The Chemiluminescence of Tetrachloroethylene Carbonate and Related Compounds

D. R. MAULDING* AND B. G. ROBERTS

American Cyanamid Company, Bound Brook,
New Jersey 08805

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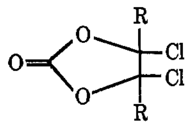
We wish to report the new chemiluminescent reaction[1] of tetrachloroethylene carbonate (**1b**) with hydrogen peroxide in the presence of a fluorescer. As shown in expt 1 of Table I, a quantum efficiency of 0.98% was obtained when 0.03 *M* **1b** was allowed to react with 98% H_2O_2 in a solution of 75% ethyl benzoate and 25% *tert*-butyl alcohol which contained 3 × 10^{-3} *M* 9,10-bis(phenylethynyl)anthracene (BPEA).[2] Moreover, in a two-phase system in which a solution of **1b** and BPEA in diethyl carbonate was stirred with 30% aqueous H_2O_2 (expt 9), a chemiluminescence efficiency of 6.5% was measured. Thus, in a homogeneous system the chemiluminescence efficiency of **1b** is comparable with the 1% reported for electronegatively substituted oxamides[3] and the well-studied reaction of luminol with hydrogen peroxide.[4] Under the best conditions, however, the reaction of **1b** with H_2O_2 is the most efficient nonbiological chemiluminescent reaction reported, with the exception of certain diaryl oxalates (8% at 0.03 *M*).[5]

TABLE I

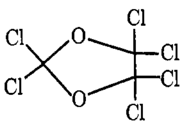
CHEMILUMINESCENCE OF **1b**, **4**, AND **5**[a,b]

Expt	Compd, *M*	H_2O_2, *M*	Quantum yield, 10^2 einstein mol^{-1}	Lifetime,[c] $T_{3/4}$, min	I_{max}[d]
1	**1b**, 0.03	0.07	0.98	8	9.2
2	**1b**, 0.03	0.03	0.85	17	3.7
3	**1b**, 0.10	0.23	0.21	4	12.5
4	**4**, 0.03	0.07	0.89	16	2.8
5	**5a**, 0.10	0.25	0.04	8	0.6
6	**5b**, 0.03	0.37	0.75	12	4.6
7	**1b**, 0.04	b	4.92	41	9.6
8[e]	**1b**, 0.04	b	4.92	108	9.1
9[f]	**1b**, 0.04	b	6.49	65	13.0
10	**1b**, 0.10	b	2.29	46	24.2
11	**1b**, 1.0	b	0.19	10	68.3
12	**4**, 0.04	b	3.40	94	2.2
13	**4**, 0.10	b	2.30	147	4.3
14	**5b**, 0.03	b	. . .	20	0.6

[a] Reaction of ester, 98% H_2O_2, and 2.3 × 10^{-3} *M* 9,10-bis(phenylethynyl)anthracene (BPEA) in 75% ethyl benzoate and 25% *tert*-butyl alcohol. [b] Hetergeneous reaction of three parts (by volume) ester and 4 × 10^{-3} *M* BPEA with one part 30% aqueous H_2O_2. [c] Time required for emission of 75% of total light. [d] Maximum intensity in foot-lamberts cm^{-1}. [e] Initial concentration of BPEA was 1.3 × 10^{-3} *M*. After 60 min of reaction time more BPEA was added to make final concentration 4 × 10^{-3} *M*. [f] Solvent for **1b** and BPEA was diethyl carbonate.



1a, R = H
b, R = Cl



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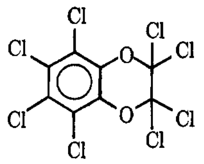

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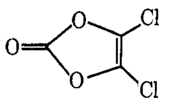

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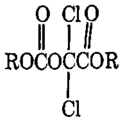
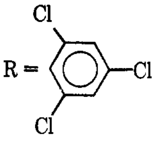


$$\overset{O}{\overset{\|}{C}}\ldots \quad ROC\overset{O}{\overset{\|}{}}O\underset{Cl}{\overset{Cl}{C}}\overset{O}{\overset{\|}{C}}OR$$

5a, R = CH_3



b, R =

The related chlorinated ethylenedioxy derivatives **1a**, **2**, and **3**, and esters **4** and **5** which were prepared from **1b** also produced light when allowed to react with H_2O_2 in the presence of BPEA. In 75% ethyl benzoate and 25% *tert*-butyl alcohol the chemiluminescence efficiencies of dichlorovinylene carbonate (**4**) and ester **5b** were 0.75–0.89%, and in a heterogeneous system the efficiency of **4** was 3.4% (see expt 4, 6, and 12). Maximum intensities of only 0.3–0.5 foot-lamberts cm^{-1} and lifetimes of 4–18 min could be obtained with dichloroethylene carbonate (**1a**), perchloro-1,3-dioxolane (**2**), and perchloro-1,4-benzodioxane (**3**) in 75% ethyl benzoate and 25% 3-methyl-3-pentanol, although in a two-phase system **3** did provide light for 1 hr (maximum intensity, 2.3 foot-lamberts cm^{-1}). It is therefore apparent from these experiments that the carbonyl and tetrachloroethylenedioxy groups in **1b** are required for efficient chemiluminescence.

A comparison of expt 1, 3, 7, 10, and 11 in Table I indicates that the chemiluminescence efficiency of **1b** is reduced at higher ester concentration. At least part of the quenching is due to the decomposition of fluorescer, since in 0.10 *M* **1b** systems unreacted carbonate was still present when BPEA fluorescence could no longer be detected by irradiation of the reaction solution with uv light. Other fluorescers such as 9,10-diphenylanthracene, rubrene, and perylene were similarly destroyed in the reaction of **1b** with H_2O_2. The development of a highly acidic medium resulting from by-product hydrogen chloride may contribute to concentration quenching, since a similar effect is observed in the chemiluminescent reaction of oxalyl chloride and hydrogen peroxide.[6] The use of weak bases, however, such as sodium acetate, sodium bicarbonate and sodium carbonate, or a phosphate buffer in the 30% aqueous peroxide solution gave no appreciable enhancement of light output.

The existence of a long-lived intermediate is indicated by a comparison of the results of expt 7 and 8 in Table I, which are also illustrated in Figure I. In expt 7 the concentration of BPEA at the beginning of the reaction was 4 × 10^{-3} *M* and was sufficient to maintain continuous emission. In expt 8 the initial concentration of BPEA was 1.3 × 10^{-3} *M* and no light was detected after 22 min. Additional BPEA was added after 60

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[1] The emitting species is the first excited singlet state of the fluorescer, since the chemiluminescence emission spectrum matched the fluorescence emission curve in each reaction reported here.

[2] D. R. Maulding and B. G. Roberts, *J. Org. Chem.*, **34**, 1734 (1969).

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

[4] Karl-Dietrich Gundermann, "Chemilumineszenz organischer Verbindungen," Springer-Verlag, West Berlin and Heidelberg, 1968, p 63.

[5] M. M. Rauhut, *Accounts Chem. Res.*, 80 (1969).

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

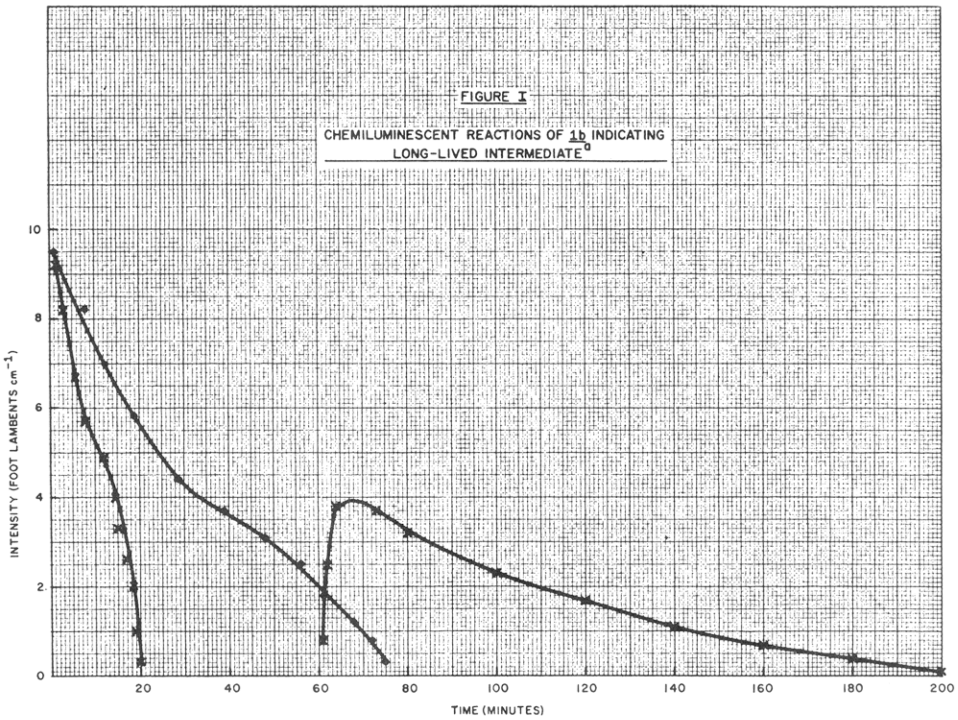
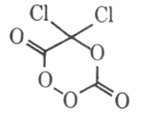


Figure 1.—Plot of the intensity-time values obtained in expt 7 and 8 described in Table I. The decay curve for expt 7 is represented by (●—●) and the curve for expt 8 by (×—×).

min of reaction time, so that the final concentration of fluorescer was 4×10^{-3} *M*. Even though the emission of light in expt 8 was interrupted, the quantum yields of the two reactions are similar.



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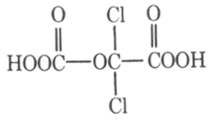
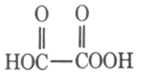


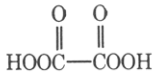
$\mathrm{HOO\overset{O}{\overset{\|}{C}}-O\underset{Cl}{\overset{Cl}{C}}-\overset{O}{\overset{\|}{C}}OOH}$

7



$\mathrm{HO\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OOH}$

8



$\mathrm{HOO\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OOH}$

9

10

By analogy with the reaction of **1b** with methanol,[7] initial attack at the carbonyl is expected in the chemiluminescent reaction of **1b** with H_2O_2, rather than displacement of a *gem*-dichloromethyl group. Thus the cyclic peroxide **6** and the diperoxy acid **7** may be key intermediates, although further reaction of **6** or **7** with 30% or 98% H_2O_2 to give monoperoxyoxalic acid (**8**), diperoxyoxalic acid (**9**), or 1,2-dioxetanedione (**10**), which have been proposed as intermediates in peroxyoxalate chemiluminescence,[5] presently can not be ruled out.

Experimental Section

In the chemiluminescence experiments 1,2-dichloroethylene carbonate supplied by J. T. Baker Chemical Co. was used without purification. Tetrachloroethylene carbonate (**1b**),[8] dichlorovinylene carbonate (**4**),[9] and the dichloroglycolates **5a** and **5b**[7] were prepared by the reported procedures.

Hexachloro-1,3-dioxolane (**2**).—Chlorine was bubbled into a refluxing solution of 7.4 g (0.10 mol) of 1,3-dioxolane and 100 ml of carbon tetrachloride, while the solution was irradiated with a Hanovia 100-W lamp (Pyrex filter) until a yellow-green color persisted. The solvent was removed by evaporation and the resulting oil was distilled twice, bp 78° (5 mm). The yield of the colorless product was 38%; ir 1010 cm^{-1}; nmr, no peaks; mass spectrum *m/e* 243 (M − Cl).

Anal. Calcd for $C_3Cl_6O_2$: C, 12.81; Cl, 75.80. Found: C, 13.15; Cl, 75.62.

Octachloro-1,4-benzodioxane (**3**).—Chlorine was bubbled into a refluxing solution of 1.55 g of 5,6,7,8-tetrachloro-1,4-benzodioxane[10] in 200 ml of carbon tetrachloride while the solution was irradiated with a Hanovia 100-W lamp (Pyrex filter) until a yellow-green color persisted. Evaporation of solvent gave 2.2 g (95%) of colorless solid, mp 128–130°.

Anal. Calcd for $C_8Cl_8O_2$: C, 23.30; Cl, 68.93. Found: C, 23.02; Cl, 68.65.

Chemiluminescence Emission Measurements.—Procedures and instrumentation for the determination of absolute emission intensities, spectra and quantum yields have been described previously.[11] The chemiluminescent reactions were initiated by injecting an aliquot of stock hydrogen peroxide solution from an all-glass syringe into solutions of the chlorinated ethylenedioxy derivative and fluorescer in a stirred 3-ml circular cuvette attached to a spectroradiometer. The data from the radiometer was converted to foot-lamberts cm^{-1} by a Scientific Data 925 computer programmed with the calibration data.

Registry No.—**1b,** 22432-68-4; **2,** 34288-86-3; **3,** 34288-87-4; **4,** 17994-23-9; **5a,** 33619-75-9; **5b,** 33661-49-3.

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(7) D. R. Maulding, *Synthesis*, 480 (1971).

(8) E. K. Ellinghoe and L. R. Melby (to Du Pont), U. S. Patent, 2,816,287 (1957); *Chem. Abstr.*, **52**, 12899 (1958).

(9) H. D. Scharf, W. Droste, and R. Liebig, *Angew. Chem., Int. Ed., Engl.*, **7**, 215 (1968).

(10) L. Horner and H. Merz, *Justus Liebigs Ann. Chem.*, **570**, 89 (1950).

(11) M. M. Rauhut, *et. al.*, *J. Amer. Chem. Soc.*, **89**, 6515 (1967).