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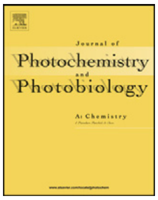

The Hammett correlation between distyrylbenzene substituents and chemiluminescence efficiency providing various ρ-values for peroxyoxalate chemiluminescence of several oxalates

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ABSTRACT

Peroxyoxalate chemiluminescence (PO-CL) was investigated using eight oxalates with various phenol moieties and the distyrylbenzene (DSB) fluorophores with various substituents. The ρ-values in the Hammett correlation between the substituent constants (σ_p^+) of the DSBs and the singlet chemiexcitation yields (Φ_S) for the PO-CL reactions varied from −0.50 to −1.01 depending on the oxalate structure, and the reactive oxalates tended to afford the higher absolute ρ-values but with a few exceptions. Based on the CIEEL mechanism, these experimental observations suggest that the aryloxy groups still remain in the 1,2-dioxetanones (DOTs), which are the postulated high-energy intermediates, and control the electronic properties of DOTs as electron-acceptors. The LUMO energies of the DOTs calculated by the ab initio method with a B3LYP/6-31g(d) basis set reveal that the lower the DOT-LUMO energies, the higher the absolute ρ-values were provided for the corresponding oxalates, as predicted by the frontier molecular orbital (FMO) theory. Thus, the chemical species interacting with the DSBs would be not unitary and will be DOTs.

1. Introduction

Since Chandross first discovered the peroxyoxalate chemiluminescence (PO-CL) reaction [1], much attention has been paid to this CL and chemists have tried to elucidate its mechanism for a long time [2–25] because of high efficiency [23] and usefulness in analytical chemistry [26,27]. Among the several peroxides proposed so far as the high-energy intermediates (HEIs) capable of generating the excited fluorophores during their decomposition, the four-membered cyclic peroxides, such as 4-aryloxy-4-hydroxy-1,2-dioxetane-3-one (DOT) and 1,2-dioxetne-3,4-dione (DOD), have been the most frequently proposed [3,4,6,7,9,10,14,19,21,22]. However, these intermediates have never been captured nor isolated. There have been studies observing labile intermediates by NMR using the highly reactive oxalates [28,29]. In addition, the EPR detection of a biradical as a trace of the formed DOD during the reaction of the oxalyl chloride and hydrogen peroxide spectra was very recently reported [30]. CIEEL (chemically initiated electron exchange luminescence) mechanism [31,32] was applied to the PO-CL [33,34], and explained experimental evidences [35–40]. According to this mechanism, an electron transfer from the fluorophores to the HEI, such as the DOTs or DOD, takes place to form a pair consisting of the carbon dioxide radical anion and the fluorophore radical cation during the decomposition of the HEI, which is followed by a back electron transfer to produce the excited fluorophores (Scheme 1). In spite of a steady accumulation of knowledge and many recent efforts made by a number of chemists, identification of the HEIs interacting with fluorophores still remains unclear.

It is important to examine the effect of the oxalate structures on the CL behavior [22], because there have been only a few reports in which a number of oxalates were employed, and new aspects can be obtained by comparing the CL behavior of the different oxalates, if the structure of the HEI as the electron-acceptors is not unitary and might depend on the oxalate structures. On the other hand, the 1,4-distyrylbenzene (DSB) derivatives are strongly fluorescent [41,42] and good emitters among the numerous fluorophores so far used for the PO-CL reactions [38,39] due to availability by the simple synthetic method and capability of modulating their electronic properties by the substituents. During our continuous studies of the DSB enhanced PO-CL, some remarkable electronic effects on the CL efficiency have been observed. Therefore, it is expected that there is a possibility of identification of the HEIs when the CL behavior using various DSBs and oxalates is investigated in detail. In this paper, we report the Hammett correlation between the DSB substituents and the behavior of the DSB enhanced PO-CL reactions employing the

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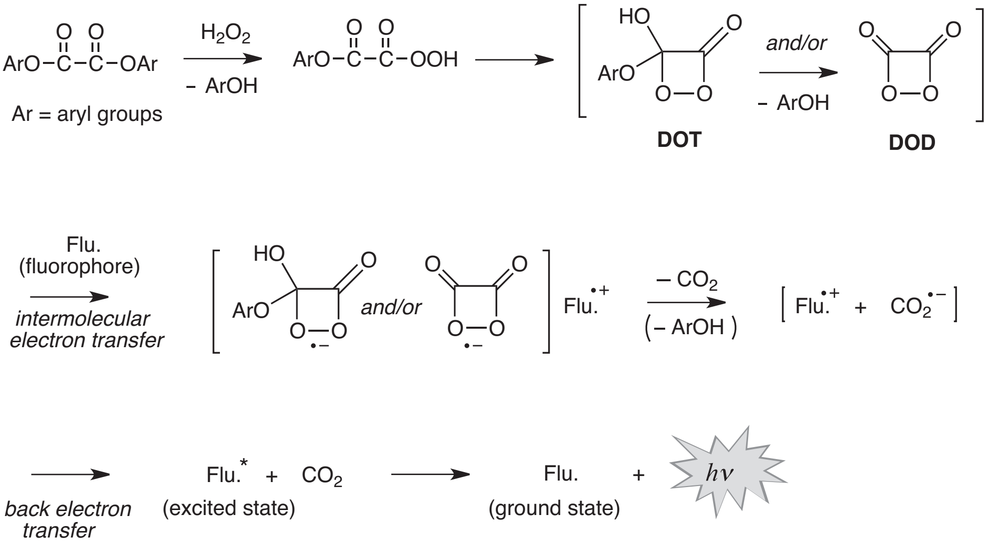


Scheme 1. A CIEEL process of peroxyoxalate chemiluminescence containing the diexetanones (DOTs) or dioxetanedione (DOD) high-energy intermediates.

eight aryl oxalates and give consideration to the HEIs in connection with the interpretation of the observed CL behavior using the frontier molecular orbital (FMO) theory.

2. Experimental details

2.1. Materials

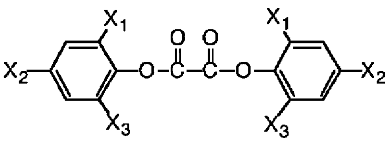
Melting points were determined using a hot stage microscope apparatus and were uncorrected. Proton nuclear magnetic resonance ^{1}H and ^{13}C NMR spectra were measured on a Bruker AVANCE-400 at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, respectively, in $CDCl_3$. The chemical shifts (δ) are reported in ppm downfield from TMS as internal standard or from the residual solvent peak for ^{1}H and ^{13}C NMR. Coupling constants (J) are reported in Hz. Low and high resolution mass spectra (MS) were recorded by the JEOL JMS-K9 spectrometers. Elemental analysis was recorded on a Perkin-Elmer 2400CHN elemental analyzer. Analytical TLC was carried out on precoated silica gel 60F-254 plates (E. Merck). Column chromatography was performed on silica gel (E. Merck). Absorption and fluorescence spectra were recorded on a U-3310 spectrometer (Hitachi) and on a RF-5000 spectrometer (Shimadzu), respectively. The measurements of the total CL quantum yield (Φ_{CL}) were carried out by a photon-counting method using a Hamamatsu Photonics R464 photomultiplier connected to a photon-counting unit (C3866) and a photon-counting board M8784, and the luminol CL [$\Phi_{CL} = 0.09$ in dimethyl sulfoxide, Lit. J. Lee, H. H. Seliger, Photochem. Photobiol. 15 (1972) 227–237] was used as the standard in DMSO for the calibration of the photomultiplier tube.

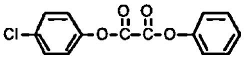
All commercially available chemicals and solvents were of the highest purity or purified by the standard method. A series of the oxalates employed in the present study, all of which are known compounds, are listed in Table 1. They were prepared from the reaction of oxalyl chloride and two equivalents of the corresponding phenols in the presence of triethylamine in benzene, while the unsymmetrical oxalate 4-CPPO was prepared from the reaction of oxalyl chloride and one equivalent phenol in the presence of triethylamine followed by the addition of another *p*-chlorophenol. DNPO [bis(2,4-dinitrophenyl) oxalate] was supplied by Tokyo Chemical Industries (TCI).

2.1.1. 1,4-Bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene

2-Ethylhexyl bromide (35 g, 180 mmol) was added dropwise to a solution of hydroquinone (10 g, 91 mmol) and potassium hydroxide (13 g, 230 mmol) in ethanol (80 mL) and stirred for 2 h at

Table 1
Structures of oxalates used in this study and p*K*a of phenols as leaving groups.



Oxalate	Abbreviation	X_1	X_2	X_3	p*K*a of phenol
Diphenyl oxalate	**DPO**	H	H	H	9.91
bis(2,4,6-Tricholorophenyl) oxalate	**TCPO**	Cl	Cl	Cl	6.00
bis(2,4-Dichlorophenyl) oxalate	**2,4-DCPO**	Cl	Cl	H	7.85
bis(2,6-Dichlorophenyl) oxalate	**2,6-DCPO**	Cl	H	Cl	6.69
bis(4-Chlorophenyl) oxalate	**4-CPO**	H	Cl	H	9.29
bis(2-Chlorophenyl) oxalate	**2-CPO**	Cl	H	H	8.41
bis(2,4-Dinitrophenyl) oxalate	**DNPO**	NO_2	NO_2	H	3.87
4-Chlorophenyl phenyl oxalate	**4-CPPO**				–