

Chemiluminescence from Reactions of Oxalic Anhydrides with Hydrogen Peroxide in the Presence of Fluorescent Compounds

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Abstract: New chemiluminescent reactions of four oxalic anhydrides with hydrogen peroxide in the presence of fluorescent compounds are reported. The reaction with bis(triphenylacetic) oxalic anhydride (I) produces an emission quantum yield of 0.13 einstein mole⁻¹ and a quarter intensity lifetime of 30 min. Effects of reactant concentrations on quantum efficiency and emission lifetime are described. Thermal decomposition of anhydride I in the presence of a fluorescer was found to provide chemiluminescent emission in the absence of hydrogen peroxide or oxygen. The chemiluminescence mechanism is discussed.

Chemiluminescent reactions in general convert chemical energy into light inefficiently.¹ Quantum yields below 0.01 einstein/mole of chemical reactant are typical.² Although much effort has been directed toward the discovery of more efficient reactions such efforts have been hampered by a lack of information relating to chemiluminescence mechanisms. Mechanism studies in turn have been hindered by the low quantum efficiencies of the available reactions since the chemiluminescence process tends to be obscured by the non-chemiluminescent processes constituting the bulk of the system. Even the positive identification of the light-emitting species is often difficult because of the absence of uniquely characteristic bands in the emission spectrum.³

In spite of these difficulties substantial insight has been gained recently into the mechanism of several chemiluminescent reactions.^{1,4,5} Notable examples are the luminol,^{4a,b} oxalyl chloride,^{4c,6} and indolyl per-

oxide^{4d} reactions. The brightest of these systems is the moderately efficient (0.03–0.05 einstein mole⁻¹) and very fast (20–40 sec half-life) oxalyl chloride–hydrogen peroxide reaction in the presence of 9,10-diphenylanthracene fluorescer.^{4c} It is clear, however, that more efficient and long-lived chemiluminescent systems are needed to facilitate definitive mechanism determinations.

In our continued search for efficient, long-lived chemiluminescent reactions⁷ we have found that reactions of several oxalic anhydrides and certain oxalic esters⁸ with hydrogen peroxide in the presence of a fluorescer produce chemiluminescent light emission with exceptionally high quantum efficiencies.

Results

Reactions of four mixed oxalic anhydrides (0.01 *M*) with 0.05 *M* hydrogen peroxide and 6×10^{-4} *M* 9,10-diphenylanthracene (DPA) in 1,2-dimethoxyethane (DME) were examined qualitatively for chemiluminescence. The anhydrides are listed below in the order of decreasing light output: bis(triphenylacetic) oxalic anhydride (I) \approx diacetic oxalic anhydride (II) > bis(4-methoxybenzoic) oxalic anhydride (III) >>> dibenzoic oxalic anhydride (IV). All four reactions were accelerated by base as indicated by increased intensity and decreased lifetime.

Anhydride I was selected for more detailed quantitative studies. The spectral distribution of chemiluminescence was found to be essentially identical with the fluorescence spectrum of 9,10-diphenylanthracene (DPA) indicating that the first singlet excited state of the fluorescer is the chemiluminescent emitter. A typical intensity decay curve is shown in Figure 1. In general, the light intensity increases rapidly after mixing and reaches a maximum in 4–6 min.⁸

Under most conditions the decay of light intensity from the maximum is rapid initially and then slows to an exponential decay. An arbitrary quantity, $t_{1/4}$ (time required for the light intensity to decay to one-quarter of its maximum value), was chosen to permit the comparison of emission lifetimes.

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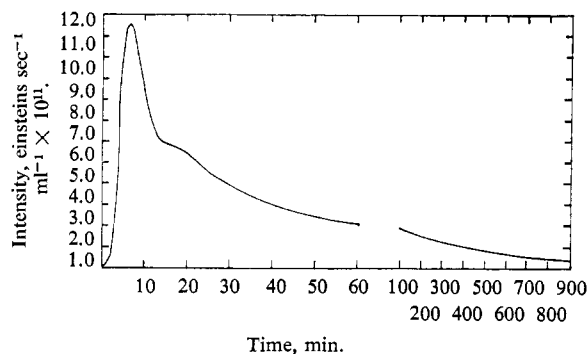


Figure 1. Intensity decay from reaction of $5.67 \times 10^{-3} M$ TPAO, $0.050 M$ H_2O_2 , and $5 \times 10^{-4} M$ DPA in DMP at 25° .

Effects of reactant concentrations on the quantum efficiency are summarized in Table I. Increasing anhydride concentration or a large excess of hydrogen

Table I. Chemiluminescence from Bis(triphenylacetic) Oxalic Anhydride (TPAO)^a

[TPAO], $M \times 10^2$	[H_2O_2], $M \times 10^2$	[DPA], ^b $M \times 10^4$	Max int, ^c 10^{10} einsteins $sec^{-1} ml^{-1}$	$t_{1/4}$, ^d min	Quantum yield, ^e 10^2 einsteins $mole^{-1}$
0.453	50.0	5.0	2.78	24.5	6.8
0.567	5.0	5.0	1.16	44.0	11.8
0.567	25.0	1.7	1.04	56.0	4.6
0.567	25.0	5.0	3.70	17.0	7.1
0.567	25.0	13.0	5.38	6.8	8.3
0.567	50.0	5.0	1.89	6.0	5.6
1.288	6.37	5.2	13.02	2.4	8.4
0.52 ^f	7.50	10.0	0.10	310	4.6
4.94 ^f	4.50	10.0	0.50	155	0.65
4.94 ^{f,g}	31.5	10.0	0.55	>300	1.2

^a Reactions at 25° in dimethyl phthalate except for *f*. ^b DPA is 9,10-diphenylanthracene. ^c Total spectrally and geometrically integrated intensity. ^d Time required for intensity to decay to one-fourth of the maximum intensity. ^e Quantum yield based on TPAO. ^f The solvent was 25 vol. % dimethyl phthalate in benzene. ^g H_2O_2 added in seven equal portions keeping intensity above 25% of its maximum.

peroxide (above a 5:1 mole ratio) decreased the quantum yield, whereas increasing DPA concentration increased the quantum yield. The light decay rate was increased by higher concentrations of all three reactants.

The effect of various additives on the chemiluminescent reaction is illustrated in Table II. Oxygen was without significant effect, but the addition of the free-radical chain inhibitor 2,6-di-*t*-butyl-4-methylphenol⁹ or the peroxide decomposer sodium diethyl dithiocarbamate¹⁰ decreased the quantum yield sharply. Small amounts of added water left the quantum yield unaffected but increased the rate of light decay moderately.

The effect of hydrogen peroxide concentration on the quantum efficiency was measured under conditions ranging from excess anhydride to excess hydrogen peroxide in an effort to examine the stoichiometry of the

Table II. The Effect of Various Additives on Chemiluminescence from Bis(triphenylacetic) Oxalic Anhydride (TPAO)^a

Additive	[TPAO], $M \times 10^2$	Max int, ^b 10^{10} einsteins $sec^{-1} ml^{-1}$	$t_{1/4}$, ^c min	Quantum yield, ^d 10^2 einsteins $mole^{-1}$
None ^e	0.453	2.78	24.5	6.8
Oxygen (saturated solution, $\sim 10^{-3} M$)	0.453	2.78	22.0	6.6
Sodium diethyldithiocarbamate ($1 \times 10^{-3} M$)	0.453	0.0
Water, $5 \times 10^{-3} M$	0.453	3.48	17.1	6.8
None ^f	1.16	26.9	5.5	7.5
2,6-Di- <i>t</i> -butyl-4-methylphenol ($1.5 \times 10^{-3} M$) ^f	1.16	12.5	1.5	1.1

^a Reactions with $0.5 M$ H_2O_2 and $5.0 \times 10^{-4} M$ 9,10-diphenylanthracene in dimethyl phthalate (except *f*) at 25° . Reactions in air except for *e*. ^b Total spectrally and geometrically integrated intensity. ^c Time required for intensity to decay to one-fourth of the maximum intensity. ^d Quantum yield based on TPAO. ^e Solution degassed and used under argon. ^f Solvent was 1,2-dimethoxyethane.

Table III. The Effect of Hydrogen Peroxide Concentration on the Chemiluminescence Quantum Yield^a

[H_2O_2], $M \times 10^2$	H_2O_2 /anhydride	Quantum yield, 10^2 einstein per mole of TPAO	H_2O_2
0.12	0.21	3.6	17.0
0.24	0.42	4.7	11.1
0.42	0.71	6.8	9.2
0.60	1.06	7.4	7.0
0.80	1.41	10.4	7.3
1.40	2.48	11.1	4.5
2.80	4.95	13.3	2.7
5.61	9.90	9.4	0.95
22.70	40.0	5.9	0.15

^a Reaction of $5.67 \times 10^{-3} M$ bis(triphenylacetic) oxalic anhydride and $5 \times 10^{-4} M$ 9,10-diphenylanthracene in dimethyl phthalate at 25° .

reaction. Results summarized in Table III indicate that the quantum yield based on hydrogen peroxide increases with decreasing hydrogen peroxide even at very low hydrogen peroxide:anhydride ratios where hydrogen peroxide is the limiting reactant, while the quantum yield based on anhydride reaches a maximum at a ratio of about 5:1. It appears from these results that a moderate excess of hydrogen peroxide is required to minimize the fraction of total anhydride diverted into nonchemiluminescent side reactions, while at the same time excess hydrogen peroxide favors other nonchemiluminescent processes. The observed results indicate a complex stoichiometry and a varying importance of dark side reactions as the hydrogen peroxide concentration is changed.

Most organic chemiluminescent reactions in solution, aside from electron transfer chemiluminescence,¹¹ in-

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volve oxygen or a peroxide as an essential reactant.¹ We found, however, that the thermal decomposition of I at temperatures above 170° in the presence of 9,10-diphenylanthracene (DPA) produced chemiluminescent emission in the absence of oxygen. Although this thermal reaction provided weaker light intensities than the reaction with hydrogen peroxide, it represents a rare peroxide-free chemiluminescent system.

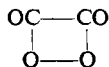
The thermal stability and hydrolytic reactivity of the four anhydrides differ substantially. Bis(triphenylacetic) oxalic anhydride (I) is fairly stable at room temperature in both solid form and in benzene solution. Pyridine catalyzes a nonchemiluminescent decomposition of I to triphenylacetic anhydride, while triphenylacetic acid is without effect. Diacetic oxalic anhydride decomposes rapidly even at 0° in agreement with Edwards and Henley's observation.¹² The decomposition is catalyzed by bases such as potassium acetate and pyridine but is unaffected by the free-radical inhibitor 2,6-di-*t*-butyl-4-methylphenol.⁹

Discussion

It is clear from the results that the chemiluminescent reaction of bis(triphenylacetic) oxalic anhydride with hydrogen peroxide and 9,10-diphenylanthracene is substantially more efficient than previously reported chemiluminescent reactions. Thus under the best conditions found a yield of 0.13 einstein mole⁻¹ was obtained in contrast to yields approaching 0.05 einstein mole⁻¹^{4c} obtained from the oxalyl chloride reaction. It is evident that high chemiluminescence efficiency is not restricted to biological systems.

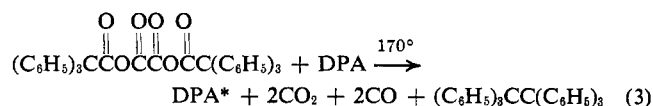
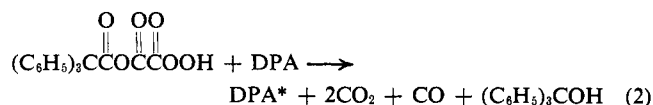
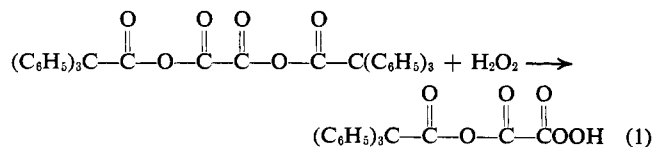
Although the chemiluminescent reaction of oxalic anhydrides with hydrogen peroxide is similar in many respects to the oxalyl chloride-hydrogen peroxide^{4c} and oxalic ester-hydrogen peroxide⁵ chemiluminescent systems, there are evident differences. In particular the effect of hydrogen peroxide concentration on anhydride chemiluminescence differs substantially from its effect on oxalyl chloride chemiluminescence (where increasing hydrogen peroxide increases the quantum yield to an asymptotic limit^{4c}) and from its effect on oxalic ester chemiluminescence (where the quantum yield based on a 1:1 stoichiometry is essentially independent of the hydrogen peroxide concentration⁵).

Mechanisms proposed for the oxalyl chloride and oxalic ester chemiluminescent reactions have suggested the formation of monoperoxyoxalic acid,^{4c} HOC(=O)-C(=O)OOH, and 1,2-dioxetanedione,⁵ respectively.



They have been suggested to decompose through a concerted bond cleavage process to provide the instantaneous energy release required for excitation of the fluorescer.¹³ Although the available evidence does not rule out either intermediate in oxalic anhydride chemiluminescence, an alternative mechanism must also be considered since concerted multiple bond

cleavage decomposition of triphenylacetyl monoperoxy oxalic acid, (C₆H₅)₃CC(=O)OC(=O)C(=O)OOH, could in principle meet the chemiluminescence energy requirement (eq 1 and 2).¹⁴ Analogously, concerted decomposition of TPOA itself (eq 3) could provide the energy release for the thermal chemiluminescence observed at 170°, although the activation energy provided under these conditions would no doubt be an important contributing factor.



Additional evidence will be required to identify the dominant mechanisms of these reactions.

Experimental Section

Materials. Solvents. Dimethyl phthalate (Eastman) was distilled under vacuum. 1,2-Dimethoxyethane (Ansul Chemical Co.) was distilled from lithium aluminum hydride under argon. Benzene (Baker & Adamson) was distilled from sodium. Residual water was determined by the Karl Fischer method.¹⁵

Anhydrous hydrogen peroxide in dimethyl phthalate was prepared from 98% hydrogen peroxide (Becco Chemical Division, FMC Corp.)¹⁶ and was assayed iodometrically.¹⁷

9,10-Diphenylanthracene (DPA) (Aldrich) was crystallized from absolute ethanol-chloroform to obtain material, mp 250–251° (lit.¹⁸ mp 250–251°).

2,6-Di-*t*-butyl-4-methylphenol (Koppers) was sublimed *in vacuo* to obtain material melting at 69–70°. Other materials were obtained from commercial sources and were purified when necessary.

Bis(triphenylacetic) Oxalic Anhydride. Triphenylacetic acid (2.889 g, 0.01 mole) and potassium hydroxide (0.6 g, 0.01 mole) were added to 300 ml of absolute ethyl alcohol in a 500-ml, one-necked flask and dissolved by boiling. The solution was cooled, and concentrated to a volume of 30 ml *in vacuo*. A white precipitate appeared and was filtered and dried in a nitrogen atmosphere to obtain 3.0 g of potassium triphenylacetate. Three grams of the acetate was slurried in 100 ml of dry benzene in a 200-ml, round-bottomed flask. Approximately 50 ml of benzene was distilled, and the condensate was checked to assure the complete removal of water from the system. The remaining slurry was cooled to room temperature under argon. Oxalyl chloride (1.48 ml, 0.015 mole) was added, and the mixture was stirred at 15 min. Using an oil pump, the mixture was filtered under argon to remove 0.9 g of solid, mostly potassium chloride. The filtrate was evaporated to dryness with an oil pump. The residue was washed with anhydrous ether in a drybox to obtain 1.9 g (60%) of white solid, mp 167–168°.

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Anal. Calcd for $C_{42}H_{30}O_8$: C, 79.98; H, 4.79; O, 15.22. Found: C, 80.60; H, 4.91; O, 15.37.

Bis(4-methoxybenzoic) Oxalic Anhydride. The procedure described above for the preparation of bis(triphenylacetic) oxalic anhydride was used. The crude product was crystallized from anhydrous ether to obtain a 7.8% over-all yield of white crystals, mp 112–113°.

Anal. Calcd for $C_{18}H_{14}O_8$: C, 60.34; H, 3.49. Found: C, 61.60; H, 4.16.

Dibenzoic Oxalic Anhydride. Sodium benzoate (7.2 g, 0.05 mole) was added to a solution of 12.7 g (0.1 mole) of oxalyl chloride in 100 ml of anhydrous ethyl acetate during 45 min. The reaction was heated at 70–73° for 3 hr and filtered to obtain 2.9 g (100%) of NaCl. Evaporation of the filtrate gave a white solid which was extracted with boiling hexane to give a hexane-insoluble solid. Benzoic acid, 2.0 g (33%), was obtained from the hexane extract. The hexane-insoluble material was crystallized from ethyl acetate-hexane to obtain 2.2 g (30%) of material, mp 98–99°. On dissolving a portion of the compound in hot water, gas was evolved, and benzoic acid (mp 121–122°, lit.¹⁹ mp 122°) was deposited from the solution on cooling.

Anal. Calcd for $C_{16}H_{10}O_8$: C, 64.43; H, 3.38; O, 32.19. Found: C, 64.19; H, 3.35; O, 32.38.

Diacetic Oxalic Anhydride.¹² Ketene, prepared by the pyrolysis of acetone²⁰ at the rate of 0.1 mole of ketene per hour, was bubbled through a stirred solution of 4.5 g (0.05 mole) of anhydrous oxalic acid in 100 ml of anhydrous ether at –50° under argon during 1.25 hr. The reaction solution was then evaporated to dryness under reduced pressure at temperatures below –5°. A white crystalline product was obtained whose infrared spectrum was in agreement with that expected. Bands characteristic of acetic anhydride or acetic acid were absent from the spectrum. The product was found to be very sensitive to moisture and to decompose at temperatures above –5°.

In a similar experiment, following completion of the reaction at –5°, the reaction mixture was maintained under a ketene atmosphere at 0° for 5.5 hr, and then analyzed by infrared spectroscopy. The resulting solution was found to contain mainly acetic anhydride together with small amounts of diacetic oxalic anhydride and acetic acid.

Determination of Chemiluminescence Spectra and Quantum Yield. A combination spectroradiometer-fluorimeter designed and calibrated under the direction of Dr. R. C. Hirt was used for the measurements.²¹ The instrument and experimental procedures have been described elsewhere.⁴⁰ (See Table IV for test results.)

Chemiluminescent Reaction of Bis(triphenylacetic) Oxalic Anhydride (I) in the Absence of Hydrogen Peroxide and Oxygen. To 15 ml of freshly distilled dimethyl phthalate, 0.3 g of anhydride I and 1 mg of 9,10-diphenylanthracene were added under argon atmosphere. After 2 hr of stirring, the slurry was centrifuged to obtain a clear, particle-free solution. The solution was degassed (three freeze-thaw cycles) under 1×10^{-4} mm pressure and was sealed into a glass tube. When the sealed tube was immersed into a 170° oil bath in a dark room readily visible blue chemiluminescent light was emitted. The light emission lasted for more than 3 min.

Infrared Study of the Solution Stability of Bis(triphenylacetic) Oxalic Anhydride in Benzene. The experiment was carried out in a drybox under an argon atmosphere. All glassware used was cleaned with chrome-sulfuric acid solution, washed with 2% aqueous ammonia and with distilled water, and dried in an oven at 110° for 1 hr.

A 0.078 M solution of bis(triphenylacetic) oxalic anhydride was prepared by shaking excess anhydride in benzene solvent for 20 min. After the undissolved material was filtered, the anhydride

Table IV. Qualitative Chemiluminescent Tests of Oxalic Anhydrides

R	Tests ^a		
	A (H ₂ O ₂)	B (H ₂ O ₂ + base)	C (H ₂ O ₂ + acid)
(C ₆ H ₅) ₃ C	VS	VS	VS
CH ₃	VS	VS	...
CH ₃ OC ₆ H ₅	MS	S	MS
C ₆ H ₅	VW	M	VW

^a The tests were carried out as follows. A: Approximately 3–5 mg of the compound to be tested is added to a 5-ml solution of about 1 mg of DPA and 0.2 ml of anhydrous H₂O₂ in anhydrous 1,2-dimethoxyethane maintained at 25°. B: Approximately 3–5 mg of the compound to be tested is added to a 5-ml slurry of 1 mg of DPA, 0.2 g of KOH (one pellet), and 0.2 ml of anhydrous H₂O₂ in anhydrous 1,2-dimethoxyethane maintained at 25°. C: Approximately 3–5 mg of the compound to be tested is added to a 5-ml solution of 1 mg of DPA and 0.2 ml CH₃SO₃H in 1,2-dimethoxyethane containing 5% water and maintained at 25°. About 0.5 ml 30% H₂O₂ is added immediately. Qualitative intensities are based on the oxalyl chloride, hydrogen peroxide reaction taken as strong (S). Other designations are M = medium; W = weak; VW = very weak, barely visible.

solution was transferred to a serum-capped bottle. Samples of the solution were withdrawn periodically by the use of a syringe and analyzed by infrared spectroscopy, measuring the absorbance of each sample at 1770 cm⁻¹ in a cell 0.0105 cm thick with a Perkin-Elmer Model 521 spectrometer. The results are summarized in Table V.

Table V. Stability of Bis(triphenylacetic) Oxalic Anhydride in Benzene at Room Temperature

Age of sample, hr	A, ^a l. mole ⁻¹ cm ⁻¹	Anhydride (% of initial concn)
5	500.6	100
70.5	483.5	96.6
94	488.4	97.6
118	482.3	96.3
142	494.5	98.8
166	488.4	97.6
238	500.6	100
334	470.1	93.9

^a Molecular absorptivity at 1770 cm⁻¹.

Decomposition of Diacetic Oxalic Anhydride. The experiments were carried out under argon with solutions of the anhydride in freshly distilled 1,2-dimethoxyethane. The reaction flasks were closed off with a mercury bubbler, fitted with serum stoppers for the withdrawal of samples, and placed in a constant temperature bath. The periodically withdrawn samples were assayed by infrared spectroscopy for diacetic oxalic anhydride at 1835, 1795, and 1767 cm⁻¹, for acetic anhydride at 890 cm⁻¹, and for acetic acid at 1740 cm⁻¹.

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