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Determination of Absolute Chemiluminescence Quantum Yields for Reactions of bis-(Pentachlorophenyl) Oxalate, Hydrogen Peroxide and Fluorescent Compounds

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Absolute chemiluminescence quantum yields (ϕ_{CL}) for reactions of bis-(pentachlorophenyl) oxalate (PCPO), hydrogen peroxide (H_2O_2) and 9:10 diphenyl anthracene (DPA) have been determined. A fully corrected chemiluminescence monitoring spectrometer was calibrated for spectral sensitivity using the chemiluminescence of the bis-(pentachlorophenyl) oxalate system as a liquid light source, the total photon output of which had previously been determined by chemical actinometry. At high (PCPO)/(H_2O_2) ratios ϕ_{CL} was found to be independent of PCPO and H_2O_2 concentrations.

Keywords Chemiluminescence; absolute quantum yields; pentachlorophenyl oxalate

INTRODUCTION

The generation of light by chemical (chemiluminescence) and biological (bioluminescence) processes has been the subject of continued and increasing activity in recent years (Seliger, 1978; Wamples, 1978) and the analytical applications of these forms of luminescence spectroscopy are considerable. The requirement, as more laboratories become involved in luminescence measurements, for well established standards is pressing, and the need for corrected luminescence spectra and quantum yield is obvious and of paramount importance. The primary use of spectral data is for comparative purposes and, without correction, interlaboratory comparison of luminescence becomes extremely difficult. Total chemiluminescence quantum yields (ϕ_{CL}) can be expressed as the product of three efficiency terms:

$$\phi_{CL} = \phi_F \, \phi_{ET} \, \phi_{EP}$$

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where ϕ_{ET} is the energy transfer efficiency between the species responsible for luminescence and an intially formed intermediate or excited state product, ϕ_{EP} is the efficiency of formation of the intermediate or excited state product from the initial reactants, and ϕ_F is the luminescence quantum efficiency of the emitting species. Experimental determinations of ϕ_{CL} and ϕ_F allow the product of chemical and excitation efficiencies to be determined.

Although the quantum yields of many chemiluminescent reactions have been measured (Mellor and Richter, 1974) the oxidation of luminol appears to be the only reaction that has been widely used and tested (Hastings and Weber, 1963; Lee and Seliger, 1965, 1972; Roberts and Hirt, 1967; Rauhut *et al.*, 1966; Bezman and Faulkner, 1971). Thus ϕ_{CL} for the luminol oxidation has been measured for radiometry using a light source comprised of a mixture of scintillators in a ^{14}C labelled solvent (Hastings and Weber, 1963) and several spectrometric methods including calibrated spectroradiometers and photomultipliers (Lee and Seliger, 1972; Roberts and Hirt, 1967; Rauhut *et al.*, 1966), matching of corrected and uncorrected spectra with that of a standard lamp viewed through filter combinations (band emission approximation method) (Lee and Seliger, 1965), and an integrating sphere detector with a quantum counter (Bezman and Faulkner, 1971; Michael and Faulkner, 1976).

We have recently investigated the aryl oxalate/hydrogen peroxide/fluor chemiluminescent reaction (Rauhut, 1969) and have developed a method for calibrating a monochromator/photomultiplier tube assembly using the chemiluminescence as a liquid light source, the total photon output of which had previously been determined by chemical actinometry (Catherall *et al.*, 1984a, 1984b). The method is of general applicability and has been used to determine ϕ_{CL} for the oxalate ester system using bis-(pentachlorophenyl) oxalate (PCPO) at high and low (PCPO)/(H_2O_2) ratios.

EXPERIMENTAL DETAILS

Actinometry

The apparatus used to measure the total photon output of the chemiluminescent reaction is shown in Fig. 1. It consisted of a cylindrical glass vessel, 4.8 cm diameter, 7.8 cm depth, with a ground glass lid 6.3 cm diameter. The outer surfaces of the vessel were silvered. Two holes provided in the lid respectively accomodated the stem of a luminescence cell (cross-section, 1 cm^2) and permitted withdrawl of actinometer solution from the vessel. A self-sealing rubber cap was fitted to the stem top of the cell and held two stainless steel syringe needles for purging by nitrogen gas and injection of reactants. The lid of the glass vessel was held in place by two spring clips. The whole assembly was fixed in a small thermostat and provision was made for the contents of the actinometer cell to be stirred magnetically. The average effective path length between the walls of the cell and the vessel was 1.8 cm which effectively became doubled by the outer reflective coating. The potassium ferrioxalate actinometer solution (0.15 mol/l), preparared according to Hatchard and Parker (1956) was found to be totally absorbing under these conditions at wavelengths shorter than 455 nm.

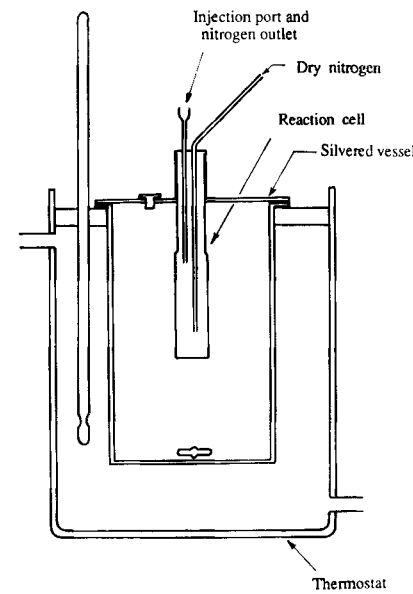

Figure 1. Actinometry cell for measurement of absolute chemiluminescence quantum yields

For the purpose of calibration, 9,10-diphenylanthracene (9,10-DPA), was chosen as the fluor because of its high quantum yield and convenient spectral range. The procedure adopted for the calibration was as follows.

Solutions of the chemiluminescent system were prepared with a known PCPO:H_2O_2 concentration ratio, and concentrations of 9,10-DPA in the range 2.5×10^{-5} mol/l to 1×10^{-3} mol/l. The required volumes of PCPO, 9, 10-DPA and solvent, chlorobenzene, were added to the reaction cell which was fixed in position in the lid of the actinometry cell. Actinometer solution (137 cm^3) was added and the lid fixed in place. The whole cell assembly was allowed to equilibrate at 298 K in a thermostat whilst the reaction cell and its contents were purged with solvent saturated nitrogen. The chemiluminescent reaction was initiated by injection of the required volume of a H_2O_2/sodium salicylate mixture in purified ethylacetate and the reaction allowed to go to completion. Two 18 cm^3 aliquots of actinometer were removed from the cell, transferred to two blackened graduated flasks and 1, 10-phenanthroline-Fe^{2+} complex prepared according to the method of Hatchard and Parker (1956). A blank determination using unexposed actinometer was also carried out. The absorption of the Fe^2 complex was measured at 510 nm using 4–cm path length cells.

Chemiluminescence monitoring spectrometer

Chemiluminescence from identical reaction mixtures to those used in the actometry experiments was monitored with time at 436 nm. The apparatus used to monitor chemiluminescence is shown in Fig. 2. A quartz cuvette (cross-section, 1 cm^2) was accomodated in a thermally controlled cell housing which had a small magnetic stirrer located underneath. Chemiluminescence emission from the cell was detected through a monochromator (Hilger and Watts D285) by a photomultiplier (RCA931A) attached to the exit slit of the monochromator. A second monochromator and photomultiplier located on the opposite side of the cell housing acted as a reference. To record the decay of chemiluminescence the emission monochromator was set to the wavelength of maximum emission and the signal from the photomultiplier fed via an amplifier to a Y-t recorder (W and W1100).

Chemiluminescence emission spectra were recorded by scanning the emission monochromator keeping the reference monochromator at a fixed wavelength close to the emission maximum and using the signal from the reference photomultiplier to compensate for the decay of chemiluminescence as the reaction proceeded. The spectral sensitivity factor S_v (Parker, 1968) for the system,

$$S_v = \frac{R_{TL}}{\lambda^3 \left(\frac{dE}{d\lambda}\right)_{TL}}$$

was determined experimentally using a standard tungsten lamp and reflecting light from it via

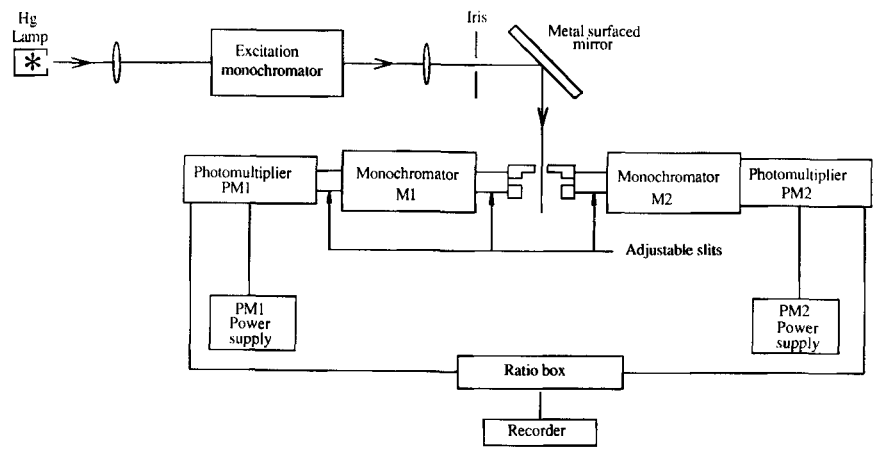

Figure 2. Schematic diagram of the chemiluminescence monitoring system showing modification for operation as a simple fluorimeter

freshly prepared magnesium oxide screen into the monochromator and photomultiplier. R_{TL} was the response of the photomultiplier to a standard light source of known spectral distribution and $(dE/dv)_{TL}$ was the calibrated output of the lamp in watts (E) per unit wavelength (λ) interval. The normalized spectral response curve (Fig. 3) for the instrument was used to obtain corrected chemiluminescence spectra expressed in the form of relative quanta per wavenumber (dQ/dv) against wavenumber (ν).

The accuracy of the spectral response curve was checked by using the instrument as a simple fluorimeter (see Fig. 2) and determining the fluorescence emission spectrum for quinine sulphate (absorbance 0.02) at an excitation wavelength of 366 nm. The correction of the observed emission spectrum by dividing the observed intensity at a given frequency by the normalized spectral sensitivity factor (S_v) at that frequency gave the corrected fluorescence emission spectrum (Fig. 4) which was in satisfactory agreement with published data (Melhuish, 1972).

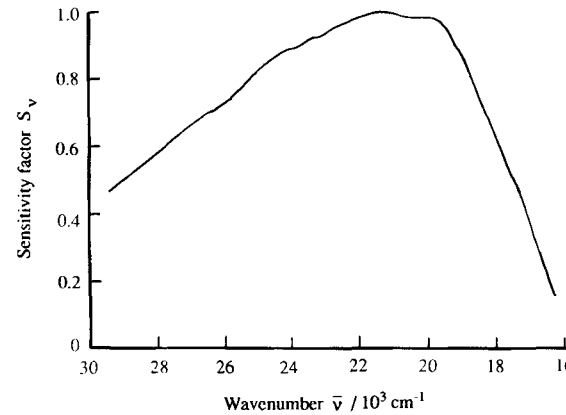

Figure. 3. Normalized spectral sensitivity curve

Materials

Quinine sulphate dihydrate (Aldrich) was purified by recrystallizing three times from warm distilled water. The recrystalized material was dried under reduced pressure over phosphorus pentoxide for five days. 9,10-DPA (Aldrich) was recrystallized twice from an ethyl alcohol-chloroform mixture and dried under reduced pressure. (Bis-(pentachlorophenyl) oxalate (PCPO) was prepared following the general method of Rauhut (Rauhut *et al.*, 1967) and Baker and Schumacher (1964). Sodium salicylate (BDH Analar) was used without further purification. Chlorobenzene (BDH Analar) was purified by fractional distillation over 'Anhydrite'. Ethyl acetate (BDH Spectroscopic grade) was fractionally distilled over anhydrous potassium carbonate before use. Solutions of hydrogen peroxide in ethyl acetate were prepared using stabilizer-free hydrogen peroxide (Laporte 86% w/w) and dried overnight using magnesium sulphate following established procedures (Greene and Kazan, 1963).

Actinometry Calculations and Absolute Calibration of Chemiluminescence Monitoring System

The total number of Fe^{2+} ions, $n_{Fe^{2+}}$, produced on exposure of the actinometer solution is given

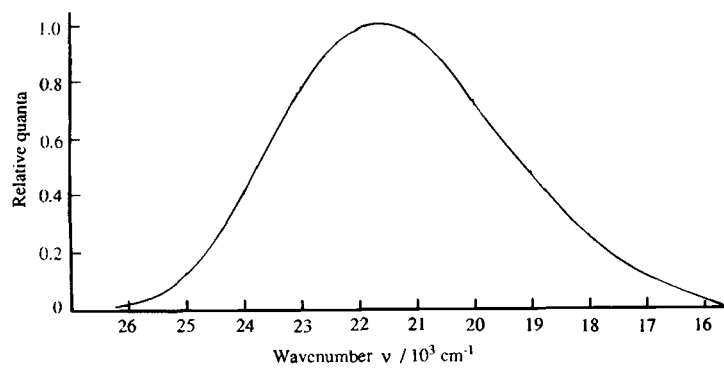

Figure 4. Corrected fluorescence emission spectrum obtained for quinine sulphate

by (Hatchard (1956):

$$n_{Fe^{2+}} = \left(\frac{V_1 V_3 A}{V_2 l_\varepsilon}\right) 6.023 \times 10^{20} \qquad (1)$$

where V_1 = volume of actinometer irradiated in cm^3; V_2 = volume of actinometer taken for analysis in cm^3; V_3 = volume to which V_2 is diluted in cm^3; A = absorbance for Fe^{2+} complex at 510 nm; l = path length of cell; ε = extinction coefficient of Fe^{2+} complex.

The number of quanta (Q_o) absorbed by the actinometer is:

$$Q_o = \frac{n_{Fe^{2+}}}{\phi^w_{Fe^{2+}}} \qquad (2)$$

where $\phi^w_{Fe^{2+}}$ is a weighted average for the wavelength dependent quantum yield for Fe^{2+} production and is given by (Bezman and Faulkner, 1971):

$$\phi^w_{Fe^{2+}} = \frac{\Sigma\{(\int_{\nu_1}^{\nu_3} S_\nu I \, d\nu)\, \phi_{Fe^{2+}}(\nu_1 \rightarrow \nu_3)\}}{\int S_\nu I d\nu} \qquad (3)$$

where $\int_{\nu_1}^{\nu_3} S_\nu I \, d\nu$ is the fractional area under the corrected chemiluminescence spectrum of 9,10-DPA between the frequency limits ν_1 and ν_3; $\phi_{Fe^{2+}}$ ($\nu_1 \rightarrow \nu_3$) is the average quantum yield between the frequency limits ν_1 and ν_3 and $\int S_\nu I \, d\nu$ is the total area under the corrected chemiluminescence emission spectrum of 9,10-DPA and is normalized to unity. The variation of $\phi_{Fe^{2+}}$ with wavelength is well established (Hatchard and Parker, 1956) and a value of 1.02 was calculated for $\phi^w_{Fe^{2+}}$ using Eq. (3).

The true number of chemiluminescence quanta, Q_T, is given by:

$$Q_T = Q_o + Q_{SA} + Q_{IA} \qquad (4)$$

where Q_{SA} is the number of quanta lost through self-absorption by 9,10-DPA and Q_{IA} is the number of quanta lost owing to incomplete absorption by the actinometer.

The effect of self-absorption by the fluor on the corrected and normalized chemiluminescence spectra is shown in Fig. 5 for 9,10-DPA in the presence of PCPO and hydrogen peroxide. At the lowest concentration of the fluor employed self-absorption was negligible. The reduction in area under the emission spectra due to self-absorption by 9,10-DPA was expressed as a fraction (A_{SA}) of the total area under the normalized emission spectrum for a solution containing 2.5×10^{-5} mol/l 9,10-DPA. The area under the corrected and normalized emission spectrum (A) is equivalent to the total number of quanta emitted at all frequencies and the reduction in total light output due to self-absorption can be equated to the fractional decrease in the areas (A_{SA}) under the emission spectra at the higher 9,10-DPA concentrations.

The fraction of chemiluminescence emission from 9,10-DPA not absorbed by the potassium ferrioxalate actinometer is shown also in Fig. 5. In an analogous manner to that described for

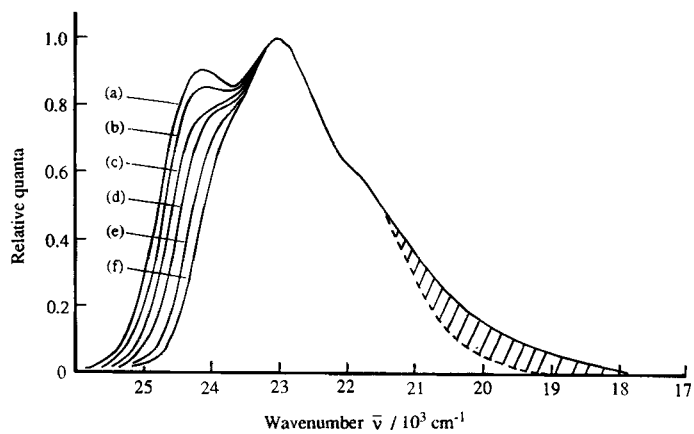

Figure 5. Effect of self-absorption on the chemiluminescence emission spectrum of 9,10-DPA. The shaded area is the region of emission not absorbed by the actinometer solution. (DPA] (a) 2.5×10^{-5} mol/l; (b) 5×10^{-5} mol/l; (c) 1×10^{-4} mol/l; (d) 2×10^{-4} mol/l; (e) 5×10^{-4} mol/l; (f) 1×10^{-3} mol/l

self-absorption by 9,10-DPA, the effect of incomplete absorption by the actinometer can be expressed in a quantitative manner as the fractional reduction in area (A_{IA}) relative to the areas (A) under the normalized and corrected chemiluminescence emission spectrum. Thus the total number of quanta (Q_T) emitted by the chemiluminescent liquid light source is given by

$$Q_T = Q_o \frac{A}{A - (A_{SA} + A_{IA})} \quad (5)$$

For the chemiluminescence monitoring system the fraction of the normalized corrected emission (F_i) detected by the photomultiplier at a frequency ν_i with an observed intensity I_{ν_i} through a monochromator with a band width, $\Delta\nu_i$ is given by

$$F_i = \frac{I_{\nu_i}\Delta\nu_i S_{\nu_i}}{\int_{\nu_L}^{\nu_U} I_\nu S_\nu d\nu} \quad (6)$$

where ν_U and ν_L are the frequency limits for the emission. At the monitoring wavelength of 436 nm (22,936 cm^{-1}) and using monochromator slits of 0.25 nm corresponding to a bandwidth of 290 cm^{-1}, the value for F_i was calculated to be 0.088 from the corrected emission spectrum for 9,10-DPA. The number of quanta (Q_{Fi}) represented by this fraction is

$$Q_{F_i} = Q_T \quad F_i = Q_o \left(\frac{A}{A - (A_{SA} + A_{IA})}\right) \left(\frac{I_{\nu_i}\Delta\nu_i S_{\nu_i}}{\int_{\nu_L}^{\nu_U} I_\nu S_\nu \, d\nu}\right) \quad (7)$$

and this number of photons is proportional to the area A_{DC} (expressed in arbitrary intensity units × time) under the experimentally observed chemiluminescence decay curve. A calibration factor (C) for the chemiluminescence monitoring system, expressed in quanta per unit area, was determined from the ratio of the number of quanta (Q_{Fi}) to the area under the chemiluminescence decay curve(A_{DC}), i.e.

$$C = \frac{Q_o}{A_{DC}} \left(\frac{A}{A - (A_{SA} + A_{IA})}\right) \left(\frac{I_{\nu_i}\Delta\nu S_{\nu_i}}{\int_{\nu_L}^{\nu_U} I_\nu S_\nu \, d\nu}\right) \quad (8)$$

RESULTS AND DISCUSSION

Values for the observed quanta from actinometric measurement of the chemiluminescence emission of serveral mixtures of PCPO and hydrogen peroxide in the presence of 9,10-DPA are presented in Table 1 together with calculations of

Table 1. Calibration of chemiluminescence monitoring spectrometer

[9,10-DPA]/10^{-5} mol l^{-1}	100	20	10	2.5
[PCPO]/10^{-3} mol l^{-1}	5	5	10	10
[H_2O_2]/10^{-2} mol l^{-1}	2	2	4	4
Observed quanta $Q_o/10^{17}$	6.02	6.02	4.65	1.50
Actinometer absorption fractional correction(A_{IA})	0.045	0.045	0.045	0.045
Fluor self-absorption fractional correction (A_{SA})	0.175	0.10	0.072	0
Total quanta $Q_T/10^{17}$	7.72	7.04	5.27	1.57
Φ^*_{CL}	0.085	0.078	0.029	0.009
F_i/A_{DC} unit area	8011	6205	4820	1527
Calibration factor (C)/10^{14} quanta (unit area)$^{-1}$	0.96	1.13	1.09	1.03

Sodium salicylate concentration 4.7 × 10^{-5} mol l^{-1},
F_i is the fraction of normalized corrected emission detected by the photomultiplier.
A_{DC} is the area under the chemiluminescence decay curve.
* Based upon total consumption of PCPO. Volume of PCPO solution used in actionometry = 3 ml.

the fraction of light not absorbed by the actinometer and the fraction of light self-absorbed by the fluor. The fraction of light not absorbed by the actinometer was found to be < 5%, but self-absorption by the fluor became significant at the higher concentrations of 9,10-DPA. The chemiluminescence quantum yields were calculated assuming a 1:1 stoichiometry between PCPO and hydrogen peroxide and complete consumption of PCPO. The mean calibration factor (C) was found to be $1.05 \times 10^{14} \pm 9\%$ quanta per unit area.

Quantum yields at high PCPO]/[H_2O_2] ratios were determined using the calibrated, fully corrected chemiluminescence monitoring spectrometer. ϕ_{CL} at high [PCPO]/[H_2O_2] ratios was found to be essentially independent of both [PCPO] and [H_2O_2] over the concentration ranges investigated (Table 2). Detailed investigations of the kinetics and mechanism of the reaction and the role of base catalyst and fluor have been reported elsewhere (Catherall *et al.*, 1984a, 1984b).

The method is capable of improvement and extension by, for example, selection of the fluor and actoinmeter such that the emission of the former and the maximum absorption region of the latter coincide. Alternatively if potassium ferrioxalate is used then selection of a fluor with a low frequency limit of 22,000 cm^{-1} for the fluorescence emission would ensure total light absorption. In the case of the aryl oxalate system the choice of fluor is determined to some extent by the dependency of ϕ_{CL} on the $E_{ox}^{1/2}$ value of the fluor (Catherall *et al.*, 1984a).

Other actinometers have been reported which show better response in the visible region than potassium ferrioxalate. Reinecke's salt actinometer may be used in the wavelength region 300–600 nm with a fairly constant quantum yield (Wegner and Adamson, 1966) but care is needed in its use, because of a thermal aquation reaction. Heterocoerdianthrone has been suggested as an actionometer for use in the wavelength range 400–580 nm (Brauer *et al.*, 1982). The method described here is applicable to chemiluminescent systems of moderate to good efficiency emitting in the near-UV–blue range if potassium ferrioxalate is used, and enables chemiluminescence emission detectors to be calibrated relatively quickly without the need for lengthy and complicated geometrical calibrations. For systems of lower efficiency the aryloxalate system* provides a useful liquid light source with a wide emission wavelength range.

Table 2. Chemiluminescence quantum yields (ϕ_{CL}) at high (PCPO]/(H_2O_2) ratios

[PCPO]/10^{-4} mol l^{-1}	[H_2O_2]/10^{-4} mol l^{-1}	ϕ_{CL}
5.0	0.50	0.15
5.0	0.25	0.15
5.0	0.17	0.15
30.0	4.00	0.16
30.0	2.00	0.17

Sodium salicylate concentration 1.17×10^{-4} mol l^{-1}, 9,10-DPA concentration 5.00×10^{-3} mol l^{-1}

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*PCPO is now commercially available from Aldrich Chemical Company, Inc., catalogue No. 33237-2.

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