mineral oil) in 3 ml of dimethylacetamide for 15 min to 40–50°. Then 0.4 ml of methyl iodide was added, and the above temperature was maintained until this reaction mixture showed a pH of 7 (after approximately 15 min). Water was added and the aqueous phase was extracted three times with methylene chloride. The combined organic phases were dried over sodium sulfate and evaporated to dryness, and the thoroughly dried residue (240 mg) crystallized from ethyl acetate to give 120 mg (68%) of 1-methyl-4-phenyl-2(1H)-quinazolinone, mp 143°. This product was again identical in melting point, mixture melting point, thin layer chromatography, and infrared spectrum with the compound obtained under A.

Since a small amount of a less polar by-product was observed in this reaction it was repeated on a larger scale (5.2 g of **8**); most of the starting material (**8**) and the N-methyl compound (**4**) were removed from the crude mixture by crystallization, and the mother liquor (1.25 g) was chromatographed on 80 g of aluminum oxide with methylene chloride as an eluent. From the first fractions (340 mg), 2-methoxy-4-phenylquinazoline (**9**) crystallized from petroleum ether: 115 mg; mp 87–89°; typical quinazoline bands[10] in ir (CH_2Cl_2) at ν_{max} 1470, 1570, and 1615 cm^{-1}; nmr ($CDCl_3$) singlet at δ 4.20 (O-methyl).

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.3; H, 5.1; N, 11.9. Found: C, 75.9; H, 5.2; N, 11.6.

Registry No.—**1**, 17629-01-5; **2**, 17629-02-6; **3**, 17629-03-7; **4**, 17629-04-8; **5a**, 17629-05-9; **5b**, 17629-06-0; **6a**, 17629-07-1; **6b**, 17629-08-2; **9**, 17629-09-3.

Chemiluminescence from the Reaction of Phthalimido Oxalate with Hydrogen Peroxide and Fluorescent Compounds

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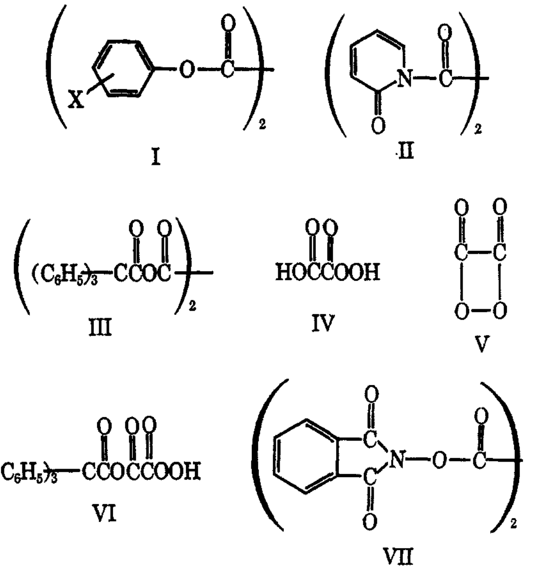
Received May 6, 1968

Chemiluminescence has been reported from a wide variety of organic reactions.[1] However, most reactions produce light with low efficiency. The quantum yields obtained from these classical reactions are below 0.01 einstein mol^{-1} the efficiency of the well known luminol reaction.[2] Unusually high emission efficiencies have been obtained from the reaction of several oxalic acid derivatives with hydrogen peroxide and fluorescent compounds. Electronegatively substituted aryl oxalates[3] (I), pyridonylglyoxals[4] (II), and certain oxalic anhydrides[5] (III) produced 0.24 0.16, and 0.14 einstein mol^{-1}, respectively, whereas oxalyl chloride[6] gave up to 0.05 einstein mol^{-1} and oxamides[7] 0.01 einstein mol^{-1}. Three peroxyoxalic acid derivatives IV, V, and VI have been suggested as intermediates depending on the oxalic acid derivative and reaction conditions.[3,5,6] The concerted multiple bond cleavage decomposition of these intermediates could release sufficient energy to excite a fluorescent compound.[8]



X is an electron-withdrawing group such as $-NO_2$, -Cl

The primary requirement for peroxyoxalate chemiluminescence appears to be an oxalic acid derivative which reacts rapidly with hydrogen peroxide. However, not all reactive oxalates produce equal emission efficiency probably due to the different competing dark side reactions and possible quenching by-products. Therefore, to further examine these points and to broaden the scope of peroxalate chemiluminescence we prepared diphthalimido oxalate VII.

Esters of N-hydroxyphthalimide react rapidly with amino acid esters and are useful intermediates of peptide synthesis.[9] Thus, diphthalimido oxalate might be expected to react readily with hydrogen peroxide and could conceivably give chemiluminescence in the presence of a fluorescer.

Preliminary qualitative experiments indicated that VII indeed produced chemiluminescent light on reaction with hydrogen peroxide and 9,10-diphenylanthracene in dimethyl phthalate solution. The light intensity was increased by bases and quenched by strong acids. A similar base–acid effect was observed in connection with the oxalic ester reaction.[3] A good agreement of the chemiluminescence and fluorescence spectra indicates that the light-emitting species is the first singlet excited state of the fluorescer.

Absolute quantum yield measurements were carried out in dimethyl phthalate and the results are collected in Table I. A quantum yield of 0.087 einstein mol^{-1} was obtained at 1×10^{-3} *M* phthalimido oxalate in the presence of the usually inefficient fluorescer 9,10-diphenylanthracene[3–5] [bis(2,4-dinitrophenyl)oxalate

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TABLE I

QUANTUM YIELD OF THE PHTHALIMIDO OXALATE REACTION[a]

Phthalimido oxalate, $M \times 10^2$	H_2O_2, $M \times 10^2$	I_{max}, ft lambert cm^{-1}	$t^1/_4$,[b] min	Quantum yield,[c] einstein mol^{-1} × 10^2
0.1	2.4	0.01	94.0	8.7
0.1[d]	3.4	0.04	6.7	2.6
1.0	2.4	0.01	307.0	2.3
1.0[d]	3.4	0.09	10.1	1.4
1.0	9.0	0.01	269.0	1.9
1.0[e]	9.0	0.03	169.0	2.7
1.0[f]	9.0	0.04	184.0	4.3

[a] In the presence of 6×10^{-4} *M* 9,10-diphenylanthracene in dimethyl phthalate solution at 25°. [b] The time of light decay from maximum to one-quarter intensity. [c] Based on phthalimido oxalate. [d] In 1,3-propylene carbonate. [e] 1×10^{-1} *M* H_2O added. [f] 8.3×10^{-6} *M* Et_3N added.

produced 0.165 einstein mol^{-1} under similar conditions, and 0.29 einstein mol^{-1} with rubrene].[3]

Increasing the concentration of VII decreased the quantum yield. The addition of triethylamine or water decreased the chemiluminescent lifetime and moderated the efficiency loss. The lifetime was shorter and the reaction was less efficient in propylene carbonate solution than in dimethyl phthalate.

The results are insufficient for a definite statement about the mechanism. However, it is likely that the phthalamido oxalate reaction proceeds through a 1,2-dioxetanedione V intermediate, first proposed in connection with the aryl oxalate reaction.[3] By analogy to the phthalamido oxalate reaction, reactive oxalates of other substituted hydroxylamines and oximes should also produce chemiluminescence. Carboxylic esters of N-hydroxypiperidine and other hydroxylamines have been prepared and used in peptide synthesis.[10] We found that the reaction of an admittedly atypical oxime ester bis(heptafluorobutyramideoxime) oxalate[11] $C_3F_7C(NH_2){=}NC(O)C(O)N{=}(NH_2)CC_3F_7$ with hydrogen peroxide and fluorescer produced only weak light emission.

Experimental Section

Materials.—Dimethyl phthalate and propylene carbonate were fractionally distilled. Oxalyl chloride and N-hydroxyphthalimide (Aldrich) were used without purification. 9,10-Diphenylanthracene (Aldrich) was recrystallized from a mixture of absolute ethanol and chloroform to obtain material, mp 250–251° (lit.[12] mp 250–251°). Hydrogen peroxide solutions were prepared from the 98% reagent (Becco Chemical Division, FMC Co.) and were analyzed iodometrically.[13]

Diphthalimido Oxalate.—To a rapidly stirred solution of 1.63 g (0.01 mol) N-hydroxyphthalimide in 100 ml of freshly distilled (from $LiAlH_4$) 1,2-dimethoxyethane, 0.43 ml (0.005 mol) of oxalyl chloride and 1.4 ml of triethylamine were added at 25°. After 1-hr stirring the mixture was evaporated to dryness under vacuum and the solid residue was digested with three 30-ml portions of chloroform to obtain a white crystalline product, mp 233–234° dec, in 42% yield which showed infrared absorption at 1817, 1795, 1758, and 1735 cm^{-1} in methylene chloride solution.

Anal. Calcd for $C_{18}H_8O_8$: C, 56.85; H, 2.12; N, 7.37. Found: C, 56.79; H, 2.08; N, 7.49.

Bis(heptafluorobutyramidoxime)oxalate was prepared by the method of H. C. Brown and C. R. Wetzel,[11] mp 180–181° (acetone–ether 1:1) [lit.[11] mp 195–196° (xylene)].

Anal. Calcd for $C_{10}H_4F_{14}N_4O_4$: C, 23.54; N, 10.98; F, 52.14. Found: C, 23.54; N, 11.0; F, 52.04.

Qualitative Chemiluminescence Tests.—Approximately 3–5 mg of diphthalimido oxalate was added to a 5-ml solution of 1 mg of 9,10-diphenylanthracene and 0.2 ml of 1 *M* H_2O_2 (in DMe) in anhydrous 1,2-dimethoxyethane (DMe) at 25°. In other experiments the solution also contained 0.2 g of KOH, 0.2 g of KOH + 0.1 ml of water, and 0.2 ml of methanesulfonic acid and 0.2 ml of water. The chemiluminescent light was observed visually in a dark room, and the results are collected in Table II.

TABLE II

QUALITATIVE CHEMILUMINESCENCE TESTS[a]

H_2O_2	H_2O_2 + KOH	H_2O_2 + KOH + H_2O	CH_3SO_3H + H_2O
S (long)	S (short)	MS (long)	W (long)

[a] Qualitative intensities are based on the oxalyl dichloride–hydrogen peroxide reaction taken as strong (S). Other designations are M, medium; W, weak but clearly visible.

Chemiluminescence Emission Measurements.—Procedures and instrumentation for the determinations of absolute emission intensities, spectra, and quantum yields have been described previously.[6,14] 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.

Registry No.—VII, 17447-57-3; hydrogen peroxide, 7722-84-1.

Acknowledgments.—Research reported in this publication was supported by the Advanced Research Project Agency under contract to the Office of Naval Research. The authors wish to thank Dr. M. M. Rauhut for discussions and encouragement. Elemental microanalysis was carried out under the direction of Mr. G. Clarke.

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Alcohol Formation in the Aprotic Bamford–Stevens Reaction. III.[1] On the Nature of the Precursors

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Received May 8, 1968

The unusual formation of alcohols from certain aldehyde tosylhydrazones **1** in the aprotic Bamford–Stevens reaction has been explained according to the mechanism outlined in Scheme I.[2] N-Methyl-2-pyrrolidone (N-MP) is particularly effective in the last step though any solvent with >CH–CO–N<: present can be used.[3] Whereas the proton donation by **1**, the intermediacy of

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