to Dr. H. Norment who collected the diffraction data and prepared it for phase determination and to Mr. S. Brenner who prepared the reiteration program using the tangent formula.

Chemiluminescence from Reactions of Electronegatively Substituted Aryl Oxalates with Hydrogen Peroxide and Fluorescent Compounds[1]

M. M. Rauhut, L. J. Bollyky, B. G. Roberts, M. Loy, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and R. A. Clarke

Contribution from the Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut 06904.

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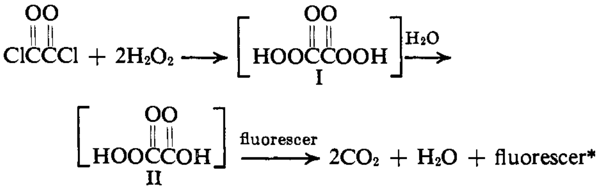
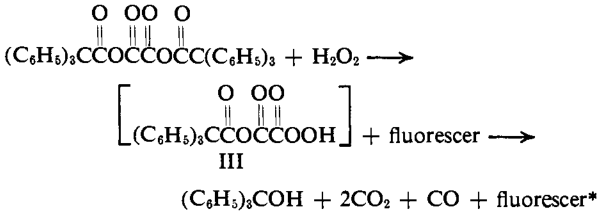
Abstract: Reactions of a series of oxalate esters with hydrogen peroxide and fluorescent compounds were examined for chemiluminescent light emission. Electronegatively substituted aryl oxalate esters were found capable of generating light with high efficiency; a quantum yield of 0.23 einstein mole^{-1} was obtained from bis(2,4-dinitrophenyl) oxalate, hydrogen peroxide, and rubrene. Comparison of chemiluminescence with fluorescence spectra indicates that the first singlet excited state of the fluorescer is the emitting species. The effects of ester, peroxide, and fluorescer structures and concentrations are reported. The reaction stoichiometry was found to be 1:1 ester:H_2O_2. The chemiluminescence efficiency is strongly dependent on the fluorescer structure. It was shown that a long-lived chemiluminescent intermediate is produced in the absence of fluorescer, and that the fluorescer catalyzes its decomposition. A tentative mechanism is discussed in terms of this and other evidence.

Chemiluminescence has been reported from reactions of hydrogen peroxide with oxalyl chloride[2,3] and certain mixed oxalic anhydrides[4] in the presence of fluorescent organic compounds such as 9,10-diphenylanthracene (DPA) (eq 1 and 2).



$$\mathrm{Cl\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl} + 2H_2O_2 \longrightarrow \underset{\mathrm{I}}{\left[\mathrm{HOO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}\right]} \xrightarrow{H_2O}$$
$$\underset{\mathrm{II}}{\left[\mathrm{HOO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OH}\right]} \xrightarrow{\text{fluorescer}} 2CO_2 + H_2O + \text{fluorescer}^* \quad (1)$$



$$\mathrm{(C_6H_5)_3C\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}C(C_6H_5)_3} + H_2O_2 \longrightarrow$$
$$\underset{\mathrm{III}}{\left[\mathrm{(C_6H_5)_3C\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}\right]} + \text{fluorescer} \longrightarrow$$
$$\mathrm{(C_6H_5)_3COH} + 2CO_2 + CO + \text{fluorescer}^* \quad (2)$$

Under suitable conditions these chemiluminescent reactions are substantially more efficient than those previously reported; light yields near 5 and 13%, respectively, have been obtained from reactions 1[3] and 2[4] in contrast to yields of 1% or less obtained from earlier reactions.[5] In reactions 1 and 2 the spectrum of the emitted light matches the normal fluorescence spectrum of the added fluorescer, indicating that the first singlet excited state of the fluorescer is the emitting species.[3,4] The results of a mechanism study of reaction 1 suggested that diperoxyoxalic acid (I) and monoperoxyoxalic acid (II) were intermediates in the chemiluminescent process, at least when carried out in ether solution.[3] A preliminary study of anhydride reaction 2 did not rule out intermediates I and II, but suggested that monoanhydride III was a possible intermediate.[4] Both mechanisms were consistent with the suggestion that concerted multiple bond cleavage decomposition of a key intermediate was essential to accommodate the substantial and simultaneous energy release required for fluorescer excitation.[6]

Providing that the essential elements of mechanisms 1 and 2 are valid, it would appear that oxalic peracids meeting the concerted decomposition requirement are particularly efficient sources of electronic excitation energy in chemiluminescence. If so, then other reactions generating such peroxyoxalates in the presence of a fluorescer should be capable of efficient chemiluminescence, providing competing, nonluminescent side reactions are minimized. To examine this point we have investigated the reactions of a series of oxalate esters with hydrogen peroxide in the presence of organic fluorescers.

Results

Preliminary Survey of Oxalate Esters for Chemiluminescence. The scope of oxalate ester chemiluminescence was quickly surveyed by visually observing the reactions of 20 esters (about 0.005 *M*) with anhydrous

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(1) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, Abstract O-169.

(2) E. A. Chandross, *Tetrahedron Letters*, 761 (1963).

(3) M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, **88**, 3604 (1966).

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(5) For reviews see: F. McCapra, *Quart. Rev.* (London), **20**, 485 (1966); K. D. Gunderman, *Angew. Chem., Intern. Ed. Engl.*, **4**, 566 (1965); V. I. Papisova, V. Y. Shlyapintokh, and R. F. Vasl'ev, *Russ. Chem. Rev.*, **34**, 599 (1965); E. J. Bowen, *Pure Appl. Chem.*, **9**, 473 (1964).

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

Table I. Chemiluminescent Reactions of Substituted Phenyl Oxalates with H_2O_2 and DPA in DMP[a]

Phenyl substituents	Ester concn, M	H_2O_2 concn, M	I_{max},[b] einsteins sec^{-1} $ml^{-1} \times 10^{11}$	$T_{3/4}$,[c] min	Quantum yield,[d] einsteins $mole^{-1} \times 10^2$
2-Nitro[e]	0.0010	0.024	1.4	76.0	5.7
2-Nitro[f,g]	0.010	0.024	14.6	54.0	2.6
4-Nitro	6.67×10^{-4}	0.4	0.3	Not calcd	0.93
4-Nitro-3-trifluoromethyl	0.0010	0.024	4.2	48.7	12.3
4-Nitro-3-trifluoromethyl	0.010	0.024	3.1	228.5	4.1
4-Nitro-3-trifluoromethyl	0.010	0.090	9.4	111.1	5.7
4-Nitro-3-trifluoromethyl	0.033	0.090	12.2	19.7	0.4
4-Nitro-2-formyl	0.0010	0.024	2.16	115.3	13.7
4-Nitro-2-formyl	0.010	0.024	20.6	102.8	8.7
4-Nitro-2-formyl	0.010	0.090	23.1	77.7	8.0
4-Nitro-2,6-dichloro[f,g]	0.010	0.097	6.5	378	4.4
4-Nitro-2,6-dichloro[f,g]	0.010	0.970	9.6	121	2.6
4-Nitro-2,6-dichloro[f-h]	0.050	0.121	5.2	670	2.1
2,4-Dinitro	0.0010	0.0027	21.4	29	15.4
2,4-Dinitro	0.010	0.024	93.5	116	8.0
2,5-Dinitro	0.0010	0.024	61.3	1.5	5.3
2,4-Dichloro[f]	0.0010	0.024	0.6	138	4.0
2,4-Dichloro[f]	0.010	0.024	4.5	160	1.7
Pentachloro	0.0010	0.0072	8.1	72.9	15.1
Pentafluoro	0.0010	0.024	14.4	22.4	14.6
Pentafluoro	0.010	0.090	10.8	140.4	7.6
3-Trifluoromethyl	0.010	0.024	0.1	1000	0.56
3-Trifluoromethyl	0.0367	0.090	0.4	193.1	0.12
3,5-Bis(trifluoromethyl)[f]	0.010	0.024	76.6	48	6.2
3,5-Bis(trifluoromethyl)[f]	0.030	0.073	4.6	73	0.3

[a] 9,10-Diphenylanthracene (DPA) was 6×10^{-4} M except where noted. Reactions were at 25° in dimethyl phthalate (DMP). [b] Absolute spectrally and geometrically integrated intensity. [c] Time required for emission of three-fourths of the total light. [d] Based on oxalate ester. [e] 1.6×10^{-5} M benzyltrimethylammonium hydroxide was added. Reaction was very slow in absence of base. [f] 1.6×10^{-4} M benzyltrimethylammonium hydroxide was added. [g] DPA consumption was complete by end of reaction. [h] The DPA concentration was 0.001 M.

hydrogen peroxide (about 0.5 M) in 1,2-dimethoxyethane containing DPA (about 0.001 M) in a dark room. Analogous reactions were carried out in the presence of excess potassium hydroxide or in the presence of methanesulfonic acid (about 0.2 M) to detect possible catalysis. Under the test conditions little emission was detected from aliphatic esters and from aryl esters substituted by electron-donating or weak electron-withdrawing groups, where R in ROC(O)C(O)OR was: ethyl, *t*-butyl, diphenylmethyl, 2-cyano-2-propyl, 2,2,2-trifluoroethyl, phenyl, 2-naphthyl, 2,6-dimethylphenyl, 4-methoxyphenyl, and *o*-phenylene. Under neutral or alkaline conditions moderate to strong chemiluminescent emission was observed from aryl esters substituted by electronegative groups (Table I). None of the reactions was appreciably chemiluminescent under acidic conditions.

Effects of Ester Structure and Concentrations. Emission lifetimes and absolute quantum yields of chemiluminescent reactions of electronegative aryl oxalate esters with anhydrous hydrogen peroxide and DPA in dimethyl phthalate are summarized in Table I. Typical plots of intensity *vs.* time are illustrated in Figure 1. The intensity decay curves did not correspond to simple first- or second-order kinetics under the conditions used, and for comparative purposes the emission lifetime was arbitrarily defined as the time required for three-quarters of total light emission. Quantum yields were generally reproducible to within 10% of the value measured. "Three-quarter intensity lifetimes" were markedly decreased by basic or polar contaminants (see below) and were less easily reproduced.

The results in Table I indicate that the quantum yield increases with increasing electronegative substitution up to a maximum quantum yield of 12–15% with DPA as the fluorescer. While emission lifetimes, in general, decreased with increasing electronegative substitution, there is no rigorous correlation between the quantum yield and emission lifetime. It is evident that the quantum yield decreases substantially with increasing ester concentration.

The Effect of Peroxide Structure and Concentration on DNPO Chemiluminescence. The quantum yields of light emission from reactions of bis(2,4-dinitrophenyl) oxalate (DNPO) with organoperoxides and with hydrogen peroxide are compared in Table II. Although the various organoperoxides are active to a minor extent, it is clear that hydrogen peroxide is specifically required for substantial efficiency.

Table II. Effect of Peroxides on the Quantum Yield of DNPO Chemiluminescence[a]

Peroxide	Concn, M	Quantum yield, einsteins $mole^{-1} \times 10^2$
Hydrogen peroxide	0.082	7.3
t-Butyl hydroperoxide	0.20	0.01
Tetralin hydroperoxide	0.10	0.008
Peroxybenzoic acid	0.10	0.003
Benzoyl peroxide	0.10	Very low

[a] Reactions with 0.010 M bis(2,4-dinitrophenyl) oxalate (DNPO) and 4.16×10^{-4} M 9,10-diphenylanthracene (DPA) in dimethyl phthalate at 25°.

The effect of the hydrogen peroxide concentration on lifetimes and quantum yields in reactions with DNPO at two concentrations is summarized in Table III. The amount of emitted light increases with increasing hydrogen peroxide up to a H_2O_2:DNPO molar ratio of about 1:1, and then remains essentially constant. Quantum yields calculated on the basis of a 1:1 stoichiometry are approximately constant with varying hydrogen peroxide concentration at a given DNPO concentration, but it is clear that lower yields are obtained at the higher DNPO concentration. A 1:1 reaction stoichiometry was also indicated by a reaction of 0.020 *M* bis(3-trifluoromethyl-4-nitrophenyl) oxalate (TFMNPO) with 0.010 *M* hydrogen peroxide in triethyl phosphate containing 6.0×10^{-4} *M* DPA, where following the completion of the reaction 0.009 *M* TFMNPO remained unchanged according to infrared spectral analysis (Table VIII).

Table III. Effect of H_2O_2 Concentration on DNPO Chemiluminescence[a]

[DNPO], $M \times 10^3$	$[H_2O_2]$, $M \times 10^3$	$T_{3/4}$,[b] min	Emitted light, einsteins $\times 10^3$	Quantum yield,[c] einsteins mole^{-1} $\times 10^2$
1.00	0.21	42	0.030	14
1.00	0.52	50	0.086	17
1.00	0.77	52	0.112	15
1.00	1.03	40	0.129	13
1.00	1.29	29	0.129	13
1.00	1.55	37	0.138	14
1.00	2.07	29	0.154	15
1.00	2.58	39	0.141	14
1.00	5.16	13	0.139	14
10.0	2.00	42	0.20	10
10.0	5.40	87	0.55	10
10.0	11.1	165	0.81	8.1
10.0	25.0	116	0.80	8.0
10.0	37.8	36	0.81	8.1
10.0	50.0	34	0.79	7.9
10.0	90.0	12	0.81	8.1

[a] Reactions of bis(2,4-dinitrophenyl) oxalate (DNPO) at 25° in dimethyl phthalate containing 6.0×10^{-4} *M* 9,10-diphenylanthracene. [b] Time required for three-quarters of total light emission. [c] Based on a 1:1 DNPO:H_2O_2 stoichiometry.

The Effects of Fluorescer Structure and Concentration. Chemiluminescence spectra were determined for reactions of DNPO with hydrogen peroxide in dimethyl phthalate containing the fluorescers 9,10-diphenylanthracene (DPA), rubrene, or 4-butylamino-N-butyl-1,8-naphthalimide (BABN), and the spectra were compared with the fluorescence spectra of these fluorescers in dimethyl phthalate. Aside from a small bathochromic shift noted in the chemiluminescence spectra, probably resulting from the more polar chemiluminescence medium, chemiluminescence and fluorescence spectra were essentially identical. Thus the first singlet excited states of the respective fluorescers were established as the emitting species. Light emission was not observed in the absence of a fluorescer.

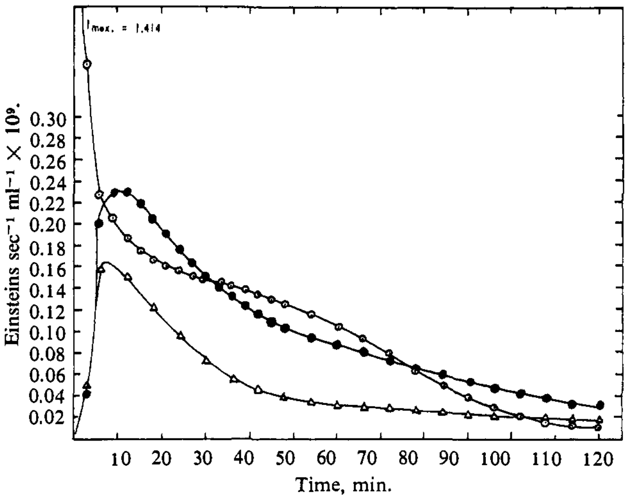


Figure 1. Emission intensity as a function of time for reactions of oxalate esters (0.0100 *M*) with hydrogen peroxide (0.0241 *M*) and 9,10-diphenylanthracene (6.0×10^{-4} *M*) in dimethyl phthalate at 25°: ○, bis(2,4-dinitrophenyl) oxalate; ●, bis(2-formyl-4-nitrophenyl) oxalate; △, bis(pentafluorophenyl) oxalate.

The results of a series of chemiluminescent reactions between DNPO and hydrogen peroxide with the fluorescers DPA, rubrene, and BABN are summarized in Table IV. At low fluorescer concentrations, early consumption of the fluorescer reduces emission yields and lifetimes. It is clear, however, that light emission is not dependent on fluorescer consumption, since even when the fluorescer is consumed, light outputs of 2 to 4 einsteins/mole of fluorescer are obtained. At fluorescer concentrations on the order of 10^{-3} *M*, the fluorescers tend to reabsorb the emitted light in a 1-cm cell and a decrease in the observed efficiency results. At intermediate fluorescer concentrations, however, neither the quantum yield nor the lifetime appears to be a function of the fluorescer concentration.

Table IV. The Effect of Fluorescer Structure and Concentration on DNPO Chemiluminescence[a]

Fluorescer	Fluorescer concn, $M \times 10^4$	$T_{3/4}$,[b] min	Quantum yield,[c] einsteins mole^{-1} $\times 10^{-2}$
DPA[d]	1.00	5[e]	3.13[e]
DPA[d]	4.16	17	8.04
DPA[d]	8.33	14	7.93
DPA[d]	21.7	12	7.13[f]
Rubrene[g]	2.92	1[e]	13.3[e]
Rubrene[g]	4.87	4	17.2
Rubrene[g]	5.84	4	16.0
Rubrene[g]	7.30	4	15.2
Rubrene[g]	8.76	4	13.3[f]
Rubrene[h]	5.00	21	23.5
BABN[i]	1.00	4.5[e]	2.2[e]
BABN[i]	4.16	25.0	5.7
BABN[i]	7.50	19.0	5.7
BABN[i]	10.00	19.6	5.6

[a] Reactions were carried out with 0.010 *M* bis(2,4-dinitrophenyl) oxalate (DNPO) except for *h* in dimethyl phthalate at 25°. [b] Time required for three-quarters of total light emission. [c] Based on DNPO. [d] The hydrogen peroxide concentration was 0.0836 *M*. [e] Consumption of the fluorescer reduced the lifetime and yield. [f] Self-absorption of emitted light by the fluorescer was observed. [g] The hydrogen peroxide concentration was 0.050 *M*. [h] The DNPO concentration was 0.001 *M*, and the hydrogen peroxide concentration was 0.025 *M*. [i] BABN is 4-butylamino-N-butyl-1,8-naphthalimide. The hydrogen peroxide concentration was 0.0168 *M*. Higher hydrogen peroxide concentrations tended to destroy the fluorescer.

As indicated in Table IV the fluorescer structure has a marked influence on emission efficiency and lifetime. Rubrene provides substantially higher quantum yields than DPA or BABN: at 0.001 *M* DNPO the yield with rubrene reaches 23.5%, and at 0.01 *M* DNPO is about twice that obtained with DPA. The

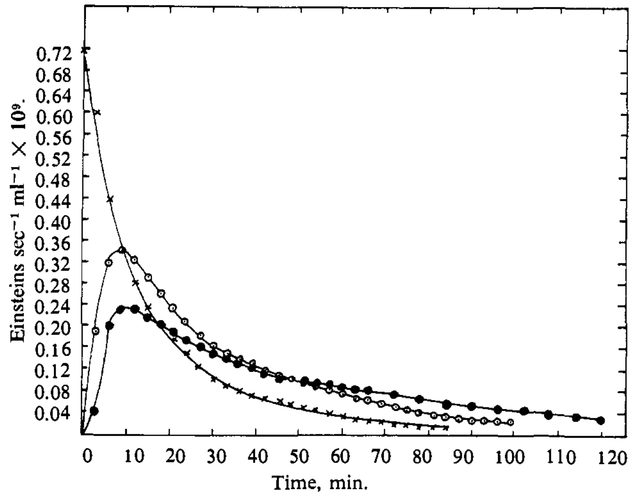


Figure 2. Effects of water and triethylamine on the intensity decay of chemiluminescence from the reaction of 0.0100 *M* bis(2-formyl-4-nitrophenyl) oxalate, 0.0904 *M* hydrogen peroxide, and 6.0×10^{-4} *M* 9,10-diphenylanthracene in dimethyl phthalate at 25°: ●, no additive; ○, 0.105 *M* water added; ×, 8.3×10^{-6} *M* triethylamine added.

lifetime is also markedly shorter with rubrene and BABN than with DPA. The chemiluminescence efficiency does not appear to correlate in a simple way with the fluorescence efficiency or singlet energy level of the fluorescer.

Effects of Certain Additives on Efficiencies and Lifetimes. Results showing the effects of water, ethanol, and two bases on DNPO chemiluminescence are summarized in Table V. It is apparent that the reaction is markedly subject to basic catalysis and is also accelerated by hydroxylic additives. Typical intensity decay curves are illustrated in Figure 2. The quantum yield is reduced slightly by water or triethylamine, but appears to be increased by benzyltrimethylammonium hydroxide. The free-radical chain inhibitor 2,6-di-*t*-butyl-4-methylphenol substantially reduces the quantum yield but has relatively little effect on the reaction lifetime.

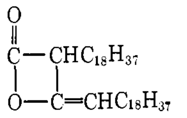
Table V. Effects of Additives on DNPO Chemiluminescence[a]

Additive	Additive concn, *M*	H_2O_2 concn, *M*	I_{max}, einsteins sec^{-1} ml^{-1} $\times 10^9$	$T_{3/4}$,[b] min	Quantum yield,[c] einsteins mole^{-1} $\times 10^2$
None	...	0.011	1.60	165	8.1
Ethanol	0.25	0.011	2.44	31	6.8
None	...	0.025	0.90	116	8.0
Water	0.21	0.025	2.56	25	7.3
None	...	0.050	1.37	22	7.9
Water	0.25	0.050	3.89	4	7.5
BTMAH[d]	8.0×10^{-6}	0.050	26.0	0.8	9.2
None	...	0.090	1.74	12	8.1
Water	0.10	0.090	2.60	7.3	7.8
$(C_2H_5)_3N$	8.3×10^{-6}	0.090	4.67	3	6.9
DTBMP[e]	0.029	0.082	0.04	18.0	0.37

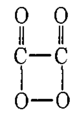
[a] Reactions with 0.010 *M* bis(2,4-dinitrophenyl) oxalate (DNPO) and 6×10^{-4} *M* 9,10-diphenylanthracene (DPA) in dimethyl phthalate at 25°. [b] Time required for three-quarters of light emission. [c] Based on DNPO. [d] Benzyltrimethylammonium hydroxide added as a 40% solution in methanol. [e] 2,6-Di-*t*-butyl-4-methylphenol.

Comparison of Intensity Decay with Ester Disappearance. An attempt was made to follow the disappearance of ester carbonyl absorption at 1806 cm^{-1} in a reaction of 0.020 *M* bis(3-trifluoromethyl-4-nitrophenyl) oxalate (TFMNPO) with 0.040 *M* hydrogen peroxide in triethyl phosphate containing 6.0×10^{-4} *M* DPA. The first observation after the reaction start, taken at 4.0 min, however, indicated an ester concentration below 0.0004 *M*; thus at least 98% of the starting ester had reacted in 4 min. However, at 4-min reaction time about 58% of the initial intensity remained as determined in a concurrent experiment. Moreover, about 75% of the total light emission appeared after the 4-min reaction time where the ester is essentially absent. It is clear that ester disappearance is substantially more rapid than intensity decay, and that a metastable chemiluminescent reaction intermediate must exist. Since other carbonyl bands were not observed between 1700 and 1800 cm^{-1} at the 4-min reaction time, it would appear that this metastable intermediate is not a simple peroxy acid or diacyl peroxide.[7a]

The possibility that the intermediate might be 1,2-dioxetanedione (V), however, was not ruled out. 1,2-Dioxetanedione would be expected to absorb near 1885 cm^{-1} [7b,c] by analogy with octadecyl ketone dimer (IV), and this spectral region was observed by serious solvent absorption in our experiments. An effort is being made to find a satisfactory reaction solvent with improved transparency.



IV



V

Effect of Delayed Fluorescer Addition. The relationship between the chemiluminescent intermediate and the fluorescer was investigated in a series of experiments where DPA was added at varying intervals to mixtures of DNPO and hydrogen peroxide in dimethyl phthalate. The results are summarized in Table VI. It is evident that substantial light emission occurs even when DPA addition is delayed as much as 70 min, while when the fluorescer is added initially to the same system less than

Table VI. Effect of Delayed Fluorescer Addition in DNPO-H_2O_2 Reactions[a]

Fluorescer addition time,[b] min	Quantum yield, einsteins mole × 10^2	Relative quantum yield, %	Relative quantum[c] yield in standard reaction, %
0	7.9	100	100
27	6.0	79	27
70	4.2	53	<2

[a] Reaction of 0.01 *M* bis(2,4-dinitrophenyl) oxalate (DNPO), 0.082 *M* hydrogen peroxide, and 6×10^{-4} *M* 9,10-diphenylanthracene in dimethyl phthalate at 25°. [b] Elapsed time between the combination of ester with hydrogen peroxide and the addition of fluorescer. [c] Per cent of light emitted beyond indicated time when fluorescer is present initially.

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(7) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964: (a) p 256; (b) p 241; (c) p 379.

2% of the emission occurs beyond 70 min. Similar results were obtained in triethyl phosphate where ester disappearance was complete in 6 min. It is again clear that a chemiluminescent intermediate exists and that it is reasonably long-lived in the absence of fluorescer. It is also clear that the fluorescer acts as a catalyst for the decomposition of the chemiluminescent intermediate, presumably in the excitation step.

Detection of a Volatile Intermediate. In a series of experiments rapid streams of argon, nitrogen, or oxygen were passed through reaction mixtures of DNPO and hydrogen peroxide in dimethyl phthalate (DMP). Such gas streams were then conducted by 1-3 ft of Pyrex tubing into solutions of 9,10-diphenylanthracene or rubrene in DMP. Irrespective of the gas used, bright, short-lived chemiluminescence was observed where the gas streams contacted the fluorescer solutions. The color of emission was characteristic of the normal fluorescence from the fluorescer used. Light was not observed when gas streams were passed through solutions of DNPO alone into solutions of rubrene and hydrogen peroxide, indicating the absence of starting material entrainment. Moreover, as discussed earlier, DNPO is consumed within about 6 min in the presence of hydrogen peroxide under the conditions used, while gas passed through DNPO-hydrogen peroxide reaction mixtures continued to generate light when passed into rubrene solutions for at least 1 hr. It is evident from the results that a reasonably volatile chemiluminescent intermediate is formed from DNPO and hydrogen peroxide. Attempts to characterize this intermediate by gas phase infrared or mass spectrometric analyses, however, have been unsuccessful; only carbon dioxide has been detected. A volatile chemiluminescent material has also been observed in the reaction of oxalyl chloride with hydrogen peroxide.[2]

The Reaction Products. The gaseous products from a reaction of 0.010 *M* DNPO with 0.50 *M* H_2O_2 and 5.6×10^{-4} *M* DPA were collected under reduced pressure in a system of known volume and analyzed by mass spectroscopy. Carbon dioxide (0.0138 mole, 69% of oxalate carbon) and carbon monoxide (0.00094 mole, 4.7% of oxalate carbon) were found. About 26% of oxalate carbon was thus not accounted for. Less than 0.0002 mole of oxygen was found. Since the quantum yield, 8.1×10^{-2} einstein mole^{-1}, was more than four times the oxygen yield it appears that oxygen is not a product of the chemiluminescent process.

In a separate experiment, infrared spectroscopic analysis of the liquid phase reaction mixture in triethyl phosphate indicated an essentially quantitative yield of 2,4-dinitrophenol. Coulometric titration of the bis(pentafluorophenyl) oxalate reaction mixture in dimethyl phthalate also showed a quantitative yield of pentafluorophenol. Oxalic acid was not detected.

An Attempt to Excite DPA with Singlet Oxygen. It has been suggested recently that (excited) singlet oxygen may play a general role in peroxide-derived chemiluminescent reactions.[8] It has been shown that singlet oxygen is a product from heterolytic peroxide decompositions,[8-11] and it has been shown that several singlet oxygen molecules may act in concert to produce radiation of substantially greater energy than possible from a single excited oxygen molecule.[12] The reasonable suggestion was thus made that peroxide-based chemiluminescence may involve the formation of singlet oxygen, followed by fluorescer excitation by a multiple of singlet oxygen molecules.[8]

Little oxygen was found, however, in oxalic ester chemiluminescent reactions. Moreover, singlet oxygen would be expected to react with DPA or rubrene to give the corresponding transannular peroxides rather than excited fluorescer.[10,11] Nevertheless in view of our observation of a volatile intermediate, it was considered desirable to provide direct evidence concerning the possible involvement of singlet oxygen. Singlet oxygen was generated from bromine and aqueous alkaline hydrogen peroxide according to the method of McKeown and Waters[11] and was allowed to bubble up through an immiscible solution of 0.001 *M* DPA in chlorobenzene. Direct contact between bromine and the organic phase was avoided. The strong red chemiluminescence typical of singlet oxygen was clearly evident; the blue emission characteristic of DPA, however, was not seen. Since red emission was not seen in oxalic ester-hydrogen peroxide reactions in the absence of fluorescer, and since only blue emission is seen in the presence of DPA, we conclude that oxalic ester chemiluminescence does not involve singlet oxygen.

Discussion

It appears evident that the chemiluminescent reactions of oxalyl chloride,[2,3] oxalic anhydrides,[4] and electronegatively substituted oxalic esters with hydrogen peroxide and fluorescers are members of a general class of chemiluminescent reactions involving peroxyoxalate intermediates. We suggest the term "peroxyoxalate chemiluminescence" as a generic name for these systems. It is clear from the high quantum yields obtained that certain peroxyoxalate derivatives are exceptionally able to accommodate the conversion of chemical energy to electronic excitation energy required in chemiluminescence. The different members of the class, however, have substantially different properties, suggesting that the reaction mechanisms differ significantly in detail depending on the oxalic acid derivative and the reaction conditions. Thus: (1) the quantum yield increases with increasing hydrogen peroxide over a broad range of H_2O_2:oxalyl chloride ratios but is independent of the hydrogen peroxide: oxalic ester ratio; (2) the oxalyl chloride reaction proceeds under acidic conditions,[2,3] while the oxalic ester reaction requires neutral or alkaline conditions; (3) chemiluminescent intermediates in the oxalyl chloride reaction are short-lived even in the absence of fluorescer, but the active intermediate in the oxalic ester reaction has an appreciable lifetime in the absence of

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(8) A. U. Khan and M. Kasha, *J. Am. Chem. Soc.*, **88**, 1574 (1966).

(9) E. J. Bowen and R. A. Lloyd, *Proc. Roy. Soc.* (London), 463 (1963); A. U. Khan and M. Kasha, *J. Chem. Phys.*, **39**, 2105 (1963); *Nature*, **203**, 1063 (1964); R. J. Browne and E. A. Ogryzlo, *Proc. Chem. Soc.*, 117 (1964); R. A. Lloyd, *Trans. Faraday Soc.*, **61**, 2173 (1965).

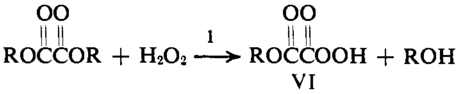
(10) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879, 3808 (1964); E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

(11) E. McKeown and W. A. Waters, *J. Chem. Soc.*, *B*, 1040 (1966).

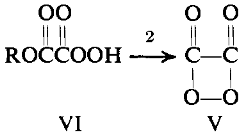
(12) S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, 40, 1769 (1964); L. W. Bader and E. A. Ogryzlo, *Discussions Faraday Soc.*, 37, 46 (1964); H. Stauff, H. Schmidkunz, and G. Hartmann, *Nature*, **198**, 281 (1963); J. S. Arnold, R. J. Browne, and E. A. Ogryzlo, *Photochem. Photobiol.*, **4**, 963 (1965); H. H. Seliger, *J. Chem. Phys.*, **40**, 3133 (1964).

fluorescer; (4) water is required for chemiluminescence in the oxalyl chloride reaction in ether solution,[3] but added water appears to have little effect on the quantum yields of oxalyl chloride[3] or oxalic ester reactions in dimethyl phthalate solution.

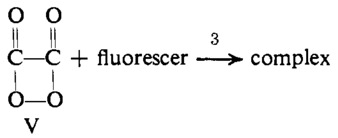
The mechanism of the oxalic ester chemiluminescent reaction is clearly complex, and the presently available evidence does not permit a definitive mechanism proposal. We are, however, currently considering the mechanism in terms of the following working hypothesis.



$$\overset{\mathrm{OO}}{\overset{\|\,\|}{\mathrm{ROCCOR}}} + H_2O_2 \xrightarrow{1} \underset{\mathrm{VI}}{\overset{\mathrm{OO}}{\overset{\|\,\|}{\mathrm{ROCCOOH}}}} + \mathrm{ROH} \qquad (3)$$



$$\underset{\mathrm{VI}}{\overset{\mathrm{OO}}{\overset{\|\,\|}{\mathrm{ROCCOOH}}}} \xrightarrow{2} \underset{\mathrm{V}}{\mathrm{C(=O)\!-\!C(=O)\!-\!O\!-\!O}} \qquad (4)$$



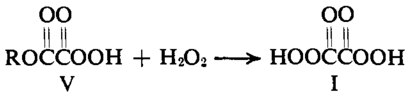
$$\underset{\mathrm{V}}{\mathrm{C(=O)\!-\!C(=O)\!-\!O\!-\!O}} + \mathrm{fluorescer} \xrightarrow{3} \mathrm{complex} \qquad (5)$$

$$\mathrm{complex} \xrightarrow{4} 2CO_2 + {}^1\mathrm{fluorescer} \qquad (6)$$

$${}^1\mathrm{fluorescer} \xrightarrow{5} \mathrm{fluorescer} + \mathrm{light} \qquad (7)$$

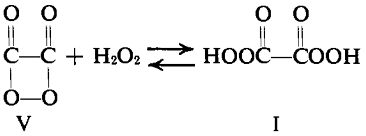
Step 1 in the tenative mechanism is analogous to the rapid reaction between hydrogen peroxide and 4-nitrophenyl acetate.[13] Monoperoxide VI, we suggest, might undergo an intramolecular nucleophilic displacement reaction to give 1,2-dioxetanedione (V) in step 2. Cyclic peroxide V might in turn form a charge-transfer complex with the fluorescer in step 3, and decomposition of the complex would form the emitting singlet excited fluorescer in step 4.

Intermediate VI cannot, itself, be the long-lived chemiluminescent intermediate since, given ample time, it would react with excess hydrogen peroxide to give diperoxyoxalic acid (I) (eq 8) in a reaction analogous to step 1.



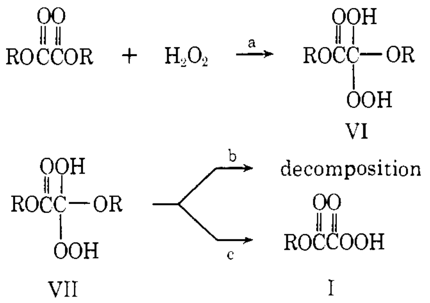
$$\underset{\mathrm{V}}{\overset{\mathrm{OO}}{\overset{\|\,\|}{\mathrm{ROCCOOH}}}} + H_2O_2 \longrightarrow \underset{\mathrm{I}}{\overset{\mathrm{OO}}{\overset{\|\,\|}{\mathrm{HOOCCOOH}}}} \qquad (8)$$

Diperoxyoxalic acid (I), in turn, cannot itself be a unique key intermediate since this would require a 2:1 H_2O_2:ester stoichiometry rather than the 1:1 stoichiometry actually observed. Moreover, infrared carbonyl absorption bands expected for intermediates VI or I were not observed in delayed fluorescer experiments. The suggestion that V, rather than VI or I, is the key chemiluminescent intermediate, would also account for the poor quantum yields obtained with organic hydroperoxides, since peroxyesters corresponding to I could not cyclize in step 2. (It appears, however, that such oxalic peresters can produce minor light emission by a different mechanism.) The observation of a volatile chemiluminescent intermediate is also in agreement with structure V and contrary to structures VI and I. It is not clear, however, why V would remain stable relative to I in the presence of excess hydrogen peroxide (eq 9), as the present evidence would appear to require.



$$\underset{\mathrm{V}}{\mathrm{C(=O)\!-\!C(=O)\!-\!O\!-\!O}} + H_2O_2 \rightleftharpoons \underset{\mathrm{I}}{\overset{\mathrm{O\;O}}{\overset{\|\;\|}{\mathrm{HOOC\!-\!COOH}}}} \qquad (9)$$

It is evident from the effect of ester structure on quantum yield that a nonchemiluminescent reaction must compete with steps 1 or 2 in reactions with poorly efficient esters. Increasing reactivity of the ester toward nucleophilic displacement of phenol by hydrogen peroxide could increase quantum yields by increasing the rate of eq 3 or 4 (or eq 8 and 9) relative to nonnucleophilic competitive steps. A possible competitive nonchemiluminescent reaction is shown in eq 10.



(10)

Intermediate VII from reaction of the ester with hydrogen peroxide[14] might undergo a radical decomposition process (eq 10) in competition with the normal elimination of phenolate in eq 10. Thus increasing electronegativity of the leaving phenolate group would facilitate step c relative to step b and increase the quantum yield. Decomposition of an intermediate similar to VII has been suggested by Milburn and Taube.[15]

The suggestion of charge-transfer complex formation in step 3 (eq 5) accommodates the observed catalysis of the decomposition of the intermediate by the fluorescer. This suggestion implies that conversion of chemical energy to electronic excitation energy in step 4 (eq 6) is more probable than the conversion of chemical energy to vibrational excitation energy in the noncatalyzed decomposition of II. This may reflect a relatively low probability for decomposition reactions leading to high vibrationally excited states of small molecules. Other experiments bearing on the mechanism of the chemiluminescent process are in progress.

The differences between oxalyl chloride, oxalic anhydride, and oxalic ester chemiluminescent reactions must be derived in part from (1) the different reactions which form the active peroxyoxalate intermediate, (2) different competing nonluminescent side reactions, and (3) the different reaction conditions employed. It is possible, in spite of their differences, that all three reactions involve a common intermediate. However, peroxyoxalate intermediates such as II, III, and V all appear capable of fluorescer excitation from other evidence,[6] and we suggest that the predominant intermediate may vary with the starting material and reaction conditions.

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[13] W. P. Jencks, *J. Am. Chem. Soc.*, **80**, 4585 (1958).

[14] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

[15] R. M. Millburn and H. Taube, *J. Am. Chem. Soc.*, **81**, 3515 (1959).

Table VII. Purification and Elementary Analysis of Oxalic Esters

Oxalate ester	Yield, %	Mp or bp, °C (mm)	Recrystn solvent	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Halogen, % Calcd	Halogen, % Found
Bis(2-nitrophenyl)	48	186.8	CH_2Cl_2	50.61	50.90	2.43	2.61	8.43	8.50	...	...
Bis(4-nitrophenyl)	66	240–242[a]	CH_3COOEt	50.61	50.30 50.64	2.43	2.78 2.87	8.43	8.40	...	...
Bis(4-nitro-3-trifluoromethyl)	73	186–189	CH_2Cl_2	41.04	41.65	1.29	1.50 1.37	5.98	6.23	24.35	24.11
Bis(4-nitro-2-formylphenyl)	83	213.5–215 dec	C_5H_5Cl	49.50	49.28	2.08	2.19	7.23	7.43	...	...
Bis(4-nitro-2,6-dichlorophenyl)	62	223.5–224.5	$CHCl_3$–Et_2O	35.78	35.84	0.86	1.16	5.96	5.88	...	...
Bis(2,4-dinitrophenyl)	38	192–194	$C_6H_5NO_2$ or EtOAc	39.83	39.97	1.43	1.65	13.27	13.47	...	...
Bis(2,5-dinitrophenyl)	66	270–274 dec	$C_6H_5NO_2$	39.83	40.27	1.43	1.63	13.27	12.88	...	...
Bis(2,4-dichlorophenyl)	38	140–141.5 dec[b]	Pet. ether	44.25	44.41	1.59	1.69	...	...	37.32	37.65
Bis(pentachlorophenyl)	65.5	228–234[c]	C_6H_5Cl	28.66	28.60	...	...	...	...	60.43	60.67
Bis(pentafluorophenyl)	74	170–172	CH_2Cl_2	39.83	40.27 39.93	...	...	...	...	45.01	44.71
Bis(3-trifluoromethylphenyl)	20	53–56	Pet. ether	50.81	50.86	2.13	2.22	...	...	30.14	29.53
Bis(3,5-di(trifluoromethylphenyl)	38.5	108–109	Pet. ether	42.04	41.70	1.18	1.37	...	...	44.34	44.15
Bis(2,6-dimethylphenyl)	15	126–126.5	...	72.46	71.83	6.08	6.11	...	...	...	...
Bis(4-methoxyphenyl)	56	157–159	C_6H_6	63.57	63.84	4.67	4.76	...	...	...	...
Diphenyl	53	133–134[d]	...	...	...	...	...	...	...	...	...
o-Phenylene	24	187–189	...	58.55	58.38	2.46	2.76	...	...	...	...
Bis(2-naphthyl)	60	187–189[e]	...	77.18	76.92	4.12	4.12	...	...	...	...
Di-*t*-butyl	59	70–71[f]	...	59.39	59.13	8.97	8.81	...	...	...	...
Bis(2-cyano-2-propyl)	53	189–190.5	C_6H_6	53.57	53.87	5.39	5.33	12.49	12.28	...	...
Bis(2,2,2-trifluoroethyl)	44	44–45 (1.8)		28.36	28.50	1.58	1.83	...	...	44.86	44.39
Bis(diphenylmethyl)	81	142–143	C_6H_6	...	...	...	...	...	...	...	...

[a] Mp 264–265° (dioxane) reported by Ya. N. Ivashchenko, V. P. Akkerman, and S. D. Moschitskii, *Zh. Obsch. Khim.*, **33**, 3829 (1963). [b] Mp 144–145° reported by J. W. Baker and I. Schumaker, *J. Chem. Eng. Data*, **9**, 584, (1964). [c] Mp 236–238° reported by J. W. Baker and I. Schumaker, *ibid.*, **9**, 584, (1964). [d] Mp 134° reported by J. Miksic and Z. Pinterovic, *J. Prakt. Chem.*, **119**, 231 (1928). [e] Mp 188–189° reported by R. Adams and H. Gilman, *J. Am. Chem. Soc.*, **37**, 2716 (1915). [f] Mp 69–70.9° reported by G. J. Karabatsos, J. M. Corbett, and K. L. Krumel, *J. Org. Chem.*, **30**, 689 (1965).

Experimental Section

Materials. Dimethyl phthalate, triethyl phosphate, and triethylamine were fractionally distilled. Oxalyl chloride and the phenols (Eastman or Aldrich) were used as received except 2,6-di-*t*-butyl-4-methylphenol (Koppers Co.) which was sublimed to obtain material melting at 69–70° (lit.[16] mp 69–70°). 9,10-Diphenylanthracene (Aldrich) was recrystallized from a mixture of absolute ethanol and chloroform to obtain material, mp 250–251° (lit.[17] mp 250–251°). Rubrene (Eastman) was not repurified. 4-Butylamino-N-butyl-1,8-naphthalimide was obtained from Dr. F. Loffelman[18] and was recrystallized from methanol to obtain material, mp 126–128°.[18] Hydrogen peroxide solutions were prepared from the 98% reagent (Becco Chemical Division, FMC Co.) and were analyzed iodometrically;[19] stock solutions were 0.78 *M* to 1.65 *M*.

Oxalic Esters. Bis(2,4-dinitrophenyl) Oxalate (DNPO). A solution of 368.2 g (2 moles) of 2,4-dinitrophenol in 5 l. of reagent grade benzene was dried by azeotropic distillation of 1 l. of solvent. The dried solution was cooled to 10° under nitrogen, and 202.4 g (2 moles) of freshly distilled triethylamine was added. Oxalyl chloride (139.6 g; 1.1 moles) was then added with stirring during 30 min using an ice bath to maintain the reaction temperature between 10 and 25°.

The resulting yellow slurry was stirred 3 hr and evaporated to dryness under reduced pressure. The solid was stirred well with 1 l. of chloroform to dissolve triethylamine hydrochloride, and the product was collected on a sintered-glass funnel, washed with chloroform, and dried under vacuum.

Recrystallization from nitrobenzene below 100° provided 151.3 g (35.8%) of pale yellow crystals, mp 189–192°.

With the exceptions noted below, other oxalate esters were prepared by essentially the same procedure (Table VII).

Bis(2,4-dichlorophenyl) Oxalate. The reaction mixture was refluxed for 4.5 hr to assure completion. Since the product is soluble in chloroform, triethylamine hydrochloride was removed by washing the crude product with water prior to recrystallization from petroleum ether.

Bis(pentafluorophenyl) Oxalate. The reaction mixture was refluxed for 20 min to assure completion of the reaction. The product was recrystallized from chlorobenzene–ether (1:1).

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(16) T. W. Campbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **74**, 1479 (1952); C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 3233 (1955); L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 3570 (1962).

(17) G. Wittig and R. W. Hoffman, *Ber.*, **95**, 2718 (1962).

(18) See M. Scalera and A. W. Joyce, U. S. Patent 2,415,373 (1947).

(19) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The MacMillan Co., New York, N. Y., 1948, p 630.

Di-*t*-butyl Oxalate. The procedure of Karabatsos, Corbett, and Krumel was used.[20]

Bis(diphenylmethyl) oxalate, bis(2,6-dimethoxyphenyl) oxalate, bis(4-methoxyphenyl) oxalate, bis(2-naphthyl) oxalate, diphenyl oxalate, and *o*-phenylene oxalate were prepared in anhydrous ether. The crude products were washed with water to remove triethylamine hydrochloride and were dried.

Gaseous Products from the Reaction of Bis(2,4-dinitrophenyl) Oxalate (DNPO), Hydrogen Peroxide, and 9,10-Diphenylanthracene (DPA). The reactions were carried out in a magnetically stirred three-necked flask equipped with a gas sample bulb, a pressure-equalized dropping funnel, a differential manometer, and a connection to a vacuum pump. The total volume of the system was 180 ml. The hydrogen peroxide and DPA solutions were placed into the flask and the DNPO solution into the funnel. The concentrations were designed to produce after mixing a solution 1×10^{-2} *M* in DNPO, 5×10^{-2} *M* in H_2O_2, and 5.6×10^{-4} *M* in DPA. The system was evacuated and isolated from the pump by a vacuum stopcock, and the solutions were stirred. This degassing procedure was repeated several times until no pressure change was observed on 30-min standing. Then the solutions were mixed under vacuum (less than 0.1 mm) and the reaction was continued until the pressure became constant. A sample of the gaseous products was analyzed with Consolidated Engineering Co. 21-103A and 21-110 mass spectrometers. The latter instrument can readily distinguish nitrogen from carbon monoxide. The gas sample contained CO_2, CO, and traces of oxygen and water, but no atmospheric contamination.

Chemiluminescence Emission Measurements. Procedures and instrumentation for the determinations of absolute emission intensities, spectra, and quantum yields have been described previously;[3] chemiluminescent reactions were initiated by injecting an aliquot of stock hydrogen peroxide solution from an all-glass syringe into the combined aliquots of the other reactants in a stirred 3-ml, cylindrical cuvette attached to a spectroradiometer. The raw intensity data from the radiometer was converted to einsteins sec^{-1} ml^{-1} by a Scientific Data 925 computer programmed with the calibration data.

Infrared Spectroscopic Studies. Procedures. Spectra were measured with a Perkin-Elmer 221 grating instrument using a compensated cell technique with a pair of stoppered 0.5-mm, NaCl cavity cells. Aliquots of stock solutions of ester, DPA, and H_2O_2 were mixed, the H_2O_2 always being added last, and the timer was started with peroxide addition. An aliquot of the reaction mixture was then transferred to the infrared cell *via* a Pyrex dropper, and the spectrum of the reaction was recorded between 1900 and 1500 cm^{-1} at the slowest speed of the instrument. When the desired portion of the spectrum had been taken, the sample cell was removed from the instrument, cleaned, and refilled with a fresh aliquot of the test solution, and another spectrum was recorded. Spectra were recorded in this manner until no further change in the spectrum with time was observed. In a separate set of experiments it was established that Beer's law holds for TFMNPO (bis(3-trifluoromethyl-4-nitrophenyl) oxalate) in the concentration range used in these experiments (see Table VIII).

Table VIII. Stoichiometry of TFMNPO–H_2O_2 Reaction in TEP[a]

TFMNPO, moles/l.	H_2O_2, moles/l.	DPA, moles/l. × 10^4	Absorbance at 1806 cm^{-1} 0.5-mm cell	Remaining TFMNPO, %
0.020	None	0	0.400M	100
0.020	0.010	0	0.175	44
0.020	0.010	6.0	0.175	44

[a] The solvent triethyl phosphate (TEP) contained water equivalent to 2.8×10^{-3} *M*. The reaction temperature was 25°.

Acknowledgments. Research reported in this publication was supported by the Advanced Research Projects Agency under contract to the Office of Naval Research. We gratefully acknowledge our great debt to the late Dr. Robert C. Hirt who designed the spectroradiometer used in this study. Coulometric titration of phenols was developed and carried out by Dr. C. A. Streuli. Infrared analyses were carried out with Mr. N. B. Colthup. Mass spectrometric analyses were carried out under the direction of Mr. T. E. Mead. Microelemental analyses were carried out under the direction of Mr. G. Clarke. Computer calculations were carried out under the direction of Mrs. T. O'Malley. Several quantum yield experiments with rubrene were carried out by Mr. R. Yaffe.

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(20) G. J. Karabatsos, J. M. Corbett, and K. L. Krumel, *J. Org. Chem.*, 30, 689 (1965).