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CHEMILUMINESCENT REACTION OF SUBSTITUTED 2,2,3,3-TETRACHLORO-1,4-BENZODIOXANE

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U.S. Cl. 252—188.3 CL 5 Claims

ABSTRACT OF THE DISCLOSURE

Novel substituted benzodioxane compounds which provide chemiluminescent light when reacted with other necessary chemiluminescent reactants in the direct generation of light from chemical energy. By "light" as referred to herein is meant electromagnetic radiation at wavelengths falling between about 350 mμ and about 1,000 mμ.

The invention herein described was made in the course of or under a contract with the Department of the Navy.

The present invention relates to novel benzodioxane compounds which obtain chemiluminescent light when reacted with other necessary chemiluminescent reactants in the direct generation of light from chemical energy. By "light" as referred to herein is meant electromagnetic radiation at wavelengths falling between about 350 mμ and about 1000 mμ.

The art of generating light from chemical energy, i.e. chemiluminescence, is continually in search of compositions which when reacted substantially improve the intensity and lifetime of light emission contrasted to known chemiluminescent compositions and reactions. Obviously, improved compositions are constantly in demand for use as signal devices, for area illumination, etc.

Various compounds have been known and proposed in the past for obtaining chemiluminescent light. One group is based on the compound tetramethylamino ethylene, reactive with oxygen. Such compounds must obviously be protected from air during storage.

Another group of compounds are derivatives of bis aryl or heterocyclic derivatives of oxalic acid. These compounds react with a peroxide in the presence of a solvent and a fluorescent compound to give chemiluminescent light. Although these oxalates are the best known chemiluminescent systems, they have the disadvantage that the oxalates are relatively expensive to prepare and are also relatively insoluble, thus limiting the amount of light obtainable from a given volume of solution.

It is an object of this invention to obtain a chemiluminescent composition and a process employing said composition whereby a high efficiency may be obtained in the conversion of chemical energy into light.

Another object is to obtain a chemiluminescent compound which produces light over an extended period of time.

Another object of this invention is to obtain a chemiluminescent composition which attains light of substantially higher intensity and with greater degree of quantum efficiency than has been obtained with former chemiluminescent compositions.

Another object of this invention is to obtain a chemiluminescent composition which may be employed to obtain light by a process which is mechanically simple and which is economically inexpensive.

Another object of this invention is to obtain a chemiluminescent reactant which is stable over a long period of time and which may be subsequently reacted to obtain chemiluminescent light.

Another object of this invention is to obtain a chemiluminescent reactant which when reacted will obtain chemiluminescent light by a process which is not hazardous.

Another object is to obtain a composition characterized by a controllable (1) length of duration of chemiluminescence and (2) intensity of chemiluminescent illumination.

Another object is to obtain a process of regulating intensity and duration of chemiluminescence.

Other objects of this invention become apparent from the above and following disclosure.

The term "aryl group" as used herein means a group which is derived from an aromatic compound by the removal of one or more atoms.

The term "chemiluminescent reactant," as used herein, means (1) a mixture which will result in a chemiluminescent reaction when reacted with other necessary reactants in the processes as disclosed herein, or (2) a chemiluminescent composition.

The term "fluorescent compound," as used herein, means a compound which fluoresces in a chemiluminescent reaction, or a compound which produces a fluorescent compound in a chemiluminescent reaction.

The term "chemiluminescent composition," as used herein, means a mixture which will result in chemiluminescence.

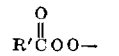
The term "admixing," as used herein, means "reacting" or sufficiently bringing together component reactants to obtain a chemiluminescent reaction.

The term "hydroperoxide compound" as used herein is limited to peroxide compounds having at least one

"HOO—"

group, or a compound which upon reaction produces a compound with such a group.

The term "peroxidic groups," as used herein, represents HHO—, R'OO—, or



R is defined for the polycarbonyl compound below, while R' is a substituent such as alkyl, cycloalkyl, α-hydroxyalkyl, substituted alkyl, for example.

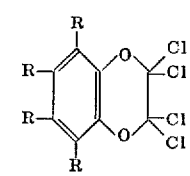
The term "diluent," as used herein, means a solvent or a vehicle which when employed with a solvent does not cause insolubility.

The term "peroxide compound," as used herein, also includes compounds which upon reaction produce the peroxide group.

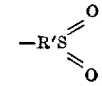
The term "hydrogen peroxide compound" includes (1) hydrogen peroxide and (2) hydrogen peroxide-producing compounds.

I have now found a new class of compounds which react with a peroxide in the presence of a solvent and a fluorescent compound to give chemiluminescent light.

These compounds are novel benzodioxane derivatives having the general structural formula:



wherein R represents an electronegative group such as, halo-, i.e. bromo, chloro, and fluoro; alkyl, aryl, —NO_2, —CN, —CF_3,



and $R'O_2C$—, where R' is alkyl or aryl, and hydrogen, provided at least one of the R substituents is always an electronegative group.

Light emission is obtained by the reaction of the substituted benzodioxane with hydrogen peroxide in the presence of a fluorescer. The light intensity is increased substantially with increased substitution of, e.g., with chloro groups. Ethyl benzoate can be used as solvent with t-butyl alcohol or 3-methyl - 3 - pentanol as cosolvents. A two phase system (9 parts/one part by volume) of ethyl benzoate with 30% hydrogen peroxide provides an intensely bright system. With such flouorescers as 9,10 - diphenylanthracene, perylene, 9,10 - bis (phenylethynyl)anthracene and 5,12 - bis - (phenylethynyl) naphthacene, blue to red emission is produced.

The hydroproxide employed in the compositions and process of this invention may be obtained from any suitable per oxide compound. For example, the hydroperoxide may be employed as sodium peroxide. Alternatively, sodium perborate may be placed in aqueous solution whereby a solution of hydrogen peroxide is obtained. Obviously, hydrogen peroxide or its solution may be employed. The peroxide employed may be obtained from anhydrous hydrogen peroxide compounds such as perhydrate of urea (ureas peroxide), perhydrate of pyrophosphate (sodium pyrophosphate peroxide), perhydrate of histidine (histidine peroxide), sodium perborate, and the like. Still another form in which the H_2O_2 may be provided in the composition is that of an anhydrous solution of H_2O_2 in a suitable solvent such as an ether, an ester, an aromatic hydrocarbon, etc. of the type which would provide a suitable diluent for the composition of this invention. Alternatively, the hydroperoxide employed in the composition or process could be any compound having a hydroperoxidic group, such as hydroperoxide

(R'OOH)

or a peroxy acid

$$\left(R'-\overset{O}{\overset{\|}{C}}-OOH\right)$$

such as t-butyl hydroperoxide and perbenzoic acid. Whenever hydrogen peroxide is contemplated to be employed, any suitable compound may be substituted which will produce hydrogen peroxide.

The hydroperoxide concentration may range from about 15 molar down to about 10^{-5}, preferably about 2 molar down to about 10^{-4} molar. The generic compound of this invention may be added as a solid or in admixture with a suitable solid peroxide reactant or in a suitable diluent, or alternatively dissolved directly in a solution containing the peroxide reactant.

Typical diluents within the purview of the instant discovery are those that do not readily react with a peroxide, such as hydrogen peroxide, and which do not readily react with the polycarbonyl compound or with the rearranged polycarbonyl compound.

Although the addition of water tends to quench the production of chemiluminescent light according to the present invention, water can serve as a partial diluent up to substantial major percentages (more than 50%). The term "water," as used herein, includes water-producing compounds such as hydrates.

Any one or more suitable diluents may be included with or in the place of the water, as long as the peroxide employed is at least partially soluble in one or more of the diluent(s), such as, for example, at least one gram of H_2O_2 per liter of diluent. The following are typical illustrative examples of the diluents or solvents which may be singly or jointly employed: non-cyclic or cyclic ethers, such as diethyl ether, diamyl ether, diphenyl ether, anisole, tetrahydrofuran, dioxane, and the like; esters such as ethyl acetate, propyl formate, amyl acetate, dimethyl phthalate, diethyl phthalate, methyl benzoate, and the like; aromatic hydrocarbons, such as benzene, xylene, toluene, and the like, acids such as acetic or propionic acids.

The fluorescent compounds contemplated herein are numerous; and they may be defined broadly as those which do not readily react on contact with the peroxide employed in this invention, such as hydrogen peroxide; likewise, they do not readily react on contact with the generic compound of this invention. Typical suitable fluorescent compounds for use in the present invention are those which have a spectral emission falling between 330 millimicrons and 800 millimicrons and which are at least partially soluble in any of the above diluents, if such diluent is employed. Among these are the conjugated polycyclic aromatic compounds having at least 3 fused rings; such as: anthracene, substituted anthracene, benzanthracene, phenanthracene, substituted phenanthracene, naphthacene, substituted naphthacene, pentacene, substituted pentacene, and the like. Typical substituents for all of these are phenyl, lower alkyl, chlorine, bromine, cyano, alkoxy (C_1–C_{16}), and other like substituents which do not interfere with the light-generating reaction contemplated herein.

Numerous other fluorescent compounds having the properties given hereinabove are well known in the art. Many of these are fully described in "Fluorescence and Phosphorescence," by Peter Pringsheim, Interscience Publishers, Inc. New York, 1949. Other fluorescers are described in "The Colour Index," 2nd ed., vol. 2, The American Association of Textile Chemists and Colorists, 1956, pp. 2907–2923. While only typical fluorescent compounds are listed hereinabove, the person skilled in the art is fully aware of the fact that this invention is not so restricted and that numerous otherfluorescent compounds having similar properties are contemplated for use herein.

It has been found that the molar (moles per liter of diluent) concentrations of the major components of the novel composition herein described may vary considerably. It is only necessary that components be in sufficient concentration to obtain chemiluminescence. The molar concentration of Benzodioxane normally is in the range of at least about 10^{-7} molar, preferably in the range of at least about 10^{-4} to about 5 molar; the fluorescent compound is present in the range from about 10^{-5} to about 5, preferably about 10^{-4} to about 10^{-1} molar; and the diluent must be present in a sufficient amount to form at least a partial solution of the reactants involved in the chemiluminescent reaction. There is no known maximum limit on the concentration of the generic compound of this invention which may be employed in the reaction, and as discussed above, intense chemiluminescent light may be obtained by employment of the high concentrations.

The ingredients of the composition of this invention may be admixed in a single stage of admixing or in a sequence of steps of admixing ingredients together or separately. Accordingly, alternative compositions may be prepared which may be stored over a period of time and which may be admixed with the final ingredient at a time when the chemiluminescent lighting is desired. For example, one such composition would be a composition which includes a generic compound of this invention and a fluorescent compound but which does not include a peroxide compound. Another alternative solid composition would be a composition which includes a peroxide, but which does not include the fluorescent compound. Another alternative composition would be a solid composition which includes a solid generic compound of this invention and a solid hydroperoxide compound, and which possibly additionally includes a solid fluorescent compound, but which does not include a diluent. Obviously, the preferred compositions which would be less than all necessary components to produce a chemiluminescent light would be a composition which would be substantially stable to a practical degree over an extended period of time; otherwise, there would be no real advantage in

forming a chemiluminescent reactant to be employed in a subsequent chemiluminescent reaction.

The wavelength of the light emitted by chemiluminescence of the compositions of this invention, i.e., the color of the light emitted, may be varied by the addition of any one or more energy transfer agents (fluorescers) such as the known fluorescent compounds discussed at length above.

The wavelength of the light emitted by the composition of this invention will vary, depending upon the particular fluorescent component employed in the reaction.

Although in the process of obtaining chemiluminescent light according to this invention, it is normally not necessary to employ a specific order to sequence of steps in the adding of the individual ingredients of the inventive chemiluminescent composition, it has been found that the fluorescent component preferably should be already in the reaction mixture at the time of addition of the last component necessary to bring about the chemical reaction and the concurrent release of chemical energy.

Additionally, it has been found that the superior intensity of chemiluminescence is obtained when the final mixture producing the luminescence is maintained at a temperature of between about −40° C. and 100° C., preferably between about 20° C. and 50° C., the luminescense of applicants' process is not limited to these ranges and temperature is not critical.

The lifetime and the intensity of the chemiluminescent light can be regulated by the use of certain regulators such as

(1) By the addition of weak bases to the chemiluminescent composition to increase intensity. Both the strength and the concentration of the base are critical for purposes of exactness in regulation.

(2) By the variation of hydroperoxide. Both the type and the concentration of hydroperoxide are critical for the purposes of exactness in regulation.

The following examples are intended to illustrate the present invention and are in no way intended to limit the invention except as limited in the appended claims.

EXAMPLE 1

Preparation of 5,6,7,8-tetrachloro-1,4-benzodioxane

To a solution of 10.6 g. of tetrachloropyrocatechol monohydrate, 78 g. of dibromoethane and 50 ml. of ethylene glycol which had been heated to 130° was added portionwise 11.6 g. of anhydrous potassium carbonate during two hours. The mixture was heated at 130° for another hour, cooled and poured into water. Extraction with 50% benzene-ethyl ether gave a solid which was washed with methanol and recrystallized from chloroform. The yield of light pink solid, M.P. 163–165° [lit.[1] M.P. 165°] was 1.60 g. or 17%.

EXAMPLE 2

Chlorination of 5,6,7,8-tetrachloro-1,4-dioxane

A refluxing solution of 1.55 g. of 5,6,7,8-tetrachloro-1,4-dioxane and 200 ml. of carbon tetrachloride was treated with chlorine gas while being irradiated with a Hanovia 100 watt lamp (Pyrex filter) until a light yellow color remained. Evaporation of solvent gave 2.20 g. (95%) of colorless solid, M.P. 128–130°.

Analysis.—Calcd. for $C_8Cl_8O_2$ (percent): C, 23.30; Cl, 68.93. Found (percent): C, 23.02; Cl, 68.78.

In another experiment incomplete chlorination of a solution of 1.64 g. of 5,6,7,8-tetrachloro-1,4-benzodioxane and 200 ml. of carbon tetrachloride gave a colorless solid, which was chromatographed on alumina and benzene to yield 1.01 g. (46%) of 2,3,5,6,7,8-hexachloro-1,4-benzodioxane, M.P. 189–192°; NMR, a singlet peak at 6.37δ.

Analysis.—Calcd. for $C_8H_2Cl_6O_2$ (percent): C, 27.98; H, 0.58; Cl, 62.09. Found (percent): C, 27.92; H, 0.67; Cl, 62.41.

[1] L. Horner and H. Merz, Ann., 570, 89 (1950).

EXAMPLES 3–5

In this example, perchloro-1,4-benzodioxane(5,6,7,8-chloro-1,4-dioxane) was examined for chemiluminescent activity. The results are shown in Table I.

TABLE I

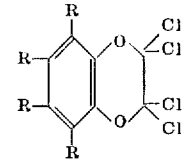
Chemiluminescence Results in Experiments with Perchloro-1,4-benzodioxane (PCBD)

Test	PCBD,[a] M	H_2O_2, M	NaOAc, M	I_{max},[b] ft. lbts. $cm.^{-1}$	Lf. Tm.,[c] mins.
1	0.10	0.66	0.66	0.48	10
1	0.10	0.27	0.66	0.43	10
3	0.01	0.066	0.066	0.28	10
4	0.10	0.66	----	0.28	4
5	0.01	0.066	----	0.29	4

[a] Experiments were run at 25° C. Solvent for PCBD and 9,10-bis(phenylethynyl)anthracene was ethyl benzoate. Solvent for hydrogen peroxide was 3-methyl-3-pentanol when base was not used. In experiments with sodium acetate, acetic acid was used as solvent.
[b] Maximum intensity.
[c] Lifetime.

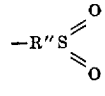
I claim:

1. A chemiluminescent composition intended to be reacted with a hydroperoxide to produce chemiluminescent light said composition comprising the ingredients, a compound of the formula



wherein R represents an electronegative substituent or hydrogen substituent, at least one of said R substituents always being an electronegative substituent; an organic fluorescent compound; and an organic solvent, said ingredients being in such ratios as to produce chemiluminescent light when reacted with hydrogen peroxide.

2. The composition of claim 1 wherein said electronegative substituent is halo, selected from the group consisting of bromo, chloro, and fluoro; alkyl; aryl; $—NO_2$; CN; $—CF_3$;



and $R''O_2C—$, where R'' is alkyl or aryl.

3. The composition of claim 1 wherein said peroxide is hydrogen peroxide.

4. The composition of claim 1 wherein said fluorescent compound is 9,10-bis(phenylethynyl)anthracene.

5. The composition of claim 1 wherein said compound is a chlorinated benzodioxane.

References Cited

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JOHN D. WELSH, Primary Examiner

U.S. Cl. X.R.

252—186; 260—333