Controlling Chemiluminescence Dynamics through Reaction Kinetics Tuned by Initiator Steric Effects

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Abstract

Chemiluminescence based on peroxyoxalate reactions underlies the operation of commercial glowsticks, which are widely used as portable light sources. Despite their practical value, a major limitation is their relatively short emission duration, which is intrinsically governed by reaction kinetics. In this study, we investigated how structural variation of the oxalate ester affects emission dynamics by comparing bis(2,4,6-trichlorophenyl) oxalate (TCPO) and bis (2,4-dinitrophenyl) oxalate (DNPO). Under identical experimental conditions, DNPO exhibited a consistently longer emission duration than TCPO. This difference can be rationalized by the distinct steric and electronic properties of the substituents. TCPO introduces steric congestion through multiple chlorine atoms, while DNPO incorporates strongly electron-withdrawing nitro groups that extend π-resonance and slow the perhydrolysis step. These findings highlight that beyond external factors such as temperature and catalyst concentration, rational modification of oxalate ester structure provides a viable strategy for tuning the brightness–lifetime trade-off in glowsticks. Our results suggest that electronic and steric descriptors, including molar refractivity (MR) and topological polar surface area (TPSA), can serve as predictive tools for guiding the design of new oxalate esters with prolonged emission, thereby offering opportunities for improved chemiluminescent devices in both practical and fundamental contexts.

Keywords: Kinetics, Steric hindrance, Chemiluminescence, Glowstick

Introduction

Chemiluminescence (CL) is the emission of light from a chemical reaction, in which the energy released during the transformation of reactants is directly converted into electronic excitation of a product molecule, typically without requiring an external light source.[1] This phenomenon underpins a wide range of natural and artificial luminescent systems, including bioluminescence (e.g., fireflies, marine organisms) and artificial devices such as glowsticks.

The chemiluminescence reaction occurring in glow sticks is classified as peroxyoxalate chemiluminescence (PO-CL). This reaction involves oxalate esters and hydrogen peroxide in the presence of a fluorescent activator and has been extensively studied due to its high quantum yield and practical applications in emergency lighting, military signaling, and analytical detection. [2,3]

The first state of the PO-CL reaction is the formation of 1,2-dioxetanedione, which is a high-energy, unstable chemiluminescent intermediate. This step is caused by a nucleophilic attack on oxalate ester by hydrogen peroxide. This process is classified as a nucleophilic acyl substitution, which is initiated by the peroxide oxygen attacking the carbonyl carbon of oxalate ester, forming a tetrahedral intermediate. Then, the leaving group – which is the 2,4,6-trichlorophenoxide group in the case of this reaction – departs and creates a monoperoyoxalic acid intermediate. Then, the second hydrogen peroxide molecule undergoes a similar reaction, leading to the formation of the desired intermediate. The mechanism for this intermediate formation is shown as Figure 1.

Glowsticks based on PO-CL are convenient light sources but exhibit an intrinsic brightness–lifetime trade-off. When PO-CL intensity increases, chemiluminescene duration time decreases. Several approaches have been attempted by changing experimental conditions such as reaction temperature, catalyst, pH, which affects to the reaction rate. [4,5]

This study has been mainly focused on elongation the glow duration by reducing the effective rate of the base-catalyzed steps through increased steric hindrance of the initiator by employing bulkier, less accessible catalytic sites to raise the activation barrier along the perhydrolysis/chemiexcitation pathway while maintaining acceptable overall chemiluminescence yield. This approach is consistent with recent mechanistic work resolving the chemiexcitation step and with comprehensive reviews that link PO-CL emission dynamics to controllable kinetic bottlenecks.

Methods

Reaction of PO-CL and measurement of chemiluminescence

The chemiluminescence was observed under equal conditions, with the same concentrations and stoichiometry. First, 0.3 g of oxalate ester was added into 15 mL vial followed by addition of 0.15 g of sodium acetate and 9,10-bis(phenylethynyl) anthracene (BPEA). And then, 15 mL of ethanol and ethyl acetate were added respectively. Lastly, 6 mL of 3 % (v/v) hydrogen peroxide (H2O2) was added and gently shaken once in 15 minutes, and each 15-minute cycle was photographed and recorded in 5-minute intervals.

In this experiment, two distinct oxalate esters, bis(2,4,6-trichlorophenyl) oxalate (TCPO) and bis(2,4-dinitrophenyl) oxalate (DNPO) were used as initiator. Molecular structure of these two oxalate esters were shown as Figure 2. TCPO consists of chlorides substituted on two benzene rings, which are again substituted to the oxalate ester. DNPO has a similar structure but has different substituents on the benzene rings: DNPO molecule consists of two nitro (-NO2) groups, which are larger substituents compared to the chloride substituents of TCPO.

Results

PO-CL of each oxalate ester have been successfully confirmed and result was shown as Figure 3. Since the photographic data of only one cycles for each TCPO and DNPO were reviewed, the rate of decay can be analyzed by the change in brightness. To perform such, the hexadecimal color codes of the sample of chemiluminescence was obtained and then converted to HSL cylindrical coordinate representation, which utilizes hue, saturation, and lightness. The lightness component of the obtained result was used as a measure to analyze brightness and shown as Table 1.

For TCPO and DNPO chemiluminescence sample, the following hexadecimal color codes and HSL (only the lightness component is included) were obtained for each stage of chemiluminescence. The following data was then plotted as a dot plot, and an exponential decay regression, which can appropriately analyze the decay of the light source, was done to each dataset and shown as Figure 4.

By using exponential regression tool, the decay constant k for the TCPO sample was 0.2027 with half-life of 3.42 steps and 17.1 minutes, and the decay constant k for the DNPO sample was 0.145 with half-life of 4.78 steps and 23.9 minutes. Thus, the DNPO chemiluminescence can be considered to decay at a slower rate and thus glow longer.

Discussion

DNPO have been exhibited a significantly longer emission duration than TCPO under identical reaction conditions. This result indicates that the molecular structure and steric hindrance of the oxalate ester plays a critical role in modulating the kinetics of the PO-CL reaction. Although both TCPO and DNPO contain strongly electron-withdrawing substituents, their steric and electronic properties differ substantially. TCPO, with chlorine atoms at the 2-, 4-, and 6-positions, introduces pronounced ortho-steric hindrance around the oxalate ester moiety. In contrast, DNPO carries nitro groups at the 2- and 4-positions and may appear less sterically congested, the nitro substituents exert strong electron-withdrawing effects and extend conjugation through π-resonance, which can stabilize the aryl ring and reduce the nucleophilic susceptibility of the oxalate carbonyl centers. As a result, the perhydrolysis step leading to the high-energy intermediate is expected to proceed more slowly, thereby prolonging the chemiluminescent emission.

Previous studies have been reported that the electronic and steric properties of substituents on diaryl oxalates strongly modulate the efficiency and kinetics of PO-CL reactions.[6] Substituents that electronically deactivate the aromatic ring or impose steric constraints on the reaction coordinate can increase the activation barrier for the chemiexcitation step, resulting in slower reaction kinetics and extended glow times.

Not only interpretation of this experimental result, computational analysis also performed for further demonstration. Computation was performed by using SwissADME, web-based pharmacokinetics analysis platform[7] and results are shown as Table 2. DNPO has larger molar refractivity (MR) and topological polar surface area (TPSA) and indicates that DNPO molecule is more sterically hindered during PO-CL reaction. However, SwissADME is optimized with pharmacokinetics analysis and other calculation by using quantum chemistry-based platform such as Gaussian is required in order to obtain more exact steric strain result.

Conclusion

In this work, we demonstrated that structural variations in oxalate esters significantly influence the emission characteristics of peroxyoxalate chemiluminescence. Direct comparison between TCPO and DNPO revealed that DNPO consistently produced a longer emission duration under identical conditions. This difference can be attributed to the interplay of steric and electronic effects. While TCPO is heavily substituted with chlorine atoms, creating steric congestion, DNPO introduces nitro groups that exert strong electron-withdrawing effects and extend π-resonance, thereby slowing the perhydrolysis step and prolonging light emission.

These findings suggest that the brightness–lifetime trade-off in glowsticks can be addressed not only through external conditions such as temperature or catalyst concentration, but also through rational molecular design of the oxalate ester itself. Incorporating electronic and steric descriptors, such as MR and TPSA, offers a framework for correlating molecular structure with emission dynamics. Ultimately, the strategic modification of oxalate esters provides a practical route to developing chemiluminescent systems with enhanced longevity and performance.

References

1. McCapra, F. (1966). The chemiluminescence of organic compounds. Quarterly Reviews, Chemical Society, 20, 485–510.

2. Silva, S. M., Casallanovo Jr, F., Oyamaguchi, K. H., Ciscato, L. F., Stevani, C. V., & Baader, W. J. (2002). Kinetic studies on the peroxyoxalate chemiluminescence reaction: determination of the cyclization rate constant. Luminescence: The journal of biological and chemical luminescence, 17(5), 313-320.

3. Cabello, M. C., Bartoloni, F. H., Bastos, E. L., & Baader, W. J. (2023). The molecular basis of organic chemiluminescence. Biosensors, 13(4), 452.

4. Ciscato, L. F., Bartoloni, F. H., Bastos, E. L., & Baader, W. J. (2009). Direct kinetic observation of the chemiexcitation step in peroxyoxalate chemiluminescence. The Journal of Organic Chemistry, 74(23),

8974-8979.

5. Stevani, C. V., Lima, D. F., Toscano, V. G., & Baader, W. J. (1996). Kinetic studies on the peroxyoxalate chemiluminescent reaction: imidazole as a nucleophilic catalyst. Journal of the Chemical Society, Perkin Transactions 2, (5), 989-995.

6. Zhou, J., Xu, Y., Wang, L., & Xu, X. (2001). Substituent effect of the peroxyoxalate chemiluminescence. Acta Physico-Chimica Sinica, 17(4), 361–364

7. Daina, A., Michielin, O., & Zoete, V. (2017). SwissADME: a free web tool to evaluate pharmacokinetics, drug-likeness and medicinal chemistry friendliness of small molecules. Scientific reports, 7(1), 42717.)

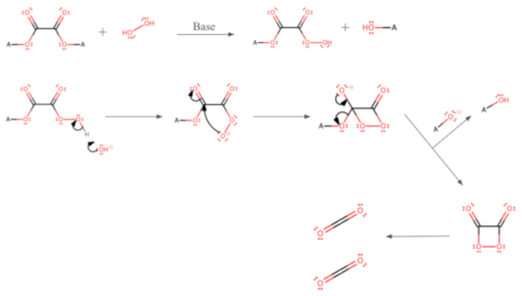

Figure 1. Reaction mechanism of peroxyoxalate chemiluminescence (PO-CL)

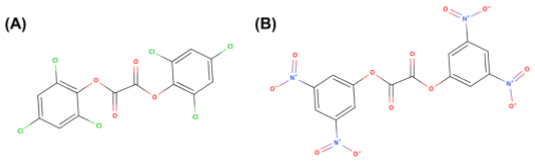

Figure 2. Molecular structure of (A) bis(2,4,6-trichlorophenyl) oxalate (TCPO) and (B) bis(2,4-dinitrophenyl) oxalate (DNPO).

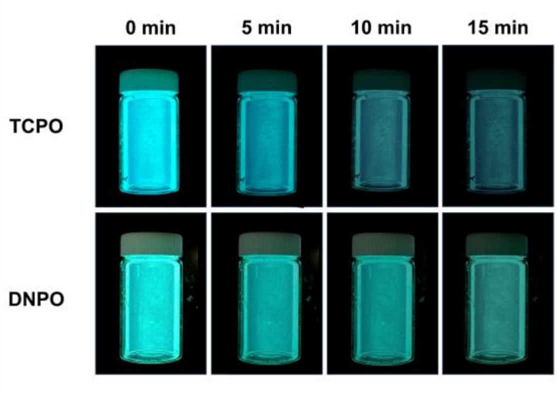

Figure 3. PO-CL result of TCPO and DNPO as a time series.

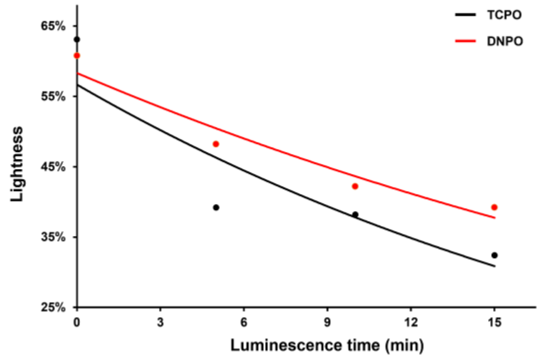

Figure 4. Luminescence time vs. lightness plot of TCPO and DNPO.

Time (min)	TCPO hex	TCPO lightness	DNPO hex	DNPO lightness
0	#43ffff	63.10%	#37ffff	60.80%
5	#00c4c8	39.20%	#30c6bc	48.20%
10	#309093	38.20%	#32a597	42.20%
15	#277d7e	32.40%	#2d9b8c	39.20%

Table 1. Hexadecimal color code and lightness of TCPO and DNPO.

Molecule	Molecular Weight (g/mol)	Molar Refractivity	Number of rotatable bonds	TPSA (Å²)
TCPO	448.9	94.21	5	52.6
DNPO	422.22	99.44	9	235.88

Table 2. Steric strain calculation result from SwissADME of TCPO and DNPO. TPSA stands for topological polar surface area.