

## THE ROLE OF DIARYL OXALATES IN PEROXIOXALATE CHEMILUMINESCENCE

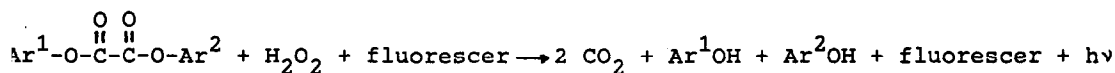
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**Abstract** - The role of symmetrical diaryl and phenyl aryl oxalates in peroxyoxalate chemiluminescence was studied. Maximum emitted light intensity and decay constant of light emission was measured as a function of oxalate, hydrogen peroxide and fluorescer concentration. Data permitted a suggestion for the mechanism of the reaction and its rate determining step.

**Introduction:** Peroxyoxalate chemiluminescence is one of the most efficient non-biological light producing systems. Its simplified equation may be written as follows [1]:



(Ar<sup>1</sup>, Ar<sup>2</sup> = aryl)

Individual steps and intermediates postulated for this process in the literature [2,3] are summarized in Fig. 1. The suggested mechanisms agree that the first relatively stable product of the reaction of a diaryl oxalate (1) and hydrogen peroxide is an aryl hydroperoxy oxalate (2), which then transforms either to a 1,2-dioxetan-3,4-dione (3) or to a 4-aryloxy-4-hydroxy-1,2-dioxetan-3-one (4). The authors assume that compound 3 or 4 are responsible for chemiluminescence; their interaction with the fluorescent molecule (fluorescer) gives the excited fluorescer. Excitation of the fluorescer proceeds probably by the CIEEL mechanism [4].

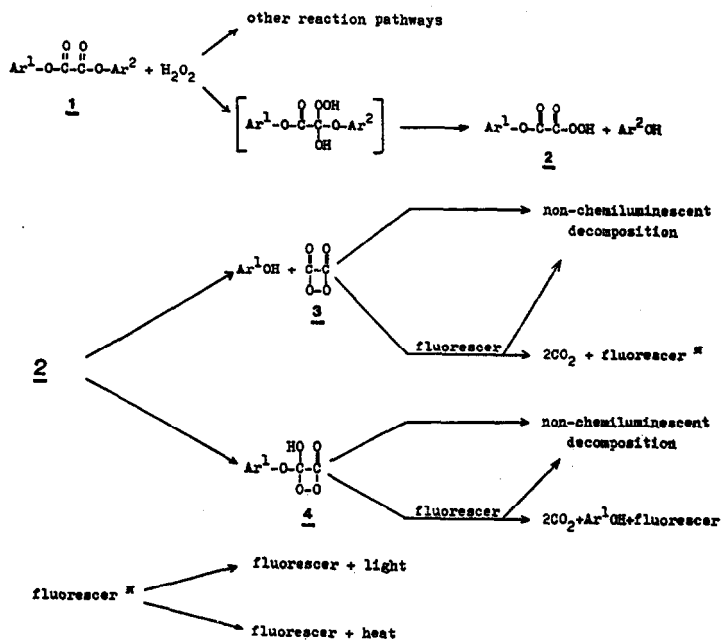


Figure 1

Proposed mechanisms of peroxyoxalate chemiluminescence

9,10-Bis(phenylethynyl)anthracene (BPEA), the fluorescer used in the experiments, which does not contain reactive groups, remains unchanged under the conditions of chemiluminescence and thus it can be assumed that its role is restricted to the transfer of chemical energy.

If the process of chemiluminescence involved a single rate-determining step (and this is our hypothesis) three steps described in the published variations of this mechanism can be postulated as being rate determining: 1) Reaction of diaryl oxalate and hydrogen peroxide. 2) Transformation of aryl hydroperoxy oxalate. 3) Decomposition of intermediates 3 or 4 by interaction with the fluorescer or without it.

To determine the rate-determining step of the chemiluminescent process we monitored, as a function of time, the chemiluminescence and the appearance of phenolic products. According to Catherall and his coworkers [3] and to De Jong *et al.* [5] after reaching a maximum, the decay of light intensity can be well approximated by the following formula:

$$I_t = I_0 \cdot \exp(-k_L \cdot t)$$

where  $I_t$  is the actual light intensity,  $t$  the time and  $k_L$  the rate constant

of exponential decay. For the characterization of emitted light  $I_{\max}$  i.e. maximum light intensity, as well as  $k_L$  is used.

The reaction can also be characterized from the point of view of products. Accordingly the rate constants of the appearance of phenols was also determined. According to our measurements the liberation of phenols can be described by the following equation:

$$C_{\text{ph}}(t) = C_{\text{ph}}(0) + (C_{\text{ph}}(\infty) - C_{\text{ph}}(0)) \cdot (1 - \exp(-k_{\text{ph}} \cdot t))$$

where  $C_{\text{ph}}(t)$  is the concentration of phenol at time  $t$ ,  $C_{\text{ph}}(0)$  the initial phenol concentration, and  $C_{\text{ph}}(\infty)$  the phenol concentration at the end of the reaction.

In the following the rate of appearance of phenol components will be characterized by the pseudo-first-order rate constant  $k_{\text{ph}}$ .

Preliminary experiments were carried out in organic solvent mixtures and permitted the following conclusions: 1) The decay constant of light emission with the generally employed weakly basic catalysts (sodium salicylate, tetrabutylammonium perchlorate) was extremely low in the case of the phenyl aryl oxalates studied. 2) Increasing the phenol concentration in the reaction mixture at the start of the chemiluminescence reaction the decay constant of light emission decreased even with oxalates containing good leaving groups [bis(2,4,6-trichlorophenyl) and bis(nitrophenyl) oxalates]. 3) At the constant excess concentration of hydrogen peroxide the decay constant of light emission decreased when the oxalate concentration increased in the range of  $10^{-3}$  -  $10^{-1}$  M.

Presumably the proton transfer processes and a shift in the acid-base equilibrium may account for these effects. To stabilize the acid-base relationships and to increase the rate of proton transfer processes the experiments discussed in this paper were carried out in aqueous buffer-organic solvent mixtures. In this solvent system the decay constant of light emission could be determined for most of the phenyl aryl oxalates, simultaneously the rate of hydrolysis had to be measured.

## RESULTS

### 1) The effect of concentration on the emitted light

First the effect of essential components of the chemiluminescent system i.e. of oxalate, hydrogen peroxide and fluorescer on the decay constant of emitted light and on maximum light intensity were studied.

In the range of  $10^{-6}$  -  $10^{-3}$  M the concentration of the fluorescer had no effect on the decay constant provided that the concentration of diaryl oxalate and hydrogen peroxide was varied in the range of  $10^{-5}$  -  $10^{-2}$  and  $10^{-4}$  -  $10^{-1}$  M.

At a given concentration of oxalate and hydrogen peroxide maximum emitted light intensity increased linearly with the concentration of fluorescer in the range of  $10^{-6}$  -  $10^{-4}$  M (Fig. 2).

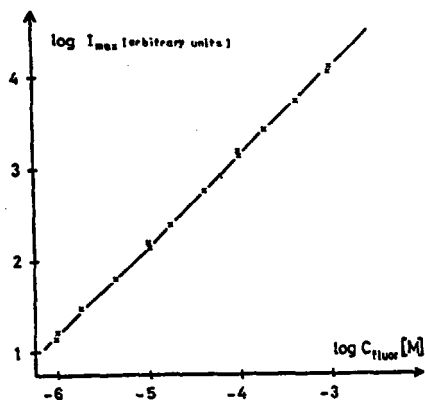


Figure 2

Maximum emitted light intensity ( $I_{\max}$ ) as a function of EPEA concentration ( $C_{\text{fluor}}$ ) at  $10^{-3}$  M bis(3,5-dichlorophenyl) oxalate and  $1.3 \cdot 10^{-2}$  M hydrogen peroxide concentration at room temperature in a 5:2 mixture of tetrahydrofuran and 0.025 M pH 4.0 potassium hydrogen phthalate buffer.

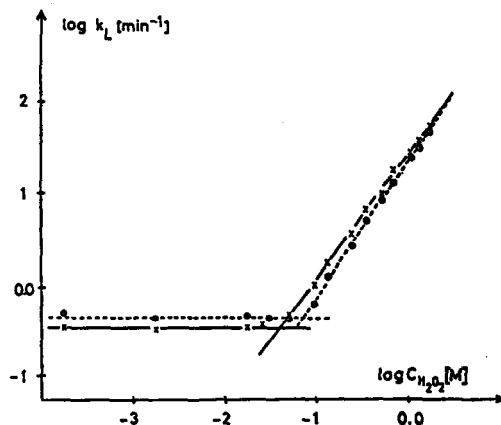


Figure 3

Decay constant of light intensity ( $k_L$ ) as a function of hydrogen peroxide concentration ( $C_{\text{H}_2\text{O}_2}$ ) at two concentrations ( $x=10^{-5}$  M and  $0=10^{-2}$  M) of bis(3,5-dichlorophenyl) oxalate and at  $4 \cdot 10^{-4}$  M EPEA concentration at room temperature in a 5:2 mixture of tetrahydrofuran and 0.025 M pH 4.0 potassium hydrogen phthalate buffer.

The effect of hydrogen peroxide concentration on the decay constant is shown in Fig. 3 for two concentrations of bis(3,5-dichlorophenyl) oxalate. The curve consists of two lines: at low hydrogen peroxide concentrations there is no change in the decay constant, while at higher concentrations a linear correlation can be established. Rate constants obtained with two different concentrations of the ester are practically identical at high and low hydrogen peroxide concentration, but are different at intermediate value. For a given oxalate concentration the following correlation holds:

$$k_L = a + b \cdot (C_{\text{H}_2\text{O}_2})^n \quad (\text{I})$$

TABLE 1. Parameters for the correlation (I) of the decay constant of light intensity and hydrogen peroxide concentration at room temperature at  $10^{-3}$ M oxalate and  $10^{-4}$ M BPEA concentration in a 5:2 mixture of tetrahydrofuran and 0.025 M pH 4.0 potassium hydrogen phthalate buffer

$\text{Ar}^1-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Ar}^2$		<u>a</u>	<u>b</u>	<u>n</u>
Ar <sup>1</sup>	Ar <sup>2</sup>	[min <sup>-1</sup> ]	$\left[ \frac{\text{dm}^3\text{n}}{\text{min}\cdot\text{mol}^{\text{n}}} \right]$	
		-	4.48	1.40
		0.04	7.60	1.40
		0.04	6.60	1.40
		0.05	13.5	1.45
		0.03	10.3	1.45
		0.06	10.7	1.35
		0.05	6.0	1.40
		0.75	76.0	1.35
		0.30	20.1	1.35
		0.60	85.0	1.50
		0.14	14.9	1.45
		0.30	16.0	1.40
		0.12	9.5	1.50
		0.18	0.71	1.15
		0.05	1.90	1.50
		38.0	-	-

where  $C_{\text{H}_2\text{O}_2}$  is the concentration of hydrogen peroxide, a, b and n are constants for a given oxalate and its concentration. Comparing equation (I) and Fig. 3 it can be established that the horizontal line in Fig. 3 at low hydrogen peroxide concentrations gives the value a, the slope of the linear function at higher hydrogen peroxide concentrations is n, its extrapolated value at  $C_{\text{H}_2\text{O}_2}=1.0$  M yields the value b. For some esters the value of a, b, and n at given ester concentration is listed in Table 1. Correlation of maximum emitted light intensity and hydrogen peroxide

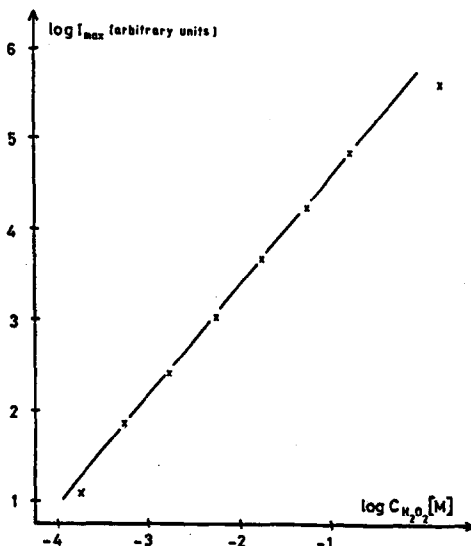


Figure 4

Maximum emitted light intensity ( $I_{\max}$ ) as a function of hydrogen peroxide concentration ( $C_{H_2O_2}$ ) at  $10^{-3}M$  bis(3,5-dichlorophenyl) oxalate and  $4 \cdot 10^{-4}M$  BPEA concentration at room temperature in a 5:2 mixture of tetrahydrofuran and 0.025 M pH 4.0 potassium hydrogen phthalate buffer

concentration for bis(3,5-dichlorophenyl) oxalate is shown in Fig. 4.

According to our measurements maximum light intensity can be given as follows:

$$I_{\max} = d \cdot (C_{H_2O_2})^m \quad (\text{II})$$

where  $C_{H_2O_2}$  is the hydrogen peroxide concentration,  $d$  and  $m$  are constants.

For different esters the value of  $m$  changes between 1 and 1.2 .

Under  $10^{-3}M$  the concentration of diaryl oxalate has practically no effect upon the decay constant of light, while beyond that it is generally the solubility of the oxalate which limits the increase of concentration. With an excess of hydrogen peroxide maximum light intensity changes in all cases linearly with ester concentration:

$$I_{\max} = e \cdot C_{\text{oxalate}} \quad (\text{III})$$

where  $e$  is constant,  $C_{\text{oxalate}}$  is the oxalate concentration.

## 2) Rate of hydrolysis

In the system organic solvent-water chemiluminescence was accompanied by hydrolysis of the oxalate. The amount of phenol liberated was determined by gas chromatography.

We found that hydrolysis followed first-order kinetics. Evaluation of experimental data permitted the conclusion that hydrolysis of diaryl oxalates proceeds in two steps:

Step 1:



Step 2:



This mechanism explains the fact that in the course of hydrolysis (in case of symmetrical oxalates) the first molar equivalent of phenol is liberated relatively fast, while the second one extremely slowly. In the case of phenyl-substituted aryl oxalates practically only the appearance of the substituted phenol component could be detected and according to our data the first step is at least by two orders of magnitude faster than the second one. In accordance with our observations Bruice found [6] that the rates of hydrolysis of ethyl 2-nitrophenyl oxalate and 2-nitrophenyl hydrogen oxalate differ by at least two orders of magnitude.

Rate constants for the first step of hydrolysis are compiled in Table 2.



























## 3) Determination of the phenol components liberated in the chemiluminescence reaction

Along with the measurement of light intensity the appearance of phenol components in the chemiluminescent system was measured in separate parallel experiments by gas chromatography.

Rate constants for large excesses of hydrogen peroxide are shown in Table 3, while those obtained with nearly equimolar oxalate and hydrogen peroxide are compiled in Table 4 along with the decay constants of light intensity. (In the calculation of rate constants results were corrected with data on hydrolysis). The tables contain for phenyl aryl oxalates the rate constants of the appearance of substituted phenol and phenol.

Under the conditions of chemiluminescence reaction - in contrast to simple hydrolysis - the liberation of both phenols was observed. At a hydrogen peroxide concentration of  $10^{-2}$  M at the end of the reaction, depending on the ester studied, 0.5-3% of the expected amount of the less acidic phenol

TABLE 2. Rate constant for the first hydrolysis step of diaryl oxalate (mean of three measurements) and its relative standard deviation (RSD) based on the appearance of the phenol component at  $10^{-3}$  M oxalate concentration at room temperature in a 5:2 mixture of tetrahydrofuran and 0.025 M pH 4.0 potassium hydrogen phthalate buffer

$\text{Ar}^1-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Ar}^2$		$k_{\text{ph}}(\text{Ar}^1\text{OH})$	RSD
Ar <sup>1</sup>	Ar <sup>2</sup>	[min <sup>-1</sup> ]	[ % ]
		$2.5 \cdot 10^{-3}$	5.5
		$3.4 \cdot 10^{-2}$	7.3
		$7.0 \cdot 10^{-3}$	6.2
		$1.3 \cdot 10^{-2}$	4.1
		$9.0 \cdot 10^{-3}$	4.7
		$1.9 \cdot 10^{-2}$	8.6
		$5.4 \cdot 10^{-3}$	7.1
		$7.0 \cdot 10^{-1}$	8.1
		$1.4 \cdot 10^{-2}$	8.9
		$2.0 \cdot 10^{-1}$	5.6
		$2.5 \cdot 10^{-2}$	6.1
		$1.1 \cdot 10^{-1}$	2.2
		$8.3 \cdot 10^{-2}$	7.3

component appeared, while at 1.2 M hydrogen peroxide concentration this value was 15-40%. These values represent the amount of diaryl oxalate bypassing simple hydrolysis. Data in Tables 3 and 4 reveal that decay of chemiluminescence and the liberation of phenols are parallel processes.



TABLE 3. Decay constant of light ( $k_L$ ), rate of appearance of the phenol components ( $k_{ph}$ ) (mean of five measurements) and their relative standard deviations (in parentheses) at  $10^{-3}$ M oxalate,  $4.0 \cdot 10^{-4}$ M BPEA and 0.13 M hydrogen peroxide concentration, at room temperature in a 5:2 mixture of tetrahydrofuran and 0.025 M pH 4.0 potassium hydrogen phthalate buffer































$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{Ar}^1-\text{O}-\text{C}-\text{C}-\text{O}-\text{Ar}^2 \end{array}$		$k_L$		$k_{ph}(\text{Ar}^1\text{OH})$		$k_{ph}(\text{Ar}^2\text{OH})$	
$\text{Ar}^1$	$\text{Ar}^2$	[min <sup>-1</sup> ]	[ % ]	[min <sup>-1</sup> ]	[ % ]	[min <sup>-1</sup> ]	[ % ]
		0.24	(5.6)	0.24	(8.3)	-	-
		0.45	(2.8)	0.45	(9.5)	-	-
		0.40	(3.8)	0.45	(10.3)	0.35	(8.6)
		1.0	(2.1)	0.90	(8.7)	-	-
		0.50	(4.7)	0.45	(11.2)	0.45	(9.4)
		0.27	(6.7)	0.32	(13.1)	0.30	(6.1)
		0.27	(2.2)	0.32	(7.2)	-	-
		0.14	(4.6)	0.17	(7.6)	0.18	(9.7)

TABLE 4. Decay constant of light ( $k_L$ ), rate of appearance of the phenol components ( $k_{ph}$ ) (mean of four measurements) and their relative standard deviations (in parentheses) at  $10^{-2}$ M oxalate,  $4.0 \cdot 10^{-4}$ M BPEA and  $1.3 \cdot 10^{-2}$ M hydrogen peroxide concentration, at room temperature in a 5:2 mixture of tetrahydrofuran and 0.025 M pH 4.0 potassium hydrogen phthalate buffer

$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{Ar}^1-\text{O}-\text{C}-\text{C}-\text{O}-\text{Ar}^2 \end{array}$		$k_L$		$k_{ph}(\text{Ar}^1\text{OH})$		$k_{ph}(\text{Ar}^2\text{OH})$	
$\text{Ar}_1^1$	$\text{Ar}_2^2$	[min <sup>-1</sup> ]	[ % ]	[min <sup>-1</sup> ]	[ % ]	[min <sup>-1</sup> ]	[ % ]
		0.072	(10.7)	0.081	(8.9)	-	-
		0.042	(10.5)	0.060	(7.8)	0.040	(7.4)
		0.029	(11.4)	0.042	(12.0)	0.032	(5.1)
		0.50	(5.2)	0.35	(16.5)	0.40	(11.0)
		0.37	(3.6)	0.40	(7.6)	-	-
		0.13	(4.8)	0.16	(11.3)	0.12	(12.4)
		0.048	(10.8)	0.051	(11.5)	0.048	(9.7)

DISCUSSIONThe rate-determining step

A comparison of the variant of the mechanism shown in Fig. 1 with the results of Fig. 3 permit the conclusion that in a given organic solvent - water system the reaction of hydrogen peroxide with diaryl oxalate is the rate-determining step in the formation of the intermediate responsible for chemiluminescence. At low hydrogen peroxide concentrations this fact is, however, overshadowed by a reaction consuming diaryl oxalate. The rate constant for the latter is represented in equation (I) by parameter a. By comparing the values of a and hydrolysis rates for the different oxalates it can be established that the corresponding values fall in the same order of magnitude and thus the value of a is controlled by hydrolytic processes.

If  $0.02 \text{ min}^{-1}$  is assumed for the a parameter of diphenyl oxalate the values of a and b in equation (I) can be well approximated as follows:

$$a(\text{phenyl-aryl}) = [a(\text{diphenyl}) \cdot a(\text{diaryl})]^{0.5} \quad (\text{IV})$$

and

$$b(\text{phenyl-aryl}) = [b(\text{diphenyl}) \cdot b(\text{diaryl})]^{0.5} \quad (\text{V})$$

(names in parentheses refer to the type of the oxalate).

The rate constant for the disappearance of the product arising from the reaction of oxalate and hydrogen peroxide is greater than the rate constant for its formation. This is also supported by data obtained by gas chromatography; liberation of the two kinds of phenols proceeds practically concurrently at the same rate. The data presented in Table 3 and 4 confirm this fact and reflect unfortunately nothing else than in the chemiluminescent process the slowest step is the first one.

2) Estimation of the amount of emitted light

With the aid of equations (I) and (II) the amount of emitted light can be estimated at a given oxalate concentration if the amount of light emitted up to reaching maximum light intensity is neglected and exponential decay is assumed beyond this point. The amount of emitted light ( $L_e$ ) can be expressed as follows:

$$L_e = d \cdot (C_{\text{H}_2\text{O}_2})^m / [a + b \cdot (C_{\text{H}_2\text{O}_2})^n] \quad (\text{VI})$$

From this expression it is apparent that the amount of light emitted as a function of hydrogen peroxide concentration ( $C_{\text{H}_2\text{O}_2}$ ) passes a maximum, i.e.

beyond a certain concentration the increase of hydrogen peroxide concentration decreases the amount of emitted light.

### 3) About the mechanism of the reaction

According to mechanisms published in the literature the first, relatively stable intermediate along the pathway leading to the chemiluminescent species is an aryl hydroperoxy oxalate (2). In analogy with the drop of reactivity observed with hydrolysis this compound is very much less susceptible towards external attack than the parent oxalate. If this intramolecular transformation (to either 3 or 4) is favoured (which is contradicted by the fact that ethyl oxalyl chloride fails to produce chemiluminescence under the conditions of peroxyoxalate chemiluminescence), this transformation may also precede the elimination of the aryl group and may result in the formation of compound 5 (Fig. 5) before 2 had been formed.

If we suppose that the intermediate is an aryl hydroperoxy oxalate it can be expected, that with phenyl aryl oxalates containing a good leaving group (in this case a common intermediate, the phenyl hydroperoxy oxalate is formed) the decay constant of light emission will not increase beyond a certain hydrogen peroxide concentration, since it is its internal transformation which becomes the rate-limiting step. This kind of behavior has not been observed with the esters studied by us although it was expected on the basis of observations with ethyl oxalyl chloride.

In equations (IV) and (V) the parameters a and b, characterizing the reactivity of phenyl aryl oxalate, are approximated by the geometric means of the symmetrical oxalates. Although a similar estimation is valid for the hydrolysis rates, the equations suggest that both ester group participate in the rate-determining step. In this case it may be supposed that the low reactivity of any ester group precludes the formation of the chemiluminescent species, thus the behavior of ethyl oxalyl chloride and phenyl aryl oxalates can be better explained.

In the postulated mechanism shown in Fig. 5 a 3,4-diaryloxy-3,4-dihydroxy-1,2-dioxetane is produced in the reaction of hydrogen peroxide and diaryl oxalate for which the following possibilities can be envisaged:

- 1) spontaneous decomposition,
- 2) reaction with other components of the reaction mixture,
- 3) further transformation to any of compounds 2, 3, or 4,
- 4) interaction in combination with compounds 3 and 4 with the fluorescer resulting in excitation of the latter.

The rate-determining step of the system is, in agreement both with the findings of Catherall et al. [3] and our results, the reaction of hydrogen peroxide and diaryl oxalate. Intermediate 5 is a labile compound, probably this is the reason that for the dependence of the decay constant of light on

hydrogen peroxide concentration an order of 1 - 1.5 was found.

Assuming the intermediacy of 5 a mechanism can be delineated which is in better agreement with both experimental data and analogies and which also includes the assumptions of Catherall.

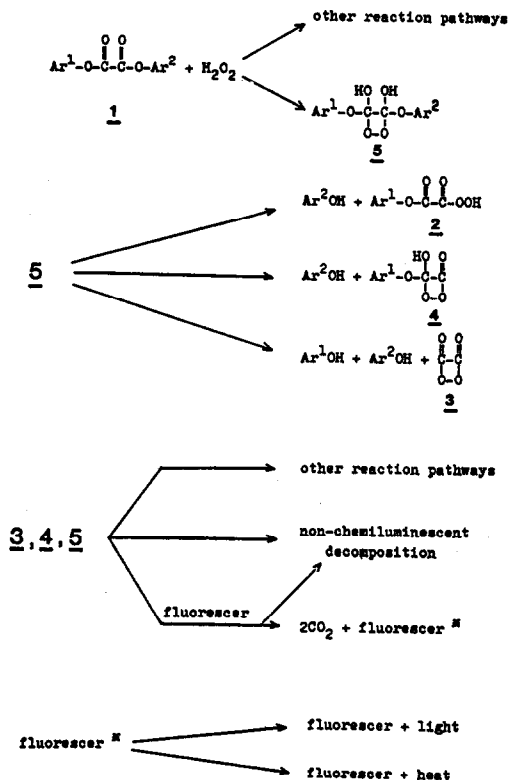


Figure 5  
Suggested mechanism for peroxyoxalate  
chemiluminescence

### EXPERIMENTAL

Diaryl oxalates were prepared by known procedures [2,7,8].

Phenyl aryl oxalates were prepared from phenyl oxalyl chloride [9] and the corresponding phenol.

General method: To a solution of phenyl oxalyl chloride (0.1 mole) in dry tetrahydrofuran (50 ml) triethylamine (0.095 mole) was added dropwise at 0-5°C with stirring within 1.5 h. Stirring was continued at room temperature for another 2 h. After filtering off triethylammonium chloride the solution was evaporated i.v. and the residue crystallized. Physical data and other

TABLE 5. Melting points, solvents of crystallisation, yields and elementary analyses for diaryl oxalates ( B - benzene, C - chloroform, CT - carbon tetrachloride, D - dioxane, EA - ethyl acetate, H - hexane, NB - nitrobenzene, T - toluene, THF - tetrahydrofuran )

Ar <sup>1</sup> -O-C(=O)-C(=O)-O-Ar <sup>2</sup>		M.p.	Solvent	Yield	Calcd.	Found
Ar <sup>1</sup>	Ar <sup>2</sup>	[°C]		[%]	[%]	[%]
		132-138	T	58	C 69.42 H 4.16 O 26.42	69.12 4.02 26.50
		118-119	T	30	C 54.05 H 2.59 O 20.57 Cl 22.79	54.24 2.47 20.42 23.40
		70-71	H	40	C 60.78 H 3.28 O 23.13 Cl 12.81	60.15 3.26 23.38 12.43
		184-188	THF	56	C 54.05 H 2.58 O 20.57 Cl 22.79	54.13 2.53 20.66 23.32
		98-100	H	77	C 60.78 H 3.28 O 23.13 Cl 12.81	59.94 3.30 23.47 12.96
		183-186	CT	59	C 42.04 H 2.02 O 16.00 Br 39.95	41.72 2.06 15.93 40.25
		89-91	CT	37	C 52.36 H 2.85 O 19.93 Br 24.88	52.12 2.88 20.21 25.11
		275-280	D	23	C 50.61 H 2.43 N 8.43 O 38.53	50.42 2.37 8.30 38.45
		128-130	CT	37	C 58.54 H 3.16 N 4.88 O 33.42	59.28 3.10 4.89 33.30
		208-211	EA	57	C 65.76 H 2.76 N 9.59 O 21.90	65.23 2.79 9.33 21.38
		85-89	CT	38	C 67.42 H 3.39 N 5.24 O 23.95	66.28 3.53 5.47 24.34
		172-176	C	49	C 44.25 H 1.59 O 16.04 Cl 37.32	42.89 1.49 16.91 37.30
		67-69	H	28	C 54.05 H 2.59 O 20.57 Cl 22.79	55.14 2.50 20.17 23.93
		190-193	B	63	C 37.46 H 0.90 O 14.26 Cl 47.39	37.81 0.83 14.51 48.07
		94-98	H	39	C 48.66 H 2.04 O 18.52 Cl 30.78	48.14 1.89 18.03 32.18
		194-197	NB	37	C 39.83 H 1.43 N 13.27 O 45.47	39.90 1.36 13.18 43.76

information of the products are compiled in Table 5. M.p.s were not corrected, elementary analyses were carried out on Carlo Erba 1106 instrument.

In the presence of excess triethylamine part of the product undergoes disproportionation to symmetrical oxalates.

Measurement of light intensity: 9,10-bis(phenylethynyl)anthracene was prepared as described in the literature [10] and brought to m.p. 252.5-253.5°C by repeated recrystallization from toluene. Tetrahydrofuran was redistilled from lithium aluminum hydride and solutions were freshly prepared every day.

Experiments were carried out with magnetic stirring in glass cells of 10 mm diameter at room temperature. The cells were flushed with nitrogen saturated with tetrahydrofuran vapors, light intensity was measured with an EMI 9826B photomultiplier. The solution of the ester and of 9,10-bis(phenylethynyl)anthracene in 5 ml tetrahydrofuran were placed into the cell and to this was pipetted the previously prepared 1:1 mixture (2 ml) of an aqueous hydrogen peroxide solution of given concentration and of a 0.05 molar pH 4.0  $\mu=0.1$  (KCl) potassium hydrogen phthalate buffer.

Measurement of hydrolysis rate: These were carried out at room temperature. Instead of hydrogen peroxide solution the buffer was mixed with water and this buffer solution, diluted to twice of its original volume, was pipetted to the solution of diaryl oxalates in tetrahydrofuran.

Gas chromatography: Measurements were carried out at 60-100°C isotherm oven temperature, on a Packard 439 instrument using a Sil 5 CB (Chrompack) capillary column of 5m x 0.25 mm ID and 0.12  $\mu$  film thickness; injector and detector (FID) temperature 150°C, carrier gas hydrogen of 50 kPa (1.8 m/s, split ratio 1:25). The temperature of the column was adjusted to give retention times less than 30 s for the phenol to be determined. The reaction mixtures were prepared as described above. At intervals samples were withdrawn for analysis.

#### REFERENCES

1. Rauhut M. M. *Acc. Chem. Res.* 1969, **2**, 80-87.
2. Rauhut M. M.; Bollyky L. J.; Roberts B. G.; Loy M.; Whitman R. H.; Ianotta A. V.; Semsel A. M.; Clarke R. A. *J. Am. Chem. Soc.* 1967, **89**, 6515-6522.
3. Catherall C. K. R.; Palmer T. F.; Cundall R. B. *J. Chem. Soc. Faraday Trans. 2*, 1984, **80**, 823-836, 837-849.
4. Schuster G. B.; Horn K. A. *Chemically Initiated Electron-Exchange Luminescence in Chemical and Biological Generation of Excited States* (Ed.s Adam W.; Cilento G.) Academic Press, N.Y. 1982, p. 229-247
5. De Jong G. J.; Lammers N.; Spruit F. J.; Frei R. W.; Brink U. A. Th. *J. Chrom.* 1986, **353**, 249-257.
6. Bruice T. C.; Holmquist B. *J. Am. Chem. Soc.* 1967, **89**, 4028-4034.
7. Bollyky L. J.; Rauhut M. M. *US Patent* 3,597,362
8. Ivashchenko J. N.; Akkerman V. P.; Moschitskij S. D. *Zh. Obsch. Khim.* 1963, **33**, 3829-3831.
9. Stollé R.; Knebel E. *Ber. dtsh. chem. Ges.* 1921, 1213-1230.
10. Ried W.; Donner W.; Schlegelmilch W. *Chem. Ber.* 1961, **94**, 1051.