When this reaction was carried out at 100° for 22 hr, most of the starting material was recovered. No other conditions were tried.

2,4-Diamino-5-phenyl-6-trifluoromethylpyrimidine.[43]—A solution of 11.5 g (0.5 mol) of sodium in 250 ml of absolute ethanol, to which had been added a mixture of 58.6 g (0.5 mol) of phenylacetonitrile and 55.0 g (0.5 mol) of ethyl trifluoroacetate, was heated under reflux for 24 hr, cooled, and poured into 2.5 l. of water. Ether extraction of the insoluble oil, and acidification of the aqueous layer to about pH 2 (H_2SO_4) produced an oil which was isolated by ether extraction. This ethereal solution was washed with saturated $NaHCO_3$, followed by water, and then dried (Na_2SO_4). Removal of the ether, followed by trituration with petroleum ether, produced a crystalline residue, 47 g (54%). This crude α-trifluoroacetylphenylacetonitrile was methylated with diazomethane according to the procedure of Russell and Hitchings.[44] A 9-g portion (*ca.* 0.047 mol) of the crude crystalline methylated product was mixed with a salt-free guanidine solution prepared from 4.5 g (0.047 mol) of guanidine hydrochloride and 1.15 g (0.05 mol) of sodium in 200 ml of butanol. After this mixture had been heated under reflux for 18 hr and chilled to 0°, a cyrstalline product separated. Recrystallization (EtOH) produced 3 g of the desired product as white crystals, mp 277–278.5°.

Anal. Calcd for $C_{11}H_9F_3N_4$: C, 51.97; H, 3.57; N, 22.04. Found: C, 51.90; H, 3.54; N, 22.11.

2,4-Diamino-5-(3′,4′,5′-trimethoxyphenyl)pyrimidine[45] was prepared from 3,4,5-trimethoxyphenylacetonitrile and ethyl formate, using procedures described by Russell and Hitchings.[44] The intermediates were not characterized. The pyrimidine was purified as the hydrochloride by recrystallization from dilute ethanol, followed by treatment with 2 *N* NaOH and recrystallization of the free base from a 90:10 acetone–water mixture. Colorless crystals were obtained, mp 190–193°.

Anal. Calcd for $C_{13}H_{16}N_4O_3$: C, 56.51; H, 5.84; N, 20.28. Found: C, 56.77; H, 6.18; N, 20.11.

Registry No.—**1**, 18588-37-9; **2**, 7132-61-8; **3**, 18588-39-1; **5**, 156-81-0; **6**, 7319-45-1; **7**, 18588-42-6; **8**, 18588-43-7; **9**, 7331-23-9; **10**, 16974-65-5; **11**, 18588-46-0; **12**, 738-70-5; **13**, 18588-48-2; **14**, 18588-49-3; **15**, 18588-50-6; **16**, 17039-14-4; **17**, 3275-44-3; **18**, 58-14-0; **19**, 18588-54-0; **20**, 18588-55-1; **21**, 7761-45-7; **22**, 18588-57-3; **23**, 18588-58-4; **24**, 18588-59-5; **25**, 7331-22-8; **26**, 18588-61-9; **27**, 3765-90-0; **28**, 18593-41-4; **29**, 18620-58-1; **30**, 7331-20-6; **31**, 18620-60-5; **32**, 18620-61-6; **33**, 18620-62-7; **34**, 18620-63-8; **36**, 18620-64-9; **37**, 15400-54-1; **38**, 18620-66-1; **39**, 18620-67-2; **40**, 18620-68-3; **41**, 18620-69-4; **42**, 16462-27-4; **43**, 18620-71-8; **44**, 18620-72-9; **45**, 18620-73-0; **46**, 16490-14-5; **47**, 1791-73-7; **48**, 1004-38-2; **49**, 3308-24-5; **50**, 3270-97-1; **52**, 18620-79-6; **53**, 18620-80-9; **54**, 18620-81-0; **55**, 18620-82-1; **56**, 18620-83-2; **57**, 18620-84-3; **58**, 156-83-2; **60**, 56-08-6; **61**, 1899-48-5; **62**, 18620-88-7; **63**, 18620-89-8; **64**, 2312-91-6; **65**, 4871-70-9; **66**, 18620-92-3; **70**, 4940-95-8; **71**, 18620-94-5; **72**, 18620-95-6; **73**, 18620-96-7; **74**, 18620-97-8; **75**, 18620-98-9.

Acknowledgment.—The authors wish to express their deep indebtedness to Professors J. F. Bunnett and Marvin Charton for their many helpful suggestions concerning the treatment of the data in this paper. We are very grateful to Dr. G. H. Hitchings for his vigorous support of this program, and for his continued advice and encouragement. Mr. Ronald R. Gauch and Mr. Neil Kaufman provided statistical and programming assistance. Discussions with Drs. Richard Baltzly, Stuart Hurlbert, and Morton Harfenist were very helpful. The room-temperature pK_a measurements on many of these pyrimidines, which were carried out by Robert Bases in 1953, provided useful orientation for the present studies. The analyses were carried out by Dr. Samuel Blackman and his staff.

[43] This compound was prepared by Dr. Stuart Hurlbert in these laboratories.

[44] See Table I, footnote *n*.

[45] This compound was prepared by Michael Salzman in these laboraories.

Chemiluminescence from the Reaction of Bis[1-(1H)-2-pyridonyl]glyoxal with Hydrogen Peroxide and Fluorescent Compounds

L. J. Bollyky, B. G. Roberts, R. H. Whitman, and J. E. Lancaster

Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut 06904

Received May 22, 1968

The reaction of 2-hydroxypyridine with oxalyl chloride gives the N-acylated product bis[1-(1H)-2-pyridonyl]-gloyoxal (V). Acid-catalyzed reaction of V with hydrogen peroxide produce strong chemiluminescent light emission in the presence of fluorescent compounds such as rubrene. Quantum yields up to 0.15 einstein mol^{-1} are obtained in dimethyl phthalate solvent in the presence of strong acid catalysts (aqueous pK_a < 2.0) such as trichloroacetic acid. A good agreement of fluorescence and chemiluminescence spectra indicates that the emitting species is the first singlet excited state of the fluorescer. The emission efficiency depends strongly on the fluorescer structure. A 1:1 hydrogen peroxide to glyoxal stoichiometry is indicated. The main products of the reaction are 2-hydroxypyridine and carbon dioxide and small amounts of carbon monoxide. Oxygen was not obtained in significant amounts. The pyridonylglyoxal reaction is considered in correlation with other peroxalate chemiluminescent reactions.

Chemiluminescence has been reported from the reaction of several oxalic acid derivatives with hydrogen peroxide and fluorescent compounds.[1–6] Unusually high quantum yields were obtained from electronegatively substituted aryl oxalates[3] (0.24 einstein mol^{-1}), oxalic anhydrides[4] (0.14 einstein mol^{-1}), phthalimido oxalate[5] (0.09 einstein mol^{-1}), and oxalyl

[1] E. A. Chandross, *Tetrahedron Lett.*, 761 (1963).

[2] M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Amer. Chem. Soc.*, **88**, 3604 (1966).

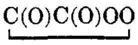
[3] L. J. Bollyky, M. Loy, B. G. Roberts, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and M. M. Rauhut, the 153 National Meeting of the American Chemical Society, Miami Beach, Fla, April 1967, Abstract 0-169; M. M. Rauhut, L. J. Bollyky, B. G. Roberts, M. Loy, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and R. A. Clarke, *J. Amer. Chem. Soc.*, **89**, 6515 (1967).

[4] L. J. Bollyky, R. H. Whitman, B. G. Roberts, and M. M. Rauhut, *ibid.*, **89**, 6523 (1967).

[5] L. J. Bollyky, R. H. Whitman, and B. G. Roberts, *J. Org. Chem.*, **33**, 4266 (1968).

[6] D. R. Maulding, R. A. Clarke, B. G. Roberts, and M. M. Rauhut, *ibid.*, **33**, 250 (1968).

chloride[2] (0.05 einstein mol^{-1}). The less efficient oxamides[6] produced 0.01 einstein mol^{-1} about the same as the quantum yield of the well-known luminol reaction.[7,8] Three peroxyoxalic acid derivatives I–III



$C(O)C(O)OO$ (I)

$(C_6H_5)_3CC(O)OC(O)C(O)OOH$ (II)

$HOC(O)C(O)OOH$ (III)

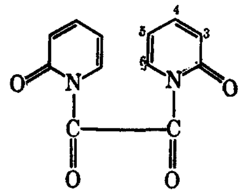
have been suggested as intermediates depending on the particular oxalate and reaction conditions.[2–4] A concerted multiple-bond cleavage decomposition of such intermediates could release sufficient energy to excite the fluorescer.[9]

All strongly chemiluminescent oxalic derivatives are compounds which would be expected to hydrolyze readily and to react with hydrogen peroxide even more rapidly.[10] Thus, the primary requirement for efficient peroxalate chemiluminescence appears to be an active oxalic acid derivative. However, the light-producing efficiency is not always proportional to the reactivity of the active oxalate. There are competing dark reactions which are dependent on reaction conditions and products. It has been shown previously that the oxalic ester reaction is best carried out in a neutral or mildly basic medium. Strong acids, such as methanesulfonic acid, are powerful quenchers of the light emission.[3] Anhydrides produce light under neutral, basic, and acidic conditions,[4,11] whereas the oxalyl chloride reaction normally takes place under acidic conditions.[1,2]

To investigate further the effect of reaction conditions and products on peroxalate chemiluminescence in general, we decided to prepare other active oxalic derivative. Esters of 2-hydroxypyridine (IV) and carbonic acids or phosphoric acid are known to undergo hydrolysis and transesterification readily.[12] We intended to prepare the oxalic ester but found that the reaction of oxalyl chloride with IV produces the unexpected N-acylated product.

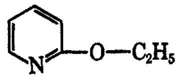
Results

Identification of Pyridonylglyoxal V.—In solution 2-hydroxypyridine exists mainly in the keto form.[13,14] Similarly, the solid sodium salt of IV consists predominantly of the keto form as demonstrated by the carbonyl band at 1640 cm^{-1}. However, all reported acylations of IV or its sodium salt led to the O-acylated product.[12,14,15] Thus, the reaction with acetyl chloride, benzoyl chloride, and phosgene produced esters exclusively as was shown by the single carbonyl band in their infrared (ir) spectra such as the band at 1796 cm^{-1} in pyridylcarbonate.[12] The product of the oxalyl chloride reaction V was strikingly different.



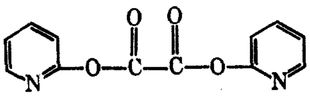
V

The ir, ultraviolet (uv), and nuclear magnetic resonance (nmr) spectra of the oxalyl chloride product V are compared in Table I with similar data for pyridine (VI), 2-ethoxypyridine (VII), 2-pyridone (IV), and

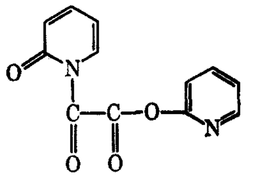


VII

1-methyl-2-pyridone (VIII). The ir stretching band of the pyridone carbonyl appears at 1683 cm^{-1} in V in addition to the oxalic bands at 1722 and 1748 cm^{-1}.[6,14,16] Similarly, the uv absorption [λ_{max} 330 mμ (ϵ 3770)] suggests a pyridone rather than pyridine chromophore.[17] These data together with the satisfactory elementary analysis establish conclusively that the correct product structure is V rather than IX or X.



IX



X

Compound V showed an interesting nmr spectrum. The spectrum consists of three groups of lines located near δ 6.5, 7.5, and 8.0. The δ 6.5 group corresponds to two and the others to one proton each. A first-order analysis of the multiplet structure yields the spin–spin couplings between each proton. The correct assignments follows from these data and are shown in Table I. The chemical shifts of V resemble the shifts of the 2-ethoxypyridine (VII) protons.[18] However, the comparison of spin–spin coupling constants, notably $J_{3,4}$ and $J_{5,6}$, clearly distinguish the two compounds VII and V. In pyridine itself these constants are 7.5 and 5.5 cps[19] and never increase above 8.2 and 5.1 cps, respectively, in a variety of substituted pyridines.[20] Thus, we find that $J_{3,4}$ is 8.2 cps in VII but it is higher, 9.5 cps in V and 9.3 and 9.1 cps in the related IV and VIII, respectively. Similarly $J_{5,6}$ is 5.0 cps in VII but it is higher, 7.2 cps in V and 6.5 and 6.7 cps in VI and VIII, respectively.

---

[7] J. Lee and H. H. Seliger, *Photochem. Photobiol.*, **4**, 1015 (1965); M. M. Rauhut, A. M. Semsel, and B. G. Roberts, *J. Org. Chem.*, **31**, 2431 (1966).

[8] For reviews, see F. McCapra, *Quart. Rev.*, **20**, 485 (1966); K. D. Gundermann, *Angew. Chem. Intern. Ed. Eng.*, **4**, 566 (1965); V. I. Papisova, V. Y. Shlyapintokh, and R. F. Vasil'ev, *Russian Chem. Rev.* (English), **34**, 599 (1965); E. J. Bowen, *Pure Appl. Chem.*, **9**, 473 (1964).

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

[10] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960); E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 314–353.

[11] Unpublished results by the authors.

[12] W. Kampe, *Angew. Chem.*, **75**, 641 (1963); *Angew. Chem. Intern. Ed. Eng.*, **2**, 479 (1963); W. Kampe, *Tetrahedron Lett.*, No. 30, 2133 (1963); W. Kampe, *Chem. Ber.*, **98**, 1038 (1965).

[13] A. R. Katritzky and J. M. Lagowski, *Advan. Heterocycl. Chem.*, 339 (1963).

[14] H. Meislich, "The Chemistry of Heterocyclic Compounds," Vol. III, part 3, Pyridine and Its Derivatives, E. Kleinberg, Ed., Interscience Publishers, New York, N. Y., 1962, p 509.

[15] T. Takahaski and F. Yoneda, *Chem. Pharm. Bull.* (Tokyo), **6**, 365 (1958); W. Kampe, *Chem. Ber.*, **98**, 1031 (1965).

[16] A. R. Katritzky and A. P. Ambler, "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 165.

[17] S. F. Mason, ref 16, p 1.

[18] R. F. M. White, ref 16, p 103.

[19] W. G. Sneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, **35**, 1487 (1957).

[20] V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **36**, 266 (1962); **37**, 2603 (1962).

TABLE I

Compound	Ir carbonyl stretching, cm^{-1} in CH_2Cl_2	Uv data, λ_{max} in mμ (ε), in $CHCl_3$	Nmr data										
			Chemical shifts of ring protons, δ				Spin–spin coupling of ring protons, cps						
			3	4	5	6	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	
Bis[1-(1H)-2-pyridonyl]glyoxal	1683, 1722, 1748	330 (3770)	6.51	7.49	6.44	8.02	9.5	1.3	1.0	6.4	2.0	7.2	(in CD_2Cl_2)
Pyridine	None[a]	263 (1680) 257 (2350) 252 (2310)											
2-Ethoxypyridine	None[a,b]		6.67	7.49	6.76	8.11	8.2	1.0	0.9	7.2	2.0	5.0	(in CD_2Cl_2)
2-Pyridone	1666–1655 ($CHCl_3$)[a,b]	301 (2400)	6.55	7.5	6.26	7.5[c]	9.3	1.2	0.58	6.7	2.1	6.47	(in CD_2Cl_2)
1-Methyl-2-pyridone	1660	304 (5200)	6.50	7.38	6.19	7.58[c]	9.1	1.37	0.74	6.65	2.12	6.70	(in $CDCl_3$)

[a] Reference 16. [b] Reference 14. [c] J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961); D. W. Turner, *ibid.*, 847 (1962).

TABLE II[a]

Glyoxal, mol $l.^{-1} \times 10^2$	H_2O_2, mol $l.^{-1} \times 10^2$	Fluorescer, mol $l.^{-1} \times 10^4$	Acid, mol $l.^{-1} \times 10^2$	I_{max},[b] ft-Lambert	Lifetimes, min[c]		Quantum yield,[d] einstein $mol^{-1} \times 10^2$
					$T_{1/4}$	$T_{3/4}L$	
A. In the Presence of Phosphoric Acid (86%)							
1.0	10	6.0 (DPA)	10	0.45	4.0		2.1
B. In the Presence of Oxalic Acid							
1.0	5.0	5.0 (DPA)	3.3	0.16	57.8	57.0	4.8
1.0	5.0	5.0 (DPA)	3.3[e]	0.11	89.0	74.2	6.3
1.0	5.0	5.0 (DPA)	3.3[f]	0.32	17.3	23.7	3.5
1.0	5.0	6.0 (rubrene)	3.3	9.72	30.4	55.8	15.2
C. In the Presence of Trichloroacetic Acid							
0.1	1.0	5.0 (DPA)	1.0	0.07	27.2	26.6	9.6
1.0	1.0	5.0 (DPA)	3.3	0.58	11.7	10.8	3.8
1.0	5.0	5.0 (DPA)	1.0	0.21	23.1	30.6	3.3
1.0	5.0	5.0 (DPA)	3.3	0.75	10.2	9.0	4.2
1.0	5.0	5.0 (DPA)	10.0	1.71	2.0	1.7	1.8
1.0	10.0	5.0 (DPA)	3.3	0.86	7.5	6.4	3.5
1.0	5.0	6.0 (rubrene)	3.3	38.0	8.4	8.9	15.2
1.33	3.33	5.0 (rubrene)	2.7	26.2	15.8	16.4	15.6
D. In the Presence of Methanesulfonic Acid							
0.1	10	6.0 (DPA)	0.03	0.67	2.0		12.9
1.0	10	6.0 (DPA)	0.03	0.28	5.0		2.3
1.0	10	6.0 (DPA)	0.33	63.0	<1.0		16.9
E. In the Presence of Trifluoroacetic Acid							
1.0	5.0	5.0 (DPA)	0.33	0.54	10.0	13.4	3.7
1.0	5.0	5.0 (DPA)	0.33[e]	0.08	100.8	75.0	3.1
1.0	5.0	5.0 (DPA)	3.3	Reaction is too fast to measure			

[a] Reaction in dimethyl phthalate at 25°. DPA is 9,10-diphenylanthracene. [b] Maximum brightness measured in a 1.0-cm-thick cell. [c] $T_{1/4}$ is the time required for the light intensity to decay to one-quarter of its maximum value. $T_{3/4}$ is the time required for the emission of three-quarters of the available light. [d] Based on pyridonylglyoxal. [e] The acid was added in several aliquots during the course of the reaction. [f] 6.7×10^{-2} *M* tetrabutylammonium perchlorate was added.

Chemiluminescence

The reaction of pyridonylglyoxal V with hydrogen peroxide was tested for chemiluminescence in the presence of 9,10-bis(phenylethylnyl)anthracene (XI) in 1,2-dimethoxyethane solution. Preliminary qualitative tests established that a strongly acidic medium is required for efficient light emission. The brightness of chemiluminescence decreased with the acidic strength of the catalyst in the order of methanesulfonic acid ($pK_a = 0.06$),[21] trichloroacetic acid ($pK_a \approx 0.63$),[22] picric acid ($pK_a = 0.29$),[22] and oxalic acid ($pK_a = 1.27$).[22] Light emission was not observed in the presence of weak acids such as 4-nitrobenzoic acid ($pK_a = 3.45$),[23] or 3,4,5-trichlorobenzoic acid ($pK_a = 4.13$).[22] A strict correlation of brightness with aqueous acidic strength naturally is not expected in dimethoxyethane.[23] Lewis acids also produced light emission and are listed in the order of decreasing brightness—$SbCl_5$, $SnCl_4$, and $BlCl_3$. Other weaker acids such as $MnCl_2$ and $CuCl_2$ were not effective.

The reaction was carried out in the presence of three fluoroescers, compound XI, rubrene (XII), and 9,19-diphenylanthracene (XIII). The chemiluminescence and the fluorescence spectra showed a good agreement for all of the three fluorescers indicating that the first singlet excited state is the light-emitting species.

The effect of catalyst and reactant concentrations on lifetime, quantum yield, and brightness are summarized in Table II. Shorter lifetimes were obtained in the

---

(21) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

(22) G. Kortum, W. Vogel, and K. Andrussow, *Pure Appl. Chem.*, **1**, 187 (1960–1961).

(23) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

presence of the two stronger acids, trifluoroacetic acid ($pK_a = 0.23$),[24] and methanesulfonic acid, than with the weaker phosphoric acid ($pK_a = 2.09$)[25] or oxalic acid. Increasing trichloroacetic acid concentration accelerated the reaction but left the quantum yield unchanged. However, the quantum yield decreased at high acid concentrations when the acid was present in large excess, perhaps indicating the instability of V at these conditions. Another observation which also points to that conclusion is that the gradual addition of acid leads to higher quantum yields and longer lifetimes than those obtained with rapid addition.

The fluorescer structure strongly influences the chemiluminescent quantum yield but not the lifetime. Under comparable conditions, rubrene with a lower singlet energy (52.3 kcal mol^{-1})[26] and lower oxidation potential (0.89 V)[28] produced a higher 0.15-einstein mol^{-1} quantum yield than 9,10-diphenylanthracene (70.8 kcal mol^{-1} [26] and 1.31 V,[27] respectively) which yielded 0.04 einstein mol^{-1}. The fluorescence efficiency of rubrene (0.71) is also lower than that of 9,10-diphenylanthracene (0.84).[28,29] In contrast to the reaction of pyridonylglyoxal V both the emission efficiency and lifetime of bis(2,4-dinitrophenyl)oxalate chemiluminescence showed a marked dependence on fluorescer structure.[3] Thus, the fluorescer does not appear to be involved in the rate determining step of the pyridonylglyoxal reaction under the conditions studied. The effect of fluorescer structure on the oxalic ester reaction is currently under investigation and will be reported elsewhere.

The pyridonylglyoxal and hydrogen peroxide concentrations exerted a much smaller effect on the reaction than did the acid strength and fluorescer structure. Increasing hydrogen peroxide concentrations accelerated the reaction mildly but left the emission efficiency unchanged. High emission efficiencies were obtained in four organic solvents in the presence of fluorescer XI as shown by the results in Table III.

Table III

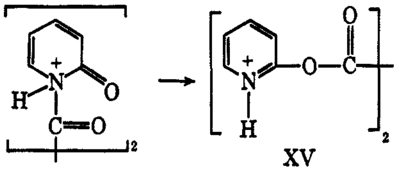
The Bis[1-(1H)-2-pyridonyl]glyoxal Reaction in Various Solvents[a]

Solvent	Glyoxal, $10^2 \times M$	H_2O_2, $10^2 \times M$	CCl_3CO_2H, $10^2 \times M$	BPEA, $10^4 \times M$	I_{max},[b] ft-Lambert	$T_{3/4}$,[c] min	Quantum yield,[d] einstein $mol^{-1} \times 10^2$
Diethyl oxalate	1.47	5.0	5.0	6.0	25.7	3.8	3.5
Dibutyl phthalate	0.72	5.0	6.7	6.0	21.6	4.1	7.4
o-Dichlorobenzene	1.5	5.0	3.3	6.0	31.9	5.3	4.8
Triethyl phosphate	4.0	10.0	34.0[e]	10.0	7.4	11.9	1.1
Triethyl phosphate	4.0	10.0	70.0[e]	10.0	22.7	7.3	1.9

[a] In the presence of 9,10-bis(phenylethynyl)anthracene (BPEA) at 25°. [b] Maximum intensity at 1-cm thickness. [c] Time required for the emission of three-quarters of the total light. [d] Based on glyoxal. [e] Catalyst, $SnCl_4$.

The nitro-substituted analog of bis[1-(1)-5-nitro-2-pyridonyl]gloyoxal (V) was also prepared and found to produce strong light emission when it reacted with hydrogen peroxide and a fluorescer. However, the nitropyridonylgloyoxal is extremely sensitive to hydrolysis and could not be prepared in an analytically pure form.

The observation that strong acids are required for efficient light emission suggests that the pyridonylglyoxal is first protonated or complexed with a Lewis acid prior to its reaction with hydrogen peroxide. To detect a possible rearrangement of the protonated glyoxal XIV to its O-acyl isomer XV the reaction was followed by ir spectroscopy in triethyl phosphate solution. In the absence of acid catalysts no reaction occurred when V (4×10^{-1} M) and hydrogen peroxide (8×10^{-2} M) were mixed for 2 hr. However, the addition of stannic chloride (8.6×10^{-2} M) led to the formation of an intermediate (ir absorption at 1797 cm^{-1}) at the expense of V. The intermediate was consumed approximately during the same time as required for light emission. The observed intermediate showed an infrared absorption expected for XV.[3] Complexes of IV and V with stannic chloride were eliminated as a possible explanation by a comparison with authentic samples.



XIV

XV

The rearrangement of N-acylpyridones to the O-acyl isomer have been suggested as an intermediate step in the formation of pyridol esters from IV and acid chlorides or anhydrides.[14] However, supporting evidence has not been presented prior to this work. Further study of the rearrangement would be desirable. In a limited number of experiments we found that the formation of XV is difficult to observe in the absence of hydrogen peroxide. Without hydrogen peroxide, and even in the presence of it XV decomposes rapidly probably through hydrolysis to give IV.

Experiments carried out to establish the stoichiometry of the pyridonyglyoxal $V-H_2O_2$ reaction in the presence of fivefold excess of trichloroacetic acid are shown in Table IV. The results indicate that the quantum yield remains constant at 1:1 through 10:1 ratios of hydrogen peroxide to pyridonylglyoxal but declines when less than 1 M equiv of hydrogen peroxide is present. Thus the light-producing reaction appears to involve 1 mol of peroxide/mol of V. The addition of small amounts of water decreased the quantum yield.

---

(24) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

(25) J. H. H. Lugg, *J. Amer. Chem. Soc.*, **53**, 1 (1931).

(26) Measured in dimethyl phthalate solvent on the basis of 0–0 bands by the method of H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(27) Measured under the direction of Dr. D. L. Maricle.

(28) Measured in dimethyl phthalate solution by the method described in ref 29. The fluorescence efficiency of unpurified rubrene (Aldrich) is 0.35.

(29) B. G. Roberts and R. Hirt, *Appl. Spectrosc.*, **21**, 250 (1967).

TABLE IV

THE EFFECT OF HYDROGEN PEROXIDE AND WATER ON THE BIS[1-(1H)-2-PYRIDONYL]GLYOXAL REACTION[a]

H_2O_2, mol l.$^{-1}$ × 10^3	H_2O, mol l.$^{-1}$ × 10^2	I_{max},[b] ft-Lambert	Lifetimes[c] $T_{1/4}$, min	$T_{3/4}$, min	Quantum yield,[d] einstein mol^{-1} × 10^2
2.5		5.8	14.6	11.8	7.5
5.0		7.6	15.7	15.7	10.8
10.0		7.5	16.1	15.1	10.8
10.0	5.0	3.6	24.3	23.7	7.5
10.0	18.0	2.3	29.8	30.0	6.0
50.0		7.5	15.5	14.4	10.1

[a] Reaction of 5 × 10^{-3} *M* bis[1-(1H)-2-pyridonyl]glyoxal, 1 × 10^3 *M* 9,10-bis(phenylethynyl)anthracene, 2 × 10^{-2} *M* CCl_3CO_2H, and hydrogen peroxide and water in dimethyl phthalate solvent at 25°. [b] Maximum intensity at 1.0-cm thickness. [c] $T_{1/4}$ is the light decay time from maximum to one-quarter intensity. $T_{3/4}$ is the time required for the emission of three-quarters of the available light. [d] Based on glyoxal.

TABLE V

GASEOUS PRODUCTS OF THE BIS[1-(1H)-2-PYRIDONYL]GLYOXAL CHEMILUMINESCENT REACTION[a]

Reactant concentrations, mol l.$^{-1}$ Glyoxal	H_2O_2	CCl_3CO_2H	Rubrene	Chemiluminescent quantum yield, einstein mol^{-1} × 10^2	Products (mol/mol of glyoxal) CO_2	CO	CO_2 + CO	O_2	Glyoxal carbon balance, %, CO_2 + CO
1.33 × 10^{-2}	3.33 × 10^{-2}	None	5 × 10^{-4}		1.598	0.075	1.673	0.095	83.7
1.33 × 10^{-2}	3.33 × 10^{-2}	2.7 × 10^{-2}	None		1.510	0.080	1.590	0.009	79.5
1.33 × 10^{-2}	3.33 × 10^{-2}	2.7 × 10^{-2}	5 × 10^{-4}	15.6	1.621	0.061	1.682	None[b]	84.2

[a] In dimethyl phthalate at 25° at 0.1 mm of mercury as described earlier.[3] [b] Less than 0.005 mol/mol of glyoxal.

Gaseous products of the pyridonylglyoxal–hydrogen peroxide–trichloroacetic acid reaction have been determined under reduced pressure (<0.1-mm of Hg) in dimethyl phthalate solution. The results are shown in Table V. The major reaction product is carbon dioxide which accounts for 81.1% of the glyoxal carbon. Although carbon monoxide and oxygen are also produced in minor amounts, their low yields rule them out as chemiluminescent products. The absence of rubrene showed no substantial effect on product distribution or yield.

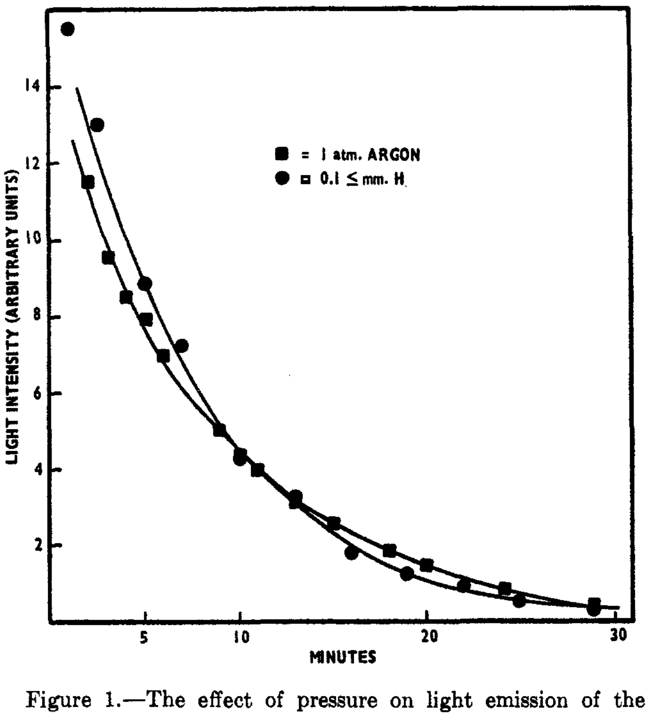


Figure 1.—The effect of pressure on light emission of the bis[1-(1H)-2-pyrodonyl]glyoxal reaction. The reactions were carried out in similarly cleaned Pyrex glassware using identical reagent stock solutions in dimethyl phthalate at 25°. Concentrations were 1.33 × 10^{-2} *M* glyoxal, 3.33 × 10^{-2} *M* H_2O_2, 2.7 × 10^{-2} *M* CCl_3CO_2H, and 5.0 × 10^{-4} *M* rubrene. ■: The solutions were degassed under vacuum and argon was added to produce 1-atm pressure. The degassing was repeated and the reaction carried out at 1-atm argon pressure. ●: The solutions were degassed under vacuum using good agitation. When no pressure change was observed after 30-min standing the reactor flask was isolated from the vacuum pump. The reaction was carried out at <0.1-mm Hg initial pressure.

A control experiment was carried out under an argon atmosphere to check the effect of pressure on light emission. The results in Figure 1 compare light emission at 1 atm of argon and under vacuum. No substantial effect of pressure was observed.

The effect of rubrene on the rate of evolution of gaseous products is indicated by Figure 2. Rubrene produced no observable change in evolution rate during

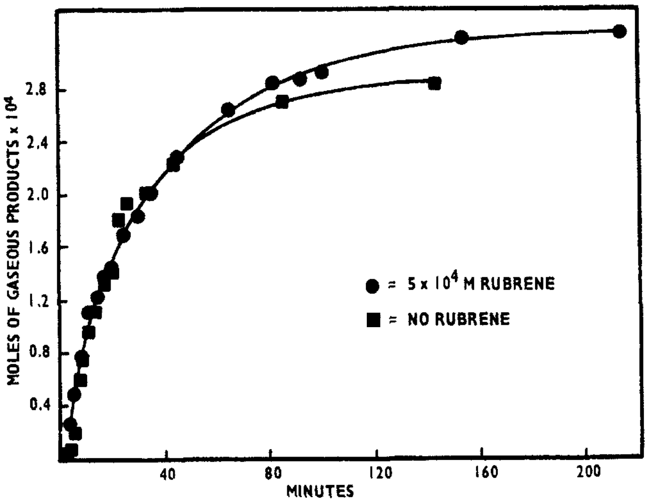


Figure 2.—The effect of rubrene on gaseous products of the bis[1-(1H)-2-pyridonyl]glyoxal reaction. Reactions were carried out in similarly cleaned glassware using identical reagent stock solutions in dimethyl phthalate under <0.1-mm Hg pressure at 25°. ●: Concentrations were 1.33 × 10^{-2} *M* glyoxal, 3.33 × 10^{-2} *M* H_2O_2, 2.7 × 10^{-2} *M* CCl_3CO_2H, and 5.0 × 10^{-4} *M* rubrene. ■: Identical with b except no rubrene was present.

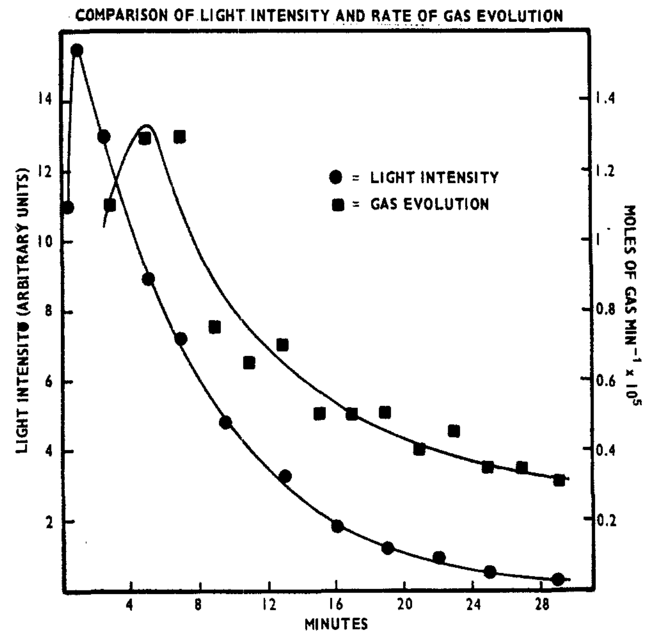


Figure 3.—Comparison of light intensity and rate of gas evolution. Concentrations were 1.33×10^{-2} *M* bis[1-(1H)-2-pyridonyl]glyoxal, 3.33×10^{-2} *M* H_2O_2, 2.7×10^{-2} *M* CCl_3CO_2H, and 5×10^{-4} rubrene. The reaction was carried out in dimethyl phthalate under 0.1-mm Hg pressure at 25°. ●: light intensity. ■: gas evolution.

the first 60 min of the reaction, but appeared to increase the rate slightly in the later dim period of reaction. This observation as well as the failure of fluorescer structure to effect chemiluminescent lifetime suggest that the fluorescer is not involved in the rate-determining step.

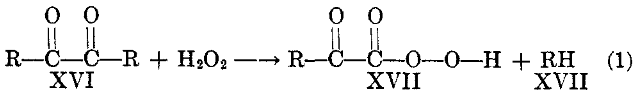
The light emission and gas evolution rates are compared in Figure 3. The results indicate that the maximum gas evolution rate follows the maximum intensity by about 4 min. This delay may reflect in part the initial saturation of the solution by carbon dioxide. Following the maximum in the gas evolution rate, at 5-min reaction time the intensity decay and gas evolution rates become similar, although the intensity decay is clearly more rapid. This second delay may result from the decrease in quantum yield (light per unit reaction) at longer reaction times caused by product quenching.

In the absence of trichloroacetic acid the reaction proceeded rather slowly and produced somewhat higher oxygen yield.

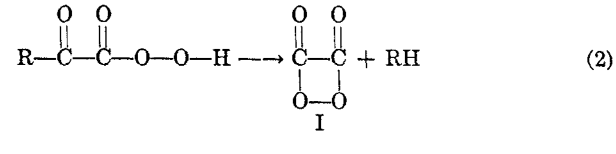
Discussion

The oxalyl chloride reaction in ether solution requires both hydrogen peroxide and water for efficient light emission. Therefore, monoperoxyoxalic acid (III) was proposed as the key chemiluminescence intermediate.[2] However, the other two, the oxalic anhydride and oxalic ester reactions, are different from that in several respects.[3,4] One important difference is that their reaction does not need water. A peracid monoanhydride has been shown as the most likely intermediate for the anhydride reaction,[4] and 1,2-dioxetanedione (I) for the ester reaction.[3]

We suggest that the absence of a common intermediate in the anhydride and ester reactions can readily be explained. The anhydride reaction may be considered as an example of peroxalate chemiluminescence where the substitution of one –R group by a hydroperoxide or peroxide in reaction 1 is sufficient to produce a chemiluminescence intermediate. Such intermediate must be capable of releasing adequate energy by a multiple-bond cleavage process for the excitation of the fluorescer. This latter requirement restricts the choice of oxalic acid derivative XVII to those capable of multiple-bond cleavage.



$$\underset{\text{XVI}}{R\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O}{\|}}{C}\text{—}R} + H_2O_2 \longrightarrow \underset{\text{XVII}}{R\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O}{\|}}{C}\text{—}O\text{—}O\text{—}H} + \underset{\text{XVII}}{RH} \qquad (1)$$



$$R\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O}{\|}}{C}\text{—}O\text{—}O\text{—}H \longrightarrow \underset{\text{I}}{\underset{\underset{O\text{—}O}{|\quad|}}{\overset{\overset{O\ \ O}{\|\quad\|}}{C\text{—}C}}} + RH \qquad (2)$$

In the oxalic ester reaction the second –R group is also replaced by hydrogen peroxide through reaction 2 to produce the postulated cyclic chemiluminescence intermediate I. Thus, oxalic derivatives XVI having –R groups which are excellent leaving groups would be expected to produce chemiluminescence similarly to electronegatively substituted aryl oxalates provided that the product of their reaction with hydrogen peroxide does not interfere. The data presented in this work suggest that the pyridonylglyoxal reaction belongs to this second group of peroxalate chemiluminescent reactions.

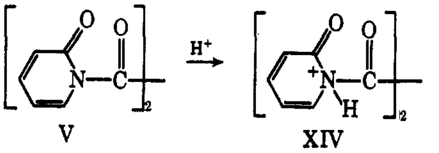
The pyridonylglyoxal reaction requires a strongly acidic medium and appears to involve 1:1 hydrogen peroxide to glyoxal stoichiometry. The main products of the reaction are carbon dioxide and 2-hydroxypyridine. These observations are well accommodated by reactions 3–7.

Pyridonylglyoxal V first is protonated to form XIV which then rearranges to XV in reaction 4. Although the ir absorption at 1797 cm^{-1} suggests that it is XV which reacts with hydrogen peroxide to produce I in reaction 5, the unrearranged XIV may also contribute to the formation of I through reaction 6. Then a concerted bond-cleavage decomposition of I could provide the excitation energy for the fluorescer (Flr). However, reaction 7 is not likely to be the rate-determining step since the chemiluminescent lifetime is independent of the fluorescer structure.

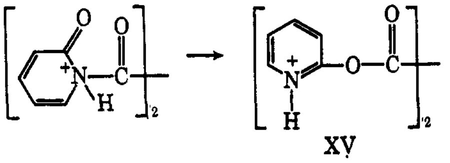
A conceivable decomposition of XIX or XX in analogy to that of the anhydride intermediate VXII would require the formation of energetic cation radicals and would produce insufficient energy to excite the fluorescer. Thus, the pyridonylglyoxal and electronegatively substituted aryl oxalate reactions appear to involve the same intermediate, I. The protonation of V converts the pyridonyl group into an excellent leaving group, similar to electronegatively substituted phenolates.[30] Further comparison of the two reactions suggest that the powerful quenching of aryl oxalate chemiluminescence by strong acids is a consequence of an interference with the formation of dioxetanedione

---

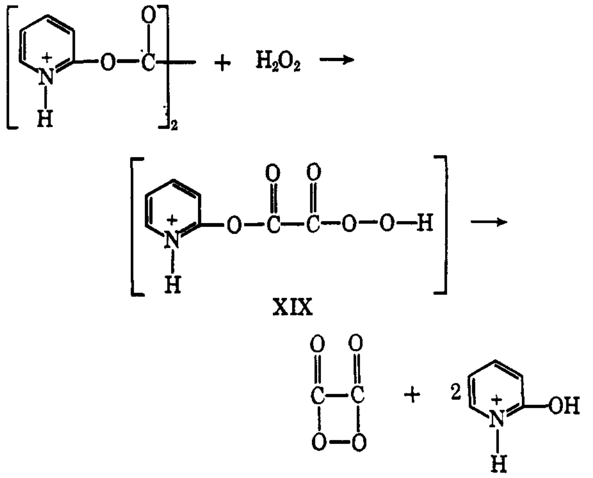
[30] For basicities, see ref 22 and V. R. Williams and J. G. Traynham, *J. Org. Chem.*, **28**, 2883 (1963).



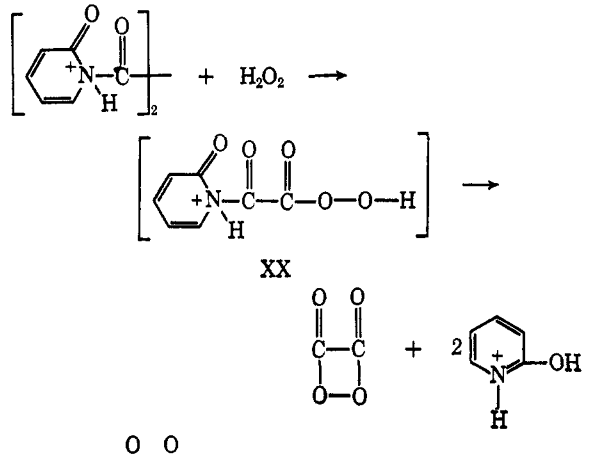
(3)



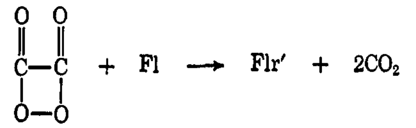
(4)



(5)



(6)



(7)

(Flr = fluorescer)

rather than with its chemiluminescent decomposition. Otherwise the strongly acidic pyridonyglyoxal reaction would not be the efficient producer of light that it is.

Experimental Section

Materials.—Dimethyl phthalate and triethyl phosphate were fractionally distilled. Oxalyl chloride, 2-hydroxypyridine, and 2-hydroxy-5-nitropyridine were used as received except where mentioned otherwise. 9,10-Diphenylanthracene (Aldrich) was recrystallized from a mixture of absolute ethanol and chloroform to obtain material of mp 250–251° (lit.[31] mp 250–251°). Rubrene (Eastman) was not purified. 9,10-Bis(phenylethynyl)anthracene was prepared by a literature procedure using anthraquinone and the anion of phenylacetylene.[32] Hydrogen peroxide solutions were prepared from the 98% reagent (Becco Chemical Division of FMC Co.) and were analyzed iodometrically.[29]

Pyridonylglyoxals. Bis[1-(1H)-2-pyridonyl]glyoxal.—To a stirred solution of 47.6 g (0.50 mol) of 2-hydroxypyridine, crystallized twice from benzene, and 50.6 g (0.50 mol) of freshly distilled triethylamine in 1.2 l. of freshly distilled (over lithium hydride) 1,2-dimethoxyethane at 25° under an argon atmosphere, oxalyl chloride (61.1 g, 0.25 mol) was added dropwise during 30 min. The mixture was refluxed for 2 hr, then evaporated to dryness under reduced pressure at 30–35°. The residue was washed three times with chloroform, then crystallized from benzene to obtain 31.2 g (51%) of crystalline product, mp 173–176.5° dec.

Anal. Calcd for $C_{12}H_8N_2O_4$: C, 59.02; H, 3.30; N, 11.47. Found: C, 59.08; H, 3.31; N, 11.46.

Gaseous Products.—The gaseous products were measured by the experimental method described earlier. A "Spectra Brightness Spot Meter" (Photo Research Co.) was used for the experiments which correlated chemiluminescent emission intensity with the role of gaseous product formation.

Chemiluminescence Emission Measurements.—Procedures and instrumentation for the determinations of absolute emission intensities, spectra, and quantum yields have been described previously.[2,29] 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 into 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 521 grating instrument using a compensated cell technique with a pair of stoppered 0.5-mm NaCl cavity cells. Aliquots of stock solutions of pyridonylgloyoxal, 9,10-bis(phenylethynyl)anthracene, and H_2O_2 were mixed, the H_2O_2 always being added last and the timer started with peroxide addition. An aliquot of the reaction mixture was then poured into the ir cell and the spectrum of the reaction was recorded between 2000 and 1600 cm^{-1} at the 16-min 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.

Oxidation Potentials.—The half-wave oxidation potential $E_{ox(1/2)}$ of rubrene and 9,10-diphenylanthracene were measured on a platinum electrode in the presence of tetrabutylammonium perchlorate electrolyte in dimethylformamide solvent (Table VI).

TABLE VI

	Oxidation potential, $E_{1/2}$ (V *vs.* sce)	Reduction potential, $E_{1/2}$ (V *vs.* sce)
Rubrene	+0.89	−1.37
9,10-Diphenylanthracene	+1.31	−1.84

Ultraviolet Spectra.—A Cary Model 15 spectrophotometer was used.

Registry No.—V, 16536-45-1; hydrogen peroxide, 7722-84-1; rubrene, 517-51-1; 9,10-diphenylanthracene, 1499-10-1.

Acknowledgments.—The authors wish to thank Dr. M. M. Rauhut for the valuable discussions and encouragement. The ir analyses were carried out with Mr. N. Colthup, oxidation potentials were determined under the direction of Dr. D. Maricle, mass spectroscopic analyses under the supervision of Mr. T. Mead, and microelemental analysis under the direction of Mr. G. Clarke. Research reported in this publication was supported by the Advanced Research Projects Agency under contract to the Office of Naval Research.

---

[31] G. Wittig and R. W. Hoffman, *Ber.*, **95**, 2718 (1962).

[32] W. Reid, W. Donner, and W. Schlegelmilch, *ibid.*, **94**, 1051 (1961); I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p 630.