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Influence of fluorescer concentration on peroxyoxalate chemiluminescence spectra

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Abstract

A study of the chemiluminescence emission spectra of the peroxyoxalate chemiluminescence system has been undertaken, and the results show that fluorescer concentration has a significant impact on the shape and λ_{max} of the spectra. As fluorescer concentration increases, the shape of the spectra changes and λ_{max} shifts gradually to longer wavelength. For the 12 substituted bis(phenylethynyl)anthracences (BPEAs) studied, a 29–38 nm bathochromic shift was generally found. Variation of oxalate, hydrogen peroxide and sodium salicylate concentration had no observable influence on the shape and λ_{max} of the spectra. © 2000 Elsevier Science Ltd. All rights reserved.

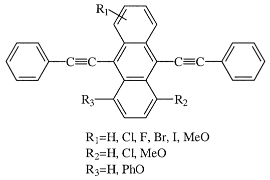
Keywords: Peroxyoxalate chemiluminescence; Spectra; Fluorescer; BPEA; TCPO; Bathochromic shift

1. Introduction

The peroxyoxalate chemiluminescence (POCL) system, which consists of a fluorescer, diaryloxalate, H_2O_2, catalyst and solvent, has been widely used in making lighting devices [1] and in luminescence studies [2–5]. The influence of oxalate, H_2O_2 and catalyst concentration on the intensity, decay and duration of chemiluminescence (CL) emission systems in the presence of the fluorescer BPEA has been studied in great detail [1]. While a CL emission maximum of 510 nm was recorded for a dimethyl phthalate solution containing BPEA (10^{-3} mol/l), bis(trichorophenyl)oxalate (TCPO) (10^{-2} mol/l), H_2O_2 (10^{-2} mol/l), detailed spectral data were not provide [6]. Studies conducted in our laboratories on 10^{-4} mol/l BPEA solutions showed that CL intensity was affected by varying experimental conditions, and that shape and λ_{max} were also affected.

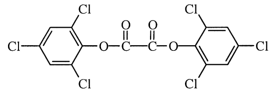
In the present paper, CL spectral changes were examined in systems employing BPEA and 11 substituted BPEAs as fluorescers, the synthesis of which was reported earlier [7].

Since the influence of various conditions on CL intensity and its decay has been examined thoroughly by others [1], our research focused on the shape and λ_{max} of the spectra, without considering intensity. Therefore, the intensity units of each spectrum were set arbitrarily.



R_1=H, Cl, F, Br, I, MeO
R_2=H, Cl, MeO
R_3=H, PhO

BPEA



TCPO

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2. Experimental

The fluorescers were prepared as reported earlier [7], and TCPO was synthesized and purified by the procedure of Mohan and Turro [8]. CL solutions with requisite concentrations were prepared by heating a mixture of required quantity of fluorescer, oxalate, and sodium salicylate and dimethyl phthalate with stirring until dissolution occurred. Test solutions were made by mixing the solutions with required quantity of H_2O_2, adjusting the volume to 10 ml, and immediately transferring a portion to a 10 mm quartz cell. Measurements were performed on a Shimadzu RF-5000 spectrophotofluorometer without external excitation. Relative intensity readings were obtained in the units of 0–100, and the units of each spectrum are not comparable. Instrument parameters such as slit width and sensitivity were found to have no influence on spectral shape and λ_{max}, and were therefore set arbitrarily.

3. Results and discussion

It was found that the oxalate, H_2O_2 and sodium salicylate concentrations had no observable influence on CL spectra, while fluorescer concentration exerted a significant impact on spectral shape and λ_{max}. To facilitate a study on the role of fluorescers, TCPO (10^{-3} mol/l), H_2O_2 (10^{-3} mol/l), and sodium salicylate (3×10^{-4} mol/l) was employed in all experiments. It was also found that, although the overall CL intensity of each test sample decays with time and that temperature can alter the decay rate, these variables had no noticeable effects on λ_{max} and the shape of the CL spectra.

3.1. Influence of the concentration of fluorescer

Examples of CL spectra obtained using BPEA at 10^{-6}–3×10^{-3} mol/l concentrations are shown in Fig. 1, and the overall influence of BPEA concentration is summarized in Fig. 2. It can be seen from Fig. 1 that two peaks (480 and 508 nm) exist in the CL spectrum of BPEA at 10^{-6} mol/l, and that increasing fluorescer concentration caused a bathochromic shift. In addition, gradual changes in the shape of the spectra occurred until at 3×10^{-3} mol/l only one peak (511 nm) remained. To simplify this discussion, we have designated the shorter wavelength peak as peak A, the longer one as peak B, and ratio of the heights of peak A/peak B as HA/HB. As the concentration was increased from 10^{-6} to 3×10^{-6} mol/l, the λ_{max} of the two peaks remained at the same position, though HA/HB decreased slightly from 2.11 to 2.01. At 3×10^{-6}–10^{-3} mol/l concentrations, significant spectral shifts were observed. Peak A shifted to a longer wavelength and its height dropped relative to that of peak B. For example, at 3×10^{-6} mol/l, peak A was observed at 481 nm and HA/HB was 2.01, while at 10^{-4} mol/l, peak A shifted to 486 nm and HA/HB decreased to 1.23. At 3×10^{-4} mol/l, peak A shifted to 490 nm and the height of peak B surpassed that of peak A, with HA/HB dropping to 0.86. At 10^{-3} mol/l, peak A became a barely noticeable shoulder, and at 3×10^{-3} mol/l, peak A disappeared completely. Compared to the remarkable bathochromic shift of peak A, the λ_{max} of peak B shifted very slightly from 508 nm at 10^{-6} mol/l to 511 nm at 3×10^{-3} mol/l.

When BPEA concentration was reduced from 10^{-6} to 3×10^{-7} mol/l, the spectrum obtained were the same as the one recorded at 10^{-6} mol/l. Also, when the concentration was increased from 3×10^{-3} mol/l to 5×10^{-3} mol/l, the spectrum was not different from the one observed at 3×10^{-3} mol/l. Thus it was clear that for the CL system studied, CL spectra shift bathochromically as BPEA concentration was varied from 10^{-6} to 3×10^{-3} mol/l.

When 11 substituted BPEAs were studied similar tendencies were observed. Table 1 contains the CL spectra data for all 12 fluorescers at 10^{-6} and 3×10^{-3} mol/l. It is clear from Table 1 that the compounds can be classified into two families. 2-Chloro-BPEA, 1-fluoro-BPEA and 1,5-diphenoxy-BPEA belong to the same family as BPEA. The CL spectra of these fluorescers afforded double peaks at low concentrations, which gradually shifted to longer wavelength and became a single peak as fluorescer concentration increased. Since the shifting behaviour was quite similar to that of the BPEA, the actual CL spectra of these three fluorescers are not presented. However, it should be pointed out that the peak at 544 nm in the CL spectrum of 1,5-diphoxy-BPEA at 10^{-6} mol/l was too weak to be resolved, but appeared

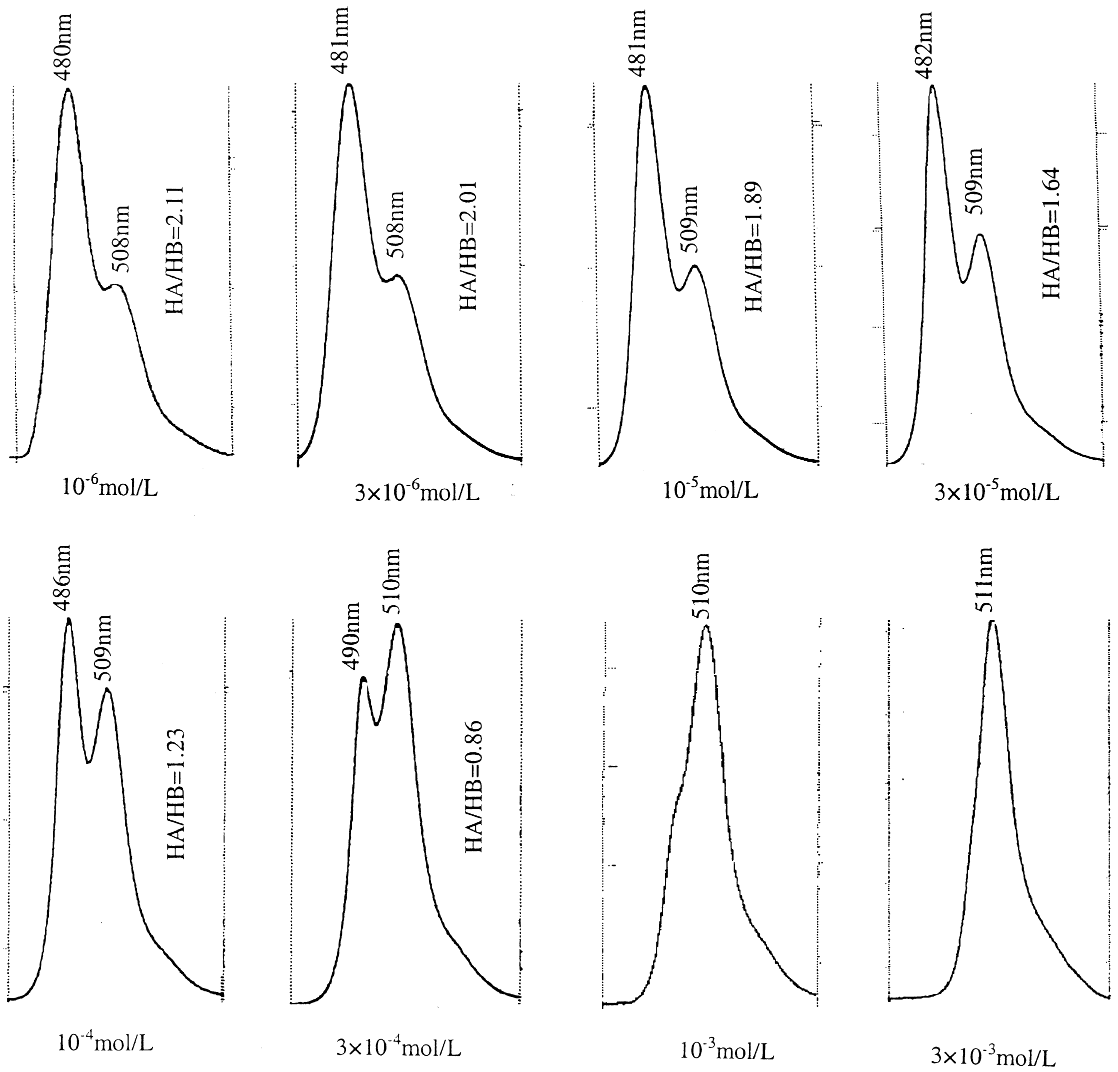

Fig. 1. CL spectra of BPEA at different concentrations.

instead as a shoulder. In this case, the peak height was about one-third the height of the peak at 514 nm. As the concentration was increased, the peak at 514 nm underwent a gradual bathochromic shift and its height decreased until only the peak at 545 nm was observed at 3×10^{-3} mol/l.

The other eight substituted-BPEAs behaved differently from the BPEA-like fluorescers, in that even at low concentrations only a single peak was observed. As fluorescer concentration was increased, the single peaks shifted gradually to a longer wavelength without significant variation in peak shape.

It can be seen from Table 1 that as the concentration increased from 10^{-6} to 3×10^{-3} mol/l, CL spectra of all 12 fluorescers exhibited a 29–38 nm bathochromic shift.

3.2. Influence of solvent

While solvent variations had no influence on the shape of the CL spectra, this did cause a slight shift in λ_{max}. This is shown in Table 2, where the λ_{max} for BPEA is reported in five solvents and at two concentrations.

Table 1
CL spectral data for 12 substituted BPEAs

Compounds	CL λ_{max} (nm) 10^{-6} mol/l	CL λ_{max} (nm) 3×10^{-3} mol/l	CL λ_{max} shift (nm)
BPEA	481.508 (0.48[a])	510	29
1-Chloro-BPEA	493	525	32
2-Chloro-BPEA	480.512 (0.45)	514	32
1,5-Dichloro-BPEA	514	543	29
1-Methoxy-BPEA	503	537	34
1,5-Dimethoxy-BPEA	513	551	38
1-Fluoro-BPEA	485.517 (0.40)	518	33
1-Bromo-BPEA	496	526	30
1-Iodo-BPEA	500	529	29
1-Phenoxy-BPEA	499	531	32
1,5-Diphenoxy-BPEA	514.544 (0.30)	545	31
1,8-Diphenoxy-BPEA	524	553	29

[a] Peak height is compared to that of the longer wavelength peak that was set as 1.00 in the same spectrum.

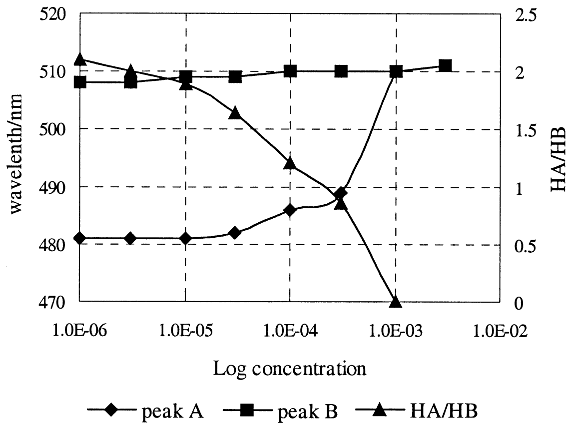

Fig. 2. Influence of BPEA concentration on CL spectra.

Table 2
Influence of solvents on BPEA spectra

Solvents	CL λ_{max} (nm) 10^{-6} mol/l	CL λ_{max} (nm) 10^{-3} mol/l
Benzene	478.506 (0.46[a])	507
Dimethyl phthalate	481.508 (0.46)	510
Dibutyl phthalate	478.507 (0.51)	507
Chloroform	478.506 (0.47)	506
THF	475.503 (0.47)	504

[a] Peak height is compared to that of the longer wavelength peak that was set as 1.00 in the same spectrum.

4. Conclusions

1. Fluorescer concentration has a significant impact on the λ_{max} and shape of POCL spectra.
2. A bathochromic shift in CL spectra occurs when the BPEA concentration is increased from 10^{-6} to 3×10^{-3} mol/l. The observed shift is 29–38 nm.
3. Solvent variations cause only small shifts in CL spectra.

Acknowledgements

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References

[1] Dowd CD, Paul DB. Aust J Chem 1984;37:73–86.
[2] Kwakman PJM, Jong GJ, Brinkman UAT. Trend in Anal Chem 1992;11:232.
[3] Honda K, Miyaguchi K, Imai K. Anal Chim Acta 1985; 177:103.
[4] Mann B, Grayeski ML. Anal Chem 1990;62:1536.
[5] Worsfolf PJ. Anal Proc 1991;28:214.
[6] Hanhela RS, Paul DB. Aust J Chem 1981;34:1701.
[7] Li B, Miao W, Cheng L. Dye Pig 1999;43:161.
[8] Mohan AG, Turro NJ. J Chem Educ 1974;51:528.