a]

[H_2O_2] × 10^2 *M*	k^1, sec^{-1} × 10^2	Q^F × 10^4	Q_W^F × 10^4	F_W	Q_W^T × 10^4	Q_W^T/Q^T
1.0	6.4	0.35	2.6	0.59	4.4	5.1
2.0	6.5	0.66	4.6	0.59	7.8	5.2
5.0	6.7	1.8	10.0	0.55	18	4.2
5.0[b]	7.5	...	...	...	6.6	1.5
10.0	7.6	4.0	13.2	0.55	24	2.8

[a] Reactions were carried out with 2.42 × 10^{-3} *M* oxalyl chloride and 2.0 × 10^{-4} *M* DPA in ether containing ~1.0 × 10^{-2} *M* water at 25°. After 30 sec of reaction an amount of water equivalent to a concentration of 3.44 × 10^{-2} *M* was injected to provide a total water concentration of 4.4 × 10^{-2} *M*. Q^F = the fractional quantum yield observed before water injection; Q_W^F = the fractional quantum yield observed after water injection; F_W = the fraction of total reaction measured after water injection; Q_W^T = the calculated total quantum yield for the reaction in the presence of water ($Q_W^T = Q_W^F/F_W$); Q^T = the total quantum yield in the absence of added water (F_W and Q^T from data in Table VIII). [b] Water was added *before* oxalyl chloride injection to provide *a total water* concentration of 4.4 × 10^{-2} *M*.

The Effect of DPA Concentration on Quantum Yield and Reaction Rate. The results of several series of experiments where DPA was varied under conditions where the initial oxalyl chloride, hydrogen peroxide, and water concentrations were held constant are summarized in Table X. It is clear that at each of the five hydrogen peroxide and water concentrations studied, the quantum yield increases with increasing DPA, with the effect becoming smaller at high DPA concentrations. Plots of quantum yield *vs.* DPA concentration are thus nonlinear (except at low concentrations). (Plots of 1/quantum yield *vs.* 1/(fluorescer) are linear as discussed in a later section.) While

Table X. Variation of Reaction Rate and Chemiluminescence Quantum Yield with Hydrogen Peroxide [H_2O_2] and 9,10-Diphenylanthracene [DPA] Concentrations in Ether Solutions[a]

	[H_2O_2], 1×10^{-2} *M* [H_2O], $\sim 1 \times 10^{-2}$ *M*		[H_2O_2], 2×10^{-2} *M* [H_2O], 1.2×10^{-2} *M*		[H_2O_2], 5×10^{-2} *M* [H_2O], $\sim 1.7 \times 10^{-2}$ *M*		[H_2O_2], 1×10^{-1} *M* [H_2O], $\sim 2.7 \times 10^{-2}$ *M*		[H_2O_2], 2×10^{-1} *M* [H_2O], $\sim 4.6 \times 10^{-2}$ *M*	
[DPA] $\times 10^4$ *M*	$K^1 \times 10^2$ sec^{-1}[b]	$QY \times 10^3$[c]	$K^1 \times 10^2$ sec^{-1}[b]	$QY \times 10^3$[c]	$K^1 \times 10^2$ sec^{-1}[b]	$QY \times 10^3$[c]	$K^1 \times 10^2$ sec^{-1}[b]	$QY \times 10^3$[c]	$K^1 \times 10^2$ sec^{-1}[b]	$QY \times 10^3$[c]
0.33	1.88	0.018	1.78	0.041	2.09	0.135	3.07	0.260	6.13	0.53
0.67	1.42	0.034	1.58	0.072	2.08	0.256	3.44	0.500	7.61	1.00
1.33	1.53	0.047	1.48	0.123	1.84	0.470	3.10	0.924	7.36	1.65
3.30	1.82	0.163	1.78	0.389	2.10	1.09	2.97	2.26	5.97	4.17
5.00	1.64	0.174	1.70	0.478	1.98	1.40	3.48	3.32	7.78	6.35
6.00	1.62	0.28	1.99	0.53	2.08	2.00	3.04	4.14	5.92	7.50
7.68	1.43	0.37	1.55	0.88	1.98	2.38	2.79	5.27	5.47	9.81
10.00[d]	1.51	0.37	1.48	0.74	2.00	3.09	3.52	6.09	7.76	11.1

[a] Reactions were run with 2.35×10^{-3} *M* oxalyl chloride in ether at 25°. [b] K^1 = pseudo-first-order rate constant. [c] QY = quantum yield of chemiluminescence based on oxalyl chloride. [d] DPA self-absorption occurs at this concentration; quantum yields are uncorrected.

Table XI. Effect of 2,6-Di-*t*-butyl-4-methylphenol (DTBMP) on Quantum Yield and Reaction Rate in Dimethyl Phthalate (DMP) and Ether Solution[a]

[DTBMP], mole l.$^{-1}$	Solvent	Maximum intensity,[b] quanta sec^{-1} ml^{-1} $\times 10^{-13}$	First half-life, sec	Quantum yield[c] $\times 10^3$	QY (inhibited)/QY (uninhibited)
0	DMP	48.6	87	41	...
0.67×10^{-3}	DMP	36.6	95	38	0.98
2.00×10^{-3}	DMP	25.2	84	23	0.59
10.0×10^{-3}	DMP	7.2	85	6.5	0.17
15.0×10^{-3}	DMP	6.1	73	4.8	0.12
15.0×10^{-3}[d]	DMP	...	..	4.7	0.12
0	Ether	1.3	24[e]	0.35	...
30×10^{-3}	Ether	0.59	25[e]	0.12	0.34
30×10^{-3}[d]	Ether	...	25[e]	0.14	0.40

[a] Initial concentrations for DMP experiments: oxalyl chloride, 2.42×10^{-3} *M;* H_2O_2, 0.20 *M;* DPA, 5.0×10^{-4} *M.* Initial concentrations for ether experiments: oxalyl chloride, 2.18×10^{-3} *M*; H_2O_2, 0.14 *M;* DPA, 2.3×10^{-4}; temperature, 25°. [b] Measured at 430 mμ and corrected to total quanta. [c] Based on oxalyl chloride. [d] DTBMP added 30 sec after reaction start; quantum yield calculated for inhibited portion of the reaction. [e] Linear log intensity *vs.* time plots.

Table XII. Effect of Hydrogen Peroxide Concentration on Quantum Yields and Reaction Rates of Inhibited Reactions in Ether[a]

	A, uninhibited reaction		B, DTBMP inhibitor[b]		C, styrene inhibitor[c]		Quantum yield ratios	
[H_2O_2], moles l.$^{-1}$	k^1, sec^{-1} $\times 10^2$	$QY \times 10^4$	k^1, sec^{-1} $\times 10^2$	$QY \times 10^4$	k^1, sec^{-1} $\times 10^2$	$QY \times 10^4$	B/A	C/A
1×10^{-2}	3.34	1.36	3.29	0.48	3.88	0.59	0.35	0.43
5×10^{-2}	3.57	5.87	3.46	2.17	4.46	3.24	0.37	0.55
10×10^{-2}	3.84	10.5	3.72	4.1	4.38	5.14	0.39	0.49
20×10^{-2}	4.92	19.1	4.81	7.3	5.28	9.5	0.38	0.50

[a] Initial concentrations: oxalyl chloride, 2.33×10^{-3} *M;* DPA, 5.0×10^{-4} *M;* water, 2.8×10^{-2} *M* at 25°. [b] DTBMP concentration, 3×10^{-2} *M.* [c] Styrene concentration, 4×10^{-1} *M.*

there is some scatter in the tabulated pseudo-first-order rate constants, the absence of any trend with changing DPA concentration indicates that DPA is not involved in a rate-determining step.

The Effect of 2,6-Di-*t*-butyl-4-methylphenol (DTBMP) and Styrene on Quantum Yield and Reaction Rate. Results of adding the free-radical inhibitors DTBMP[19,20] and styrene[21-23] to oxalyl chloride–hydrogen peroxide–DPA reactions under a variety of conditions are summarized in Tables XI and XII. The results in Table XI indicate that DTBMP seriously reduces quantum yields in both dimethyl phthalate and ether solutions, but has little effect on reaction rates. The reduction in quantum yield is not a consequence of fluorescence quenching of DPA emission, since the fluorescence quantum yield of 4.6×10^{-4} *M* DPA in deoxygenated ether (0.82) was unchanged by the presence of 0.015 *M* DTBMP. Moreover, the fluorescence quantum yield (0.84) of DPA (6×10^{-4} *M*) was unchanged following a reaction of 2.5×10^{-3} *M* oxalyl chloride with 0.1 *M* hydrogen peroxide in the presence of 0.015 *M* DTBMP. The absence of an appreciable effect on the reaction rate indicates that, in contrast to ethanol, DTBMP does not reduce the quantum yield by competing with water in a rate-determining step. Moreover, in contrast to water, delayed addition of DTBMP produced the same decrease in quantum yield as DTBMP present at the reaction start. The possibility of a direct, nonradical reaction between DTBMP and peroxy acids or hydrogen peroxide was examined by ultraviolet spectroscopic analysis of a mixture of DTBMP (0.03 *M*), peroxy-4-nitrobenzoic acid (0.005 *M*), and hydrogen peroxide (0.1 *M*) in ether. The spectrum represented a linear combination of the spectra of the separate components and remained unchanged during 15 min, indicating the absence of appreciable reaction.

Results showing the effects of DTBMP and styrene at varying hydrogen peroxide concentrations are sum-

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marized in Table XII. It is seen that the ratio of inhibited to uninhibited quantum yields is not a function of hydrogen peroxide concentration, and that styrene is a less effective inhibitor than DTBMP.

Discussion

The mechanism of the processes involving oxalyl chloride and hydrogen peroxide and the process leading to chemiluminescence must be consistent with the following observations.

(A) Disappearance of acyl chloride constituents from oxalyl chloride–hydrogen peroxide reaction mixtures in ether is fast relative to the disappearance of total carbonyl constituents and to the rate of intensity decay as indicated by infrared analysis.

(B) The reaction rate is first order with respect to a derivative of oxalyl chloride under pseudo-first-order conditions in ether.

(C) The reaction rate increases with increasing water, even when water addition is delayed.

(D) The reaction rate increases with increasing ethanol.

(E) The reaction rate is independent of the hydrogen peroxide concentration.

(F) The reaction rate is independent of the fluorescer concentration.

(G) The reaction rate is independent of 2,6-di-*t*-butyl-4-methylphenol [DTBMP] and styrene concentrations.

(H) The intensity increases with increasing water in both ether and in dimethyl phthalate solutions showing that water is involved in a step leading to chemiluminescence.

(I) The quantum yield increases with increasing water at low water levels in ether, but decreases somewhat in dimethyl phthalate solution.

(J) The quantum yield is substantially higher when water addition is delayed than when water is present initially, particularly at low hydrogen peroxide concentrations.

(K) The quantum yield increases with increasing hydrogen peroxide even at high hydrogen peroxide/water ratios.

(L) The quantum yield increases with increasing fluorescer concentration.

(M) The quantum yield is essentially independent of the initial oxalyl chloride concentration at high hydrogen peroxide–oxalyl chloride ratios in ether.

(N) The quantum yield decreases with increasing ethanol.

(O) The quantum yield decreases with increasing DTBMP or styrene, even when inhibitor addition is delayed. The inhibition is independent of the peroxide concentration.

(P) The quantum yield is substantially higher in dimethyl phthalate than in ether.

(Q) The singlet excited state of the fluorescer is the emitting species.

(R) Emission of excited DPA is strongly quenched by oxalyl chloride.

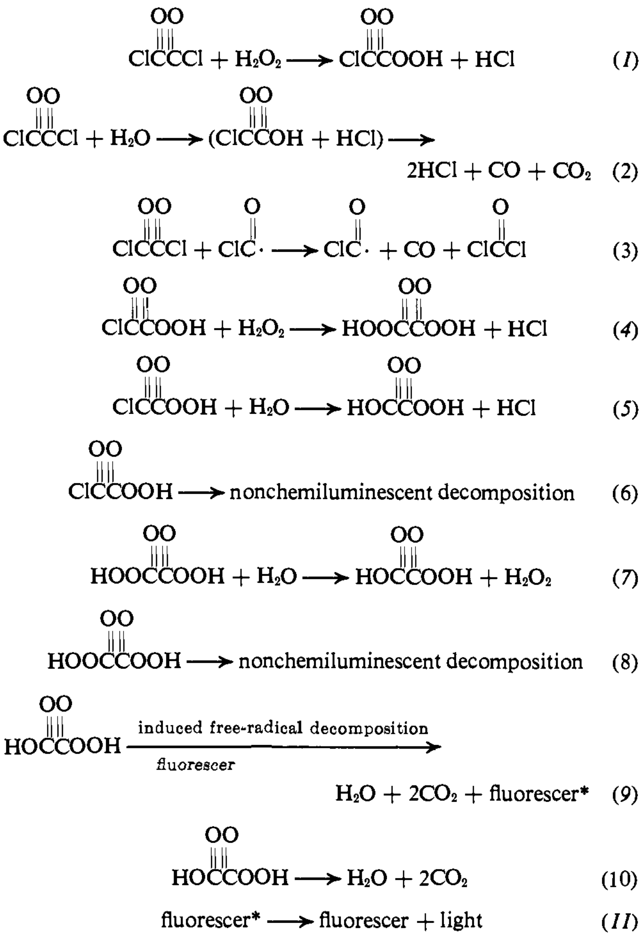
(S) Emission of excited DPA is not quenched by DTBMP.

(T) The major reaction products are hydrochloric acid, carbon monoxide, and carbon dioxide. Oxygen was not found in significant amounts.

(U) Phosgene is a product in dimethyl phthalate solution at high oxalyl chloride concentrations when the ratio of hydrogen peroxide to oxalyl chloride is low.

A paritial mechanism for the over-all process in accord with the above observations is suggested in Chart I. The proposed steps leading to chemiluminescence are in italic to distinguish them from nonluminescent side reactions. The mechanism is not a complete description of the process since the evidence at hand does not permit a detailed analysis of steps 6, 8, 9, and 10, although all of the steps have close analogies.

Chart I. Proposed Partial Mechanism



$$\mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} + \mathrm{H_2O_2} \longrightarrow \mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{HCl} \qquad (\mathit{1})$$

$$\mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} + \mathrm{H_2O} \longrightarrow (\mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} + \mathrm{HCl}) \longrightarrow 2\mathrm{HCl} + \mathrm{CO} + \mathrm{CO_2} \qquad (2)$$

$$\mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} + \mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot \longrightarrow \mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot + \mathrm{CO} + \mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} \qquad (3)$$

$$\mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{H_2O_2} \longrightarrow \mathrm{HOO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{HCl} \qquad (\mathit{4})$$

$$\mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{H_2O} \longrightarrow \mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{HCl} \qquad (\mathit{5})$$

$$\mathrm{Cl}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} \longrightarrow \text{nonchemiluminescent decomposition} \qquad (6)$$

$$\mathrm{HOO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{H_2O} \longrightarrow \mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{H_2O_2} \qquad (\mathit{7})$$

$$\mathrm{HOO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} \longrightarrow \text{nonchemiluminescent decomposition} \qquad (8)$$

$$\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} \xrightarrow[\text{fluorescer}]{\text{induced free-radical decomposition}} \mathrm{H_2O} + 2\mathrm{CO_2} + \text{fluorescer*} \qquad (\mathit{9})$$

$$\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} \longrightarrow \mathrm{H_2O} + 2\mathrm{CO_2} \qquad (10)$$

$$\text{fluorescer*} \longrightarrow \text{fluorescer} + \text{light} \qquad (\mathit{11})$$

Steps 1–6 involve reactions of acyl chlorides and in ether solution are evidently complete prior to the bulk of light emission as indicated by the separate observations A, M, B, E, and J. Thus, observation A indicates by direct observation that acid chloride disappears from the chemiluminescent system more rapidly than a carbonyl-containing intermediate and more rapidly than light decay; observations M and B indicate the absence of fluorescence quenching of DPA by oxalyl chloride in the chemiluminescent experiments although fluorescence quenching would occur if oxalyl chloride were present (R); observation E indicates that reactions of hydrogen peroxide are not rate determining, and since reactions involving hydrogen peroxide would be expected in the early steps, such reactions must be essentially complete prior to light emission; and observation J indicates that direct reaction of water with oxalyl chloride is substantially reduced when water addition is delayed.

The less extensive results from experiments in dimethyl phthalate, where solvent absorption prevented spectroscopic determination of acid chloride disappearance, suggest that oxalyl chloride consumption is less rapid than in ether. Thus, linear first-order plots were not obtained until substantial excesses of water and hydrogen peroxide were present, the effect of delayed water addition on quantum yield was minor relative to the effect in ether, and the over-all reactions were substantially less rapid.

Step 2 (and the analogous step 5) seems required to account for the large increase in quantum yield produced by delayed water addition, relative to the small increase produced by water added initially (J). Thus, initially present water acting in nonchemiluminescent step 2 would act to lower the quantum yield. The reaction of oxalyl chloride with water has been reported to give carbon monoxide and carbon dioxide rapidly and quantitatively and attempts to trap the intermediate monoacid chloride with aniline have been reported to be unsuccessful.[24] Since hydrogen peroxide is substantially more reactive than water in nucleophilic reactions,[25] however, steps 1 and 4 should dominate steps 2 and 5 at high hydrogen peroxide/water ratios.

Step 3 is included to accommodate phosgene formation in dimethyl phthalate solution (U) and is in agreement with previously reported work.[14] This reaction would not be expected in ether solution where the primary chain carrier would be the radical $CH_3CH\text{-}OCH_2CH_2$,[19,21,22,26] although induced decomposition remains possible. At the high hydrogen peroxide/oxalyl chloride ratios used in the chemiluminescence experiments step 3 should have minor importance.

Competitive steps 4 and 6 appear required by the pronounced increase in quantum yield with increasing hydrogen peroxide concentration (observation K). This result is not accounted for by competitions between hydrogen peroxide and water in steps 1 and 2 or in steps 4 and 5 since the effect of hydrogen peroxide concentration on quantum yield remains large even at hydrogen peroxide/water ratios of 10:1 where steps 1 and 4 are already dominant.[25] Observation K thus suggests a separate nonluminescent reaction involving chloroperoxyoxalic acid but not involving hydrogen peroxide or water. A rapid spontaneous decomposition of chloroperoxyoxalic acid, as indicated in step 6, seems reasonable in view of the rapid decomposition of chlorooxalic acid[24] (step 2) and the general instability of peroxyoxalate derivatives[22,27,28] Thus, according to Chart I, increasing hydrogen peroxide favors step 4 over step 6 and increases the quantum yield. Step 6 probably involves a decomposition to the $Cl\dot{C}{=}O$ and $\cdot OH$ radicals along with CO_2. The $Cl\dot{C}{=}O$ radical (through hydrogen abstraction and reactions *via* (3)) is a likely source of the carbon monoxide observed at low hydrogen peroxide/oxalyl chloride ratios (observation T). Our failure to observe oxygen as a significant product would appear to rule out decomposition of chloroperoxyoxalic acid by a cyclic transition state involving direct HCl formation.[11]

The constancy of quantum yield with changing oxalyl chloride concentration (observation M) indicates that processes second order in oxalyl chloride or a derived intermediate are absent at low oxalyl chloride concentrations. Such a second-order process in competition with steps 1 through 6 would result in increased quantum yields with increasing oxalyl chloride if it led to light emission or decreased quantum yields if it did not.

Step 7 is evidently required to account for the marked effects of water on the system. Thus the increase in intensity with increasing water (observation H) demonstrates that water is involved in a step leading to chemiluminescence. But this cannot be step 5 alone, since the increase in intensity is even more pronounced when water is added after the bulk of acid chloride disappearance (observation J). Moreover, water is involved in a rate-determining step (observation C) and this cannot be a step such as (5) where hydrogen peroxide is in competition, because hydrogen peroxide is not involved in a rate-determining step (observation E). The increase in reaction rate produced by water cannot be accounted for in terms of increased solvent polarity, since hydrogen peroxide, while highly polar,[29] does not affect the rate (E). Moreover, the increase in rate with increasing ethanol (observation D) is consistent with a competition between ethanol and water for an intermediate involved in a rate-determining step, while the decrease in quantum yield produced by ethanol (observation N) shows that water is specifically required for chemiluminescence.

Finally, the assignment of diperoxyoxalic acid as the reactant with water in a rate-determining step is consistent with observations A and B which require a rate-determining step involving a non-acid chloride, carbonyl intermediate derived from oxalyl chloride. The proposed acid-catalyzed hydrolysis of diperoxyoxalic acid in step 7 is consistent with the observed acid hydrolysis of simple peroxy acids[30] and seems necessary to account for the experimental results. The possibility remains, however, that steps 7 and 9 should be combined so that water acts in concert with the fluorescer on diperoxyoxalic acid in the excitation step.

Step 8 is suggested, at least in ether solution, by observation I since added water acting in step 7 would increase the reaction rate and the light intensity but would not be expected to increase the quantum yield in the absence of a competing nonluminescent reaction. Step 8 is evidently less important or absent in dimethyl phthalate solution, however, since quantum yields remain high at low water concentrations, and are less affected by increased water.

Since a rapid decomposition of acyl peroxides is known to be specifically induced by ether (eq 12),[19,21,22,26] ether-induced decomposition in steps 6 and 8 might account for the low quantum yields in ether relative to dimethyl phthalate (observation P), and for the larger effect of water on quantum yield in ether than in dimethyl phthalate (observation I). However,

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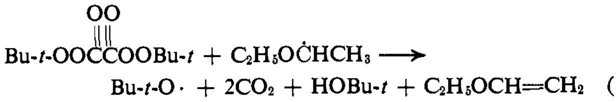
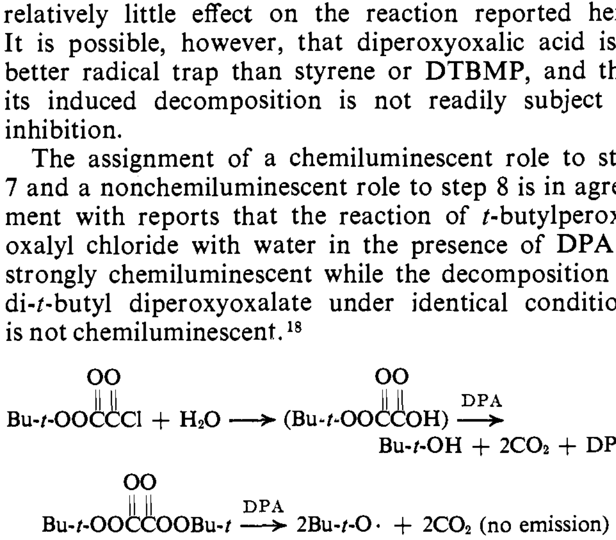


$$\text{Bu-}t\text{-OO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOBu-}t + C_2H_5O\dot{C}HCH_3 \longrightarrow \text{Bu-}t\text{-O}\cdot + 2CO_2 + \text{HOBu-}t + C_2H_5OCH{=}CH_2 \quad (12)$$

ether-induced decompositions of simple acyl peroxides,[21] and of di-*t*-butyl diperoxyoxalate[22] are eliminated by the addition of styrene, and styrene has relatively little effect on the reaction reported here. It is possible, however, that diperoxyoxalic acid is a better radical trap than styrene or DTBMP, and that its induced decomposition is not readily subject to inhibition.

The assignment of a chemiluminescent role to step 7 and a nonchemiluminescent role to step 8 is in agreement with reports that the reaction of *t*-butylperoxyoxalyl chloride with water in the presence of DPA is strongly chemiluminescent while the decomposition of di-*t*-butyl diperoxyoxalate under identical conditions is not chemiluminescent.[18]



$$\text{Bu-}t\text{-OO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{Cl} + H_2O \longrightarrow (\text{Bu-}t\text{-OO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OH}) \xrightarrow{\text{DPA}} \text{Bu-}t\text{-OH} + 2CO_2 + \text{DPA*}$$

$$\text{Bu-}t\text{-OO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOBu-}t \xrightarrow{\text{DPA}} 2\text{Bu-}t\text{-O}\cdot + 2CO_2 \text{ (no emission)}$$

Step 9 specifies that the decomposition of monoperoxyoxalic acid provides the energy required for excitation of the fluorescer. While the involvement of monoperoxyoxalic acid in this key step seems indicated by the preceding discussion, the present evidence does not provide the detailed mechanism of the energy conversion process leading to excitation. It is possible that step 9 represents several distinct steps.

Step 9 is evidently subject to interference by free-radical inhibitors (observation O). Thus, the loss in efficiency from delayed addition of DTBMP (O) shows that the inhibitor does not interfere with steps 1 through 6; the absence of a rate effect from added inhibitor (observation G) shows that it does not react with diperoxyoxalic acid in competition with rate-determining step 7, and that it must affect a fast subsequent step; the absence of fluorescence quenching by DTBMP (observation S) shows that it does not interfere with the emission step 11. With these alternatives eliminated, it seems clear that inhibitors reduce the quantum yield by reducing the rate or the efficiency of step 9. While it remains possible that the inhibitors could interfere with step 9 by reacting directly with monoperoxyoxalic acid or by interfering in some way with the energy conversion process, it seems more likely that step 9 requires an induced free-radical decomposition which is subject to free-radical inhibition. The appearance of phosgene in dimethyl phthalate (observation U) also indicates the presence of a free-radical process. Since steps 6 and 8 might also be subject to induced decomposition[14,22] and its inhibition, the effect of inhibitors in reducing the quantum yield may indicate that induced decomposition in step 9 is more readily inhibited than in steps 6 or 8. As noted in Table XI, inhibitors reduce the quantum yield less in ether than in dimethyl phthalate, suggesting that inhibition of induced decomposition by ether in step 6 or 8 may partly compensate inhibition in step 9. It is clear that step 9 must be fast relative to rate-determining step 7 (observation F), and that step 7 remains rate determining even in the presence of inhibitors (observation G).

It is clear from the increase in quantum yield with increasing fluorescer concentration (observation L) that decomposition of monoperoxyoxalic acid also takes place in the absence of fluorescer, and that excitation approximates a bimolecular process. The low fluorescer concentrations required along with the absence of a rate effect from the fluorescer (observation F) indicate that the excitation process is rapid; the high quantum yields in dimethyl phthalate indicate that the process is efficient.

Step 10 seems required to account for the decrease in quantum yield with increasing inhibitor concentration (observation O). Inhibition of step 9 might slow the light decay rate but would not be expected to reduce the quantum yield in the absence of an alternative noninduced, nonluminescent pathway from monoperoxyoxalic acid decomposition. Thus, added inhibitor is suggested to favor step 10 relative to step 9 and thereby reduce the quantum yield. Step 10 like step 9 must be fast relative to rate-determining step 7 to account for the absence of a rate effect from added inhibitors. Step 11 accommodates the observed emission from the excited singlet state of the fluorescer (observation Q).

Under conditions where the water/hydrogen peroxide ratio is small, steps 2 and 5 in Chart I should be dominated by steps 1 and 4 and have little influence on the quantum yield. Similarly at low oxalyl chloride concentrations step 3 should be unimportant. These conditions are met at least approximately by the experiments in Tables VIII through XII. Since the yield of a product from a competitive process is determined under pseudo-first-order conditions by the ratio of its rate of formation to the sum of the rates of all the competitive processes,[31] the mechanism in Chart I predicts the effects of reactant concentrations on quantum yields according to eq III.

$$Q = \left(\frac{k_4[\text{Cl}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}][H_2O_2]}{k_4[\text{Cl}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}][H_2O_2] + k_6[\text{Cl}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}]}\right) \times \left(\frac{k_7[\text{HOO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}][H_2O]}{k_7[\text{HOO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}][H_2O] + k_8[\text{HOO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}]}\right) \times \left(\frac{k_9[\text{HO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}][F][R\cdot]}{k_9[\text{HO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}][F][R\cdot] + k_{10}[\text{HO}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\text{OOH}]}\right)K \qquad \text{(III)}$$

$$1/Q = \frac{1}{K}\left(1 + \frac{k_6}{k_4[H_2O_2]}\right)\left(1 + \frac{k_8}{k_7[H_2O]}\right)\left(1 + \frac{k_{10}}{k_9[R\cdot][F]}\right) \qquad \text{(IV)}$$

The first product term is the predicted yield of HOOC(=O)C(=O)OOH; the second product term is the predicted yield of HOC(=O)C(=O)OOH from

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(31) See: C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1957, p 245.

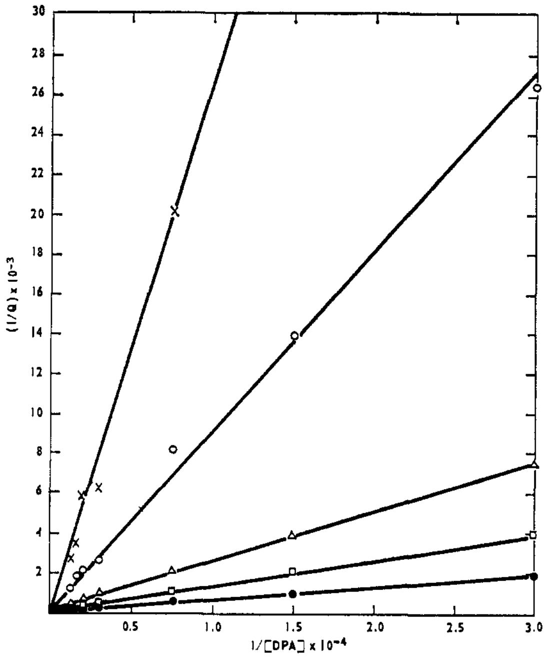


Figure 6. Relationship of quantum yield (Q) and DPA concentration (data from Table X): ●, $[H_2O_2] = 20 \times 10^{-2}\ M$; □, $[H_2O_2] = 10 \times 10^{-2}\ M$; △, $[H_2O_2] = 5 \times 10^{-2}\ M$; ○, $[H_2O_2] = 2.0 \times 10^{-2}\ M$; ×, $[H_2O_2] = 1.0 \times 10^{-2}\ M$.

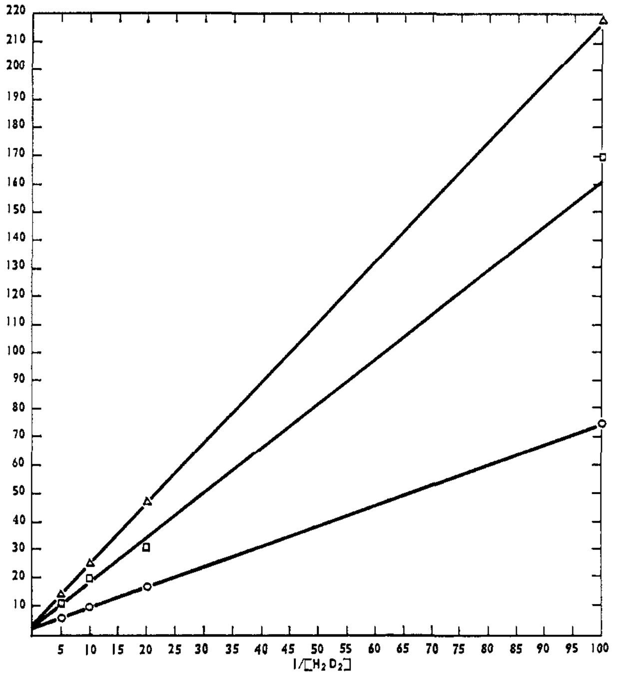


Figure 7. Effect of inhibitors on the relationship of quantum yield (Q) and hydrogen peroxide concentration (data from Table XII): ○, uninhibited reaction; □, styrene inhibition; △, DTBMP inhibition.

HOOC(=O)C(=O)OOH; the third product term, where [F] is the fluorescer concentration and [R·] is the steady-state radical concentration, is the predicted yield of excited fluorescer from HOC(=O)C(=O)-OOH; K is the fluorescence yield of the fluorescer, and the quantum yield Q is the product of the separate yields. Simplification and inversion of eq III gives eq IV which permits several tests of the proposed mechanism in terms of the experimental data.

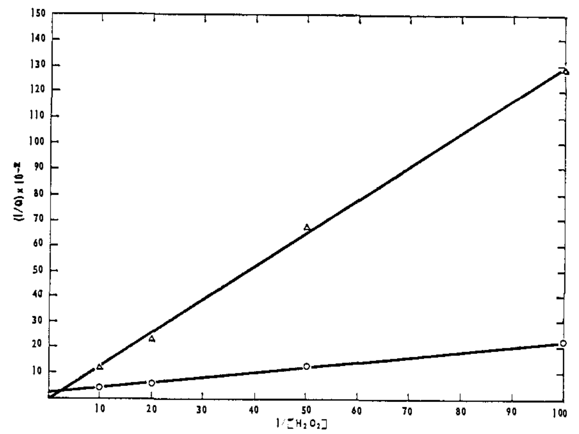


Figure 8. Effect of water on the relationship of quantum yield (Q) and hydrogen peroxide concentration: ○, $[H_2O] = 0.034\ M$ (Table IX); △, $[H_2O] = \sim 0.01\ M$ (Table VIII).

In a series of experiments where the fluorescer concentration is varied at constant hydrogen peroxide and water concentrations, a linear plot of $1/Q$ *vs.* $1/[F]$ would be expected. Moreover, the slopes of such linear plots should decrease as the hydrogen peroxide and water concentrations of the experimental sets increase. The data from Table X are plotted accordingly in Figure 6, where the predicted relationships are found.

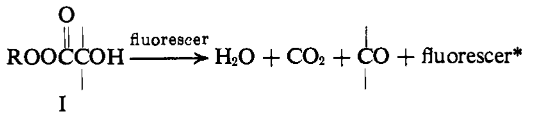
In experiments carried out with constant water and fluorescer concentrations but where hydrogen peroxide is varied, a linear plot of $1/Q$ *vs.* $1/[H_2O_2]$ would be expected. Moreover, the slopes of such plots should decrease as the steady-state concentration of free radicals increases. The data of Table XII are plotted accordingly in Figure 7, where the predicted relationships are found. Equation IV also indicates that the slopes of $1/Q$ *vs.* $1/[H_2O_2]$ plots should decrease with increasing water concentration. The data of Tables VIII and IX are plotted in Figure 8, where the expected relationship is found.

In experiments carried out with constant hydrogen peroxide, water, and fluorescer concentrations, but where the inhibitor concentration is varied, a linear plot of $1/Q$ *vs.* [inhibitor] would be expected from eq IV and V. Equation V is only approximate since its

$$[\mathrm{R}\cdot] = \frac{\text{rate of radical formation}}{k_{\text{inhib}}[\text{inhibitor}]} \qquad \text{(V)}$$

derivation by the steady-state assumption ignores termination steps not involving the inhibitor. Nevertheless, a reasonable linear plot of $1/Q$ *vs.* [inhibitor] is obtained from the data in Table XI, as indicated in Figure 9.

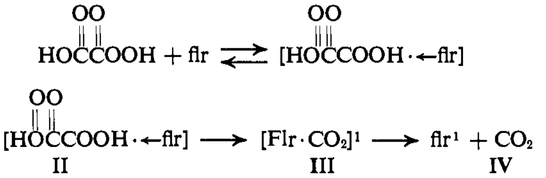
The mechanism in Chart I indicates that decomposition of monoperoxyoxalic acid uniquely provides the energy required to provide the excited state of the fluorescer. The assignment of step 9 to this key chemiluminescent role is in agreement with related work which has demonstrated chemiluminescence involving decomposition of a number of related peroxides[9,18] (structure I). The chemiluminescent char-



$$\underset{\text{I}}{\mathrm{ROO\overset{O}{\overset{\|}{C}}\underset{|}{\overset{|}{C}}OH}} \xrightarrow{\text{fluorescer}} \mathrm{H_2O + CO_2 + \underset{|}{\overset{|}{C}}O} + \text{fluorescer}^*$$

acter of peroxides I can in part be accounted for in terms of their ability to undergo concerted multiple bond cleavage decomposition[32] where the simultaneous formation of several stable product molecules accommodates the synchronous release of the substantial energy required for excitation.[18]

In the absence of experimental evidence, however, the mechanism by which chemical energy is converted to electronic excitation energy of the fluorescer can only be considered speculatively. In principle, decomposition of monoperoxyoxalic acid might produce excited singlet carbon dioxide, which might undergo a collisional or resonance energy transfer process[13] with the fluorescer as has been suggested.[18] However, quenching of excited carbon dioxide by oxygen, which would be expected to occur at a diffusion-controlled rate,[33] would seriously compete with transfer to the fluorescer and would limit the quantum yield. Since high quantum yields were obtained in the present study even at low fluorescer concentration in oxygen-saturated solutions, collisional energy transfer seems unlikely. An alternative possibility would be the formation of a charge-transfer complex[34] between monoperoxyoxalic acid and the fluorescer followed by decomposition to give a short-lived mixed eximer[35] of the fluorescer and carbon dioxide. Since the energy of excited singlet DPA (71 kcal) is lower than the energy of excited singlet carbon dioxide (~105 kcal)[36] such an excimer would have a lower excitation energy than excited carbon dioxide, thus providing a lower energy transition state for the decomposition. The excimer would also have a higher energy than the excited fluorescer so that its dissociation to ground-state carbon dioxide and excited fluorescer should be energetically favored, perhaps to the extent that the conversion of II to IV would be essentially synchronous. If this latter



$$\mathrm{HO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH} + \mathrm{flr} \rightleftharpoons [\mathrm{HO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}\cdot\!\leftarrow\!\mathrm{flr}]$$

$$\underset{\mathrm{II}}{[\mathrm{HO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}\cdot\!\leftarrow\!\mathrm{flr}]} \longrightarrow \underset{\mathrm{III}}{[\mathrm{Flr}\cdot\mathrm{CO_2}]^1} \longrightarrow \underset{\mathrm{IV}}{\mathrm{flr}^1} + \mathrm{CO_2}$$

mechanism is correct, the fluorescer should act as a catalyst for the decomposition of monoperoxyoxalic acid. The details of the energy conversion process are currently being investigated.

Experimental Section

Materials. Solvents. Anhydrous ether (Mallinckrodt reagent grade) was further dried by passage through a 30-cm neutral alumina column,[37] or by distillation over lithium aluminum hydride under argon. Dimethyl phthalate (Eastman) was distilled under vacuum. Residual water was estimated by the Karl Fischer method.[38]

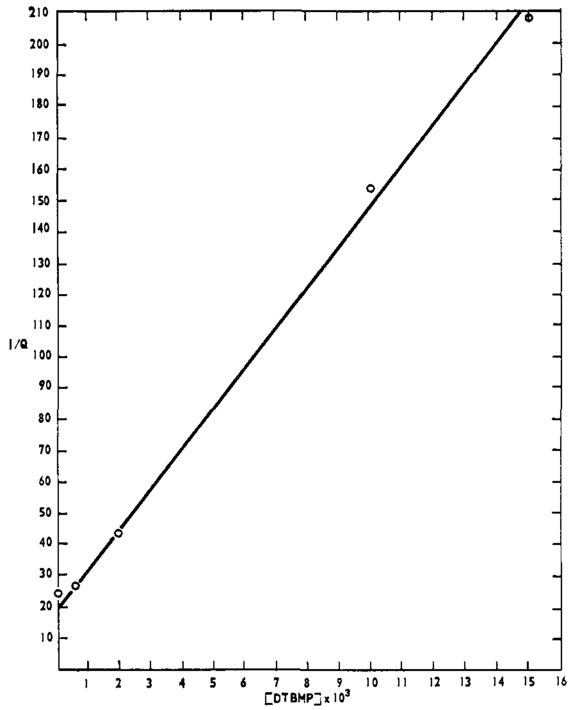


Figure 9. Relationship between quantum yield (Q) and inhibitor concentration (data from Table XI).

Oxalyl chloride (Aldrich) was distilled through a 10 × 1 cm Vigreux column under argon to obtain a fraction, bp 64° (1 atm) (lit.[24] bp 63.5–64° (763 mm)). Standard solutions of oxalyl chloride in ether or dimethyl phthalate (1.11×10^{-1} to $1.50 \times 10^{-1}M$) were analyzed gravimetrically by conversion to oxanilide with excess aniline. This reaction was shown to be quantitative in preliminary large-scale experiments.

Anhydrous hydrogen peroxide in ether was prepared from 98% hydrogen peroxide (Becco Chemical Division, FMC Corp.) dissolved in ether to a concentration of 25%, and dried by shaking for 16 hr with excess anhydrous magnesium sulfate.[39] Water estimation of the dried solution by infrared analysis at 1640 cm^{-1} indicated that residual water was below 2.9×10^{-2} M. Standard solutions of hydrogen peroxide (0.758 to 1.65 M) were prepared from this solution and anhydrous ether and were analyzed iodometrically.[40] Anhydrous hydrogen peroxide solutions in dimethyl phthalate were prepared similarly.

9,10-Diphenylanthracene (DPA) (Aldrich) was recrystallized from absolute ethanol–chloroform to obtain material, mp 250–251° (lit.[41] mp 250–251°).

2,6-Di-*t*-butyl-4-methylphenol (Koppers Co., Inc.) was sublimed *in vacuo* to obtain material melting at 69–70° (lit.[22] mp 69–70°). Other materials were obtained from commercial sources and were recrystallized or redistilled before use.

Gaseous Products from Oxalyl Chloride–Hydrogen Peroxide Reactions. The reactions in Table II were carried out in an apparatus consisting of a 500-ml, round-bottom flask equipped with a magnetic stirrer and fitted with two evacuated gas sample bulbs, a 10-ml dropping funnel, and a three-way stopcock leading to a helium tank, a differential manometer, and a vacuum pump. The total volume of the system was 620 ml. A solution of hydrogen peroxide in ether or dimethyl phthalate containing 10 mg of 9,10-diphenylanthracene was placed in the flask and cooled to −78°, and the system was evacuated. The system was tested for leaks by observing changes in pressure with the manometer after isolating the vacuum pump by means of the stopcock. The cooling bath was removed and oxalyl chloride was added from the dropping funnel. When chemiluminescence had ceased, the pressure and temperature of the system were observed and a sample of gas was

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Table XIII. Stability of Fluorescers in Oxalyl Chloride–Hydrogen Peroxide Reactions

Fluorescer concn, mole l.$^{-1}$	Solvent	[$OxCl_2$], moles l.$^{-1}$	[H_2O_2], mole l.$^{-1}$	Emission max, mμ	Florescence intensity arbitrary units: Before reaction	After reaction
		DPA				
1.0×10^{-4}	Ether	2.5×10^{-3}	0.10	430	73	72
1.0×10^{-3}	Dimethyl phthalate	2.4×10^{-3}	0.15	430	85	83
1.0×10^{-3}	Dimethyl phthalate	1.0×10^{-2}	0.15	430	85	<5.0
		Perylene				
1.0×10^{-4}	Ether	2.4×10^{-3}	0.05	465	70	70
		Rubrene				
1.0×10^{-4}	Ether	2.0×10^{-3}	0.05	550	80	74

taken for the analysis by mass spectroscopy. The system was then raised to atmospheric pressure with helium and a sample of gas was taken for analysis by vapor phase chromatography (vpc). Mass spectroscopic analysis provided the mole fractions of ether, CO, CO_2, O_2, and phosgene present and thus allowed the calculation of the yields of the various products from the observed pressure, temperature, and volume of the reaction system. Since only the CO_2 determination was free from possible interference by peaks from other components of the system, the reliability of oxygen and carbon monoxide analyses was checked by vpc analysis which gave ratios of the various components to CO_2. These ratios were compared with the unambiguous CO_2 yield obtained by mass spectroscopy to determine the reported vpc yields.

In vpc analyses,[42] oxygen, nitrogen, and carbon monoxide were determined concurrently on a 6 ft 13X molecular sieve column operated at 26° in an F and M Model 119 instrument. Carbon dioxide was determined separately on a 2-ft silica gel column at 26° in the same instrument. Gas sampling was accomplished by means of an Aerograph gas sampling valve. The instrument was calibrated with pure CO, CO_2, O_2, and N_2 samples.

Infrared Analyses of Oxalyl Chloride–Hydrogen Peroxide Reaction Mixtures. Aliquots of 1.5×10^{-1} *M* oxalyl chloride and hydrogen peroxide solutions in ether were mixed rapidly and transferred to a 0.25-mm infrared cell. Absorption bands at 1790 and 750 cm^{-1} corresponding, respectively, to carbonyl and chlorocarbonyl were determined as a function of time at 25°. Typical results are shown in Figure 3.

Stoichiometry Experiments. A magnetically stirred, 150-ml, three-necked flask, fitted with a 50-ml buret and attached to a constant-pressure nitrogen manifold, was flushed well with nitrogen and charged with 10.0 ml (1.020 mmoles) of 0.102 *M* hydrogen peroxide in anhydrous diethyl ether and 5 mg of 9,10-diphenylanthracene (DPA). The buret, also attached to the manifold, was filled with 0.075 *M* oxalyl chloride solution in anhydrous diethyl ether, and the entire assembly was placed under slight positive nitrogen pressure. Oxalyl chloride was added in 1.0- to 0.5-ml portions. The chemiluminescence was allowed to decay to zero intensity between additions. The end point was reached when further addition failed to produce light and occurred at 16.0 ml (1.200 mmoles) of oxalyl chloride solution. This is a ratio of 1.18 moles of oxalyl chloride per mole of hydrogen peroxide. Until very near the end point, each addition of oxalyl chloride solution produced a bright chemiluminescent emission which required in excess of 10 min to decay. Titration of 0.075 *M* oxalyl chloride with 0.102 *M* hydrogen peroxide gave an oxalyl chloride/hydrogen peroxide ratio of 0.94.

Determinations of Light Intensities, Spectra, and Quantum Yields. Instrumentation. A combination spectroradiometer–fluorimeter, designed and calibrated under the direction of Dr. R. C. Hirt, will be described elsewhere in detail.[43] The instrument consisted of a Bausch and Lomb grating monochromator (Model 33-86-25), an Aminco photomultiplier power supply and amplifier, and a IP21 photomultiplier tube. The entrance and exit slits of the monochromator were fixed at 1.34 and 0.75 mm. For fluorescence measurements, the instrument was equipped for a G.E. F4T 5/BLB fluorescent tube, mounted to provide front-side excitation of the sample. The amplifier output was fed to a Brown variable speed Electronik recorder or to a Leeds and Northrup integrating recorder for tracking spectral and intensity decay curves. The instrument was used without change for both fluorescence and chemiluminescence measurements. The liquid sample cell was a 10.0-mm thick, 22-mm diameter cylindrical quartz cuvette of 3.0-ml capacity. The instrument was calibrated using a National Bureau of Standards tungsten lamp, operated at a color temperature of 2864°K, and the accepted fluorescence yield (0.55) for 1×10^{-3} *M* quinine sulfate[44] in 0.1 *N* H_2SO_4 according to standard procedures.[45,46] The absolute intensity of exciting light incident on the cuvette was determined by ferrioxalate actinometry;[47] the fraction of incident light absorbed in fluorescence experiments was calculated from the emission spectrum of the exciting light and from absorbance data determined with a Cary Model 14 spectrophotometer.

Calculation of Fluorescence and Chemiluminescence Quantum Yields. Fluorescence quantum yields were calculated from the formula

$$Q_{\mathrm{Fl}} = \frac{I(\mathrm{emission})}{I(\mathrm{absorbed})} = \frac{aa'\left(\int_{\lambda}^{\lambda_2} b_\lambda I_\lambda \mathrm{d}\lambda\right)}{I(\mathrm{absorbed})} = \frac{\int_{\lambda}^{\lambda_2} C_\lambda I_\lambda \mathrm{d}\lambda}{I(\mathrm{absorbed})}$$

where I_λ is the observed intensity at wavelength λ; b_λ is the wavelength sensitivity calibration factor for I_λ provided by the standard lamp; a is the reciprocal of the fraction of emitted light reaching the detector and a' is the conversion factor to absolute units, where aa' is determined by reference to quinine sulfate; C_λ is the product $aa'b_\lambda$. Since the instrument is unchanged for chemiluminescence measurements the factors C_λ are unchanged, permitting the determination of absolute chemiluminescence quantum yields.

Fluorescence quantum yields in deoxygenated solutions measured with the instrument agreed well with literature values: fluorescein in 0.1 *M* aqueous K_2CO_3, 0.88 (lit.[48] 0.92); eosin in 0.1 *N* aqueous NaOH, 0.17 (lit. 0.15,[49] 0.23[45]); rhodamine B in ethanol, 0.92 (lit.[48] 0.97); anthracene in ethanol, 0.25 (lit.[49] 0.27); 9,10-diphenylanthracene in benzene, 0.84 (lit.[50] 0.84).

The chemiluminescence quantum yields in einsteins mole^{-1} were calculated from the equation

$$QY = \frac{\left(\int_0^\infty C_{\lambda'} I_{\lambda'} \mathrm{d}T\right)\left(\dfrac{\int_{\lambda_1}^{\lambda_2} C_\lambda I_\lambda{}^T \mathrm{d}_\lambda}{C_{\lambda'} I_{\lambda'}{}^T}\right)}{3.0 \times 10^{-3}\,[\text{oxalyl chloride}]\,6.02 \times 10^{23}}$$

The first product term in the numerator corresponds to the area of the corrected intensity *vs.* time decay plot at observed wavelength λ', where $I_{\lambda'}$ is the observed intensity and $C_{\lambda'}$ is the instrument

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[42] The vpc analytical method was developed by Dr. R. A. Paylor, Research Service Department, American Cyanamid Co.

[43] B. G. Roberts and R. C. Hirt, Research Service Department, American Cyanamid Co. The instrument was described at the 19th Annual Instrument Society of America Conference, New York, N. Y., Oct 12–15, 1964, Preprint No. 2.2-2-64.

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calibration factor for λ'. This term was measured graphically. The second product term in the numerator corresponds to the unit spectral area at time T. The spectral distribution and therefore the unit spectral area did not change appreciably during an experiment so that this was a constant factor for an experiment. This term can be calculated graphically from the area of a plot of $C_\lambda I_\lambda{}^T/C_{\lambda'}I_{\lambda'}{}^T$ *vs.* λ, but was actually determined with a Burroughs Datatron 205 computer, programmed with the calibration data.

Procedure for Chemiluminescence Experiments. The light measurement experiments were carried out by combining appropriate aliquots of standardized stock solutions of hydrogen peroxide, DPA, and water in ether or dimethyl phthalate with appropriate aliquots of solvent in a 3.0-ml magnetically stirred cylindrical cuvette attached to the radiometer. The stirrer was positioned vertically against the rear, flat side of the cuvette and provided efficient, rapid mixing. The shutter to the radiometer was opened, the recorder was started, and an aliquot of standarized oxalyl chloride was injected from an all-glass syringe. The intensity of emission of a 5-mμ-wide wavelength segment, usually selected at the spectral maximum, was recorded as a function of time from the point of oxalyl chloride injection. Spectral distributons were determined for representative experiments at several times during a single experiment. The time required for spectral scan was short relative to the intensity decay rate; however, the intensities were corrected for intensity decay. The spectral distributions did not change with time during an experiment under the conditions studied. Corrections of the spectra for reabsorption of emitted light was not necessary with DPA concentrations below 1×10^{-3} M; at 1×10^{-3} M, however, minor reabsorption was noted as a relative loss of intensity at short wavelength. The experiments were not thermostated but were run at room temperature, 25°, which was constant within 1°. Exotherms were not observed at the low reactant concentrations used in several experiments where the temperature was followed with a thermocouple. Typical spectra are shown in Figures 1 and 2. A typical intensity decay plot is is shown in Figure 4.

Stability of Fluorescers in Oxalyl Chloride–Hydrogen Peroxide Chemiluminescent Systems. In a typical experiment, the fluorescence spectrum of 2.95 ml of a solution containing 1×10^{-4} M DPA and 0.1 M H_2O_2 in ether was recorded. A 0.05-ml aliquot of 1.5×10^{-1} M ethereal oxalyl chloride was injected to provide an oxalyl chloride concentration of 2.5×10^{-3} M. After 10 min the chemiluminescence emission decayed essentially to zero and the fluorescence spectrum was again measured. Similarly both perylene and rubrene spectra before and after chemiluminescent reaction were obtained. The results are summarized in Table XIII. Ultraviolet absorption spectra of a reaction of 1.5×10^{-2} M oxalyl chloride, 2.0×10^{-1} M hydrogen peroxide, 1.2×10^{-2} M water, and 6.7×10^{-5} M DPA in ether also indicated essentially no change in fluorescer concentration following the reaction.

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Perfluorodiazo Compounds

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Abstract: Members of a new class of perfluoroalkyldiazomethanes $(R_f)_2CN_2$ and the first member of the class of perfluoroalkyldiazirines have been prepared by lead tetraacetate oxidation of the corresponding hydrazones and diaziridine, respectively. The chemistry of these compounds has been investigated with emphasis on the formation and chemistry of carbenes $(R_f)_2C$:, which are sufficiently electrophilic to add to benzene. The ultraviolet spectrum of tropylidene XXVI suggests that the ring is very nearly planar.

Perfluoroalkyldiazomethanes or diazirines have not been reported previous to the start of this investigation.[1-4] Detailed studies of the reactions of the dihalocarbenes have revealed that they are less electrophilic than methylene.[5] This lower electrophilicity has been attributed to a resonance stabilization by the halogen of the electron-deficient carbon, which offsets any inductive destabilization.[6] The method of generation may also be an important consideration in carbene reactivity; for example, chlorocarbene generated from chlorodiazomethane is more reactive than "chlorocarbene" generated in solution from methylene chloride and an organolithium reagent.[7] Recent studies[8] of partly fluorinated carbenes (containing a hydrogen and perfluoroalkyl group attached to the electron-deficient carbon) have led to examples of addition to haloolefins. In the present study, it was hoped that the decomposition of a bis(perfluoroalkyl)diazomethane or diazirine

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(1) A preliminary communication describing a portion of this work has appeared: D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965). While this work was in progress, reports of the synthesis of bis(trifluoromethyl)diazomethane[2] and bis(trifluoromethyl)diazirine[3] by alternate routes have appeared. The properties and chemistry of difluorodiazirine have been reported.[4] See ref 1–4 for a summary of the literature of partly fluorinated diazo compounds.

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(5) For recent reviews, see J. Hine, "Divalent Carbon," Ronald Press New York, N. Y., 1964; W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

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