Substituent Effect of the Peroxyoxalate Chemiluminescence

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Most well-known and efficient chemiluminescent reactions are based on the oxidation of a diaryl oxalate by hydrogen peroxide in the presence of a fluorescent compound, which had permitted the wide use for both civilian and military purposes[1–6] . As shown in the following scheme, it was proposed [1] that the first step is the base-catalyzed nucleophilic addition of hydrogen peroxide to ester carbonyl, known to be rapid with electronegatively substituted aryl acetates, the intermediate in momentary existence could undergo the normal elimination of ROH to give peroxyacid, and will finally give rise to a high energy intermediate, a cyclic peroxide 1, 2-dioxetanedione, which is responsible for the light emitting process in a complex form. This has been verified by the recent kinetic study [6, 7]. This important intermediate was thought to be produced by the reaction of hydrogen peroxide and active oxalate esters. Therefore, the intensity and duration of light output was recognized to be primarily dependent on the reactivity of the diaryl oxalate towards nucleophilic attack by hydrogen peroxide [5].

However, up to now, there has been no minute description about the crystal structure because the oxalates are not so stable. The electron density distribution of the diaryl oxalate, which is necessary for the in-depth knowledge of the nucleophilic reaction mechanism, have not been found either. For this reason, the
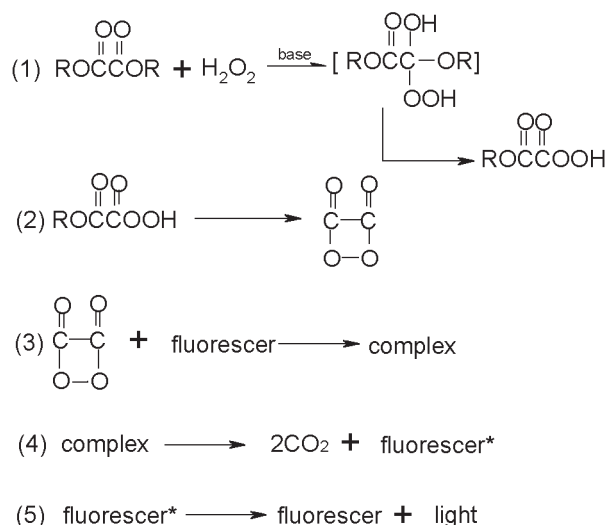
The suggested chemiluminescent mechanism

single crystal and theoretical studies on the peroxyoxalate chemiluminescent systems were reported here. As described in Fig. 1, four typical oxalate esters were
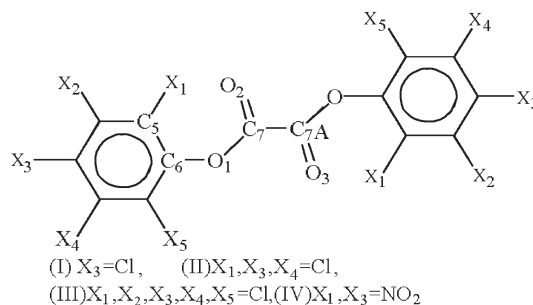

(I) X_3=Cl,   (II)X_1,X_3,X_4=Cl,
(III)X_1,X_2,X_3,X_4,X_5=Cl,(IV)X_1,X_3=NO$_2$

Fig. 1   Molecular structures of the studied compounds

Table 1   Crystal data and structure refinement for compound III

Identification code	Compound III
Empirical formula	$C_{14}Cl_{10}O_4$
Formula weight	586. 64
Temperature	293(2) K
Wavelength	0. 071073 nm
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	$a = 0.55257(6)$ nm $\alpha = 95.456(7)°$
	$b = 0.60352(6)$ nm $\beta = 90.600(9)°$
	$c = 1.52560(13)$ nm $\gamma = 98.040(8)°$
Volume	0. 50134(9) nm³
Z	1
Density (calculated)	1. 943 mg · m⁻³
Absorption coefficient	1. 410 mm⁻¹
F(000)	286
Crystal size	0. 3 mm × 0. 5 mm × 1. 0 mm
Theta range for data collection	2. 68 to 25. 00°.
Index ranges	$-1 \leq h \leq 6, -7 \leq k \leq 7, -18 \leq l \leq 18$
Reflections collected	2351
Independent reflections	1766[$R_{(int)} = 0.0260$]
Completeness to theta = 25. 00°	99. 9 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1766/0/128
Goodness-of-fit on F^2	1. 069
Final *R* indices[$I > 2sigma(I)$]	$R_1 = 0.0367, wR_2 = 0.0911$
R indices (all data)	$R_1 = 0.0497, wR_2 = 0.0988$
Extinction coefficient	0. 022(3)
Largest diff. peak and hole	2. 67 × 10⁻⁴ and -2. 55 × 10⁻⁴ e · nm⁻³

synthesized by the traditional method [1, 5] . Among them, the single crystal of (III) was grown from hexane. Intensity data were collected on Simens P4 diffractometer, Mo- *K*$_\alpha$ radiation. The structure was resolved by the direct method with SHELXS and refined with SHELXL. The obtained crystal data and structure refinement were listed in Table 1.

     By using the RF540 fluorescence spectrometer with the xenon light off, the relative light-emitting intensity was recorded when 0. 01 mol · L⁻¹ oxalates were mixed with 0. 5 mol · L⁻¹ hydrogen peroxide in the presence of fluorescer 9, 10-bis(phenylethynyl) anthracene of 0. 0012 mol · L⁻¹.

     As shown in Fig. 2, bis(pentachlorophenyl) oxalate (III) has an inversion center. Its backbone is made of two aromatic ring linked by an oxalic group. The planes that are composed of the side phenyl rings are parallel to each other. The torsion angles, C (4) − C(5) − C(6) − O(1) of 173. 6(2)°, C(7) − O (1) − C(6) − C(5) of 86. 8(3)° and C(6) − O(1) −
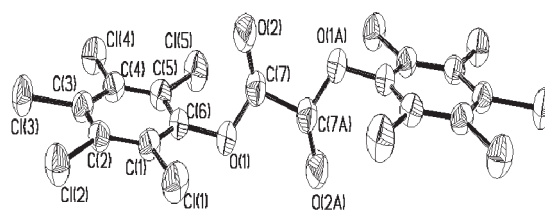

Fig. 2   The ORTEP view of III. Thermal ellipsoids are drawn at the 50% probability level

C(7) − O(2) of 1. 0(5)°, indicate that the plane of the oxalic group is almost vertical to side phenyl rings. This may be a result of the steric effect imposed by the five chlorine substituents. The single crystal study reveals that the relative orientation of the two carbonyl bonds is not *cis* as in the scheme, but *trans* as similar to the molecular structure of oxalic acid [8]. The C(7) − O(1) bond length of 0. 1388 nm is also similar to that of oxalic acid as 0. 1336 nm. On the other hand, the C(7) = O(2) and C(7) − C(7A) bond lengths of 0. 1181 nm and 0. 1536 nm, respectively,

are a little contracted as compared with those of oxalic acid, i. e., 0. 1205 and 0. 1544 nm, respectively.

As found in other experimental studies [1, 5], the relative light-emitting intensity of these diaryl oxalates increases with the more electronegative groups, namely I < II < III < IV. To obtain insights into the electronic nature of this sequence, the hybrid Hartree-Fock-Density-Functional-Theory（HF-DFT）model B3LYP together with the STO-3G* basis set（it has 230 basis functions and 600 primitive gaussians for III）in *Gaussian* 98 [9] were adopted to fully optimize all molecular structures, and then perform the natural orbital population analysis on all component atoms. The density functional study extends the single crystal characterization of compound III to other compounds. For instance, the two carbonyl bonds of the central moiety in all studied compounds are found to be kept in the *trans* orientation, which suggests that this may be valid for all diaryl oxalates in chemiluminescent systems. The calculated torsion angle, $C(7) - O(1) - C(6) - C(5)$, increases in the order of I< IV< II < III, which demonstrates the steric effect by the number of substituents in the studied compounds. It is interesting to note that after investigating all the electron density distribution of the component atoms, only the formal charges of $C(7)$ or $C(7A)$, 0. 256, 0. 260, 0. 265, and 0. 275 *e* corresponding to the compounds I, II, III, IV, respectively, that have the same tendency of the relative light-emitting intensity in these typical chemiluminescent systems. So the more positively charged reaction center according to the proposed mechanism will improve the nucleophilic reactivity by hydrogen peroxide, which may enhance the yield of the presumed intermediate. In this way, the resultant chemiluminescent efficiency is increased as observed in the experiments.

References

1　Rauhut M M, Bollyky L J, *et al. J. Am. Chem. Soc.,* **1967, 89**: 6515

2　Mccapra F. *J. Photo. Chem. Photo. Bio. A*, **1990, 51**: 21

3　Bollyky L J, Rauhut M M. U. S. Pat., 1971, 3597362

4　Maulding D R. U. S. Pat., 1972, 3704309

5　Dowd C D, Paul D B. *Aust. J. Chem.,* **1984, 37**: 73

6　Baader W J. Biolumin. Chemilumin., Proc. Int. Symp., 1997, 9th, 16

7　Schaap A P, Chen T -S, Handley R S, *et al. Tetrahedron Lett.,* **1987, 28**: 1155

8　"CRC Handbook of Chemistry and Physics", 78th Ed., Florida, CRC Press. 1997

9　Gaussian 98, Revision A. 7, Frisch M J *et al.* Gaussian, Inc., Pittsburgh PA, 1998

过氧草酸酯结构和取代基对其化学发光的影响

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摘要　　通过单晶测定和理论研究阐述了过氧草酸酯化学发光中取代基的影响．几种典型的芳基草酸酯所观察的化学发光效率随着羰基碳原子的正电荷增加而递增．通过电子密度函数的计算印证了芳基草酸酯对过氧化氢亲核进攻的活泼性．

关键词：　化学发光，　晶体结构，　密度函数计算，　取代基影响