Electrogenerated chemiluminescence. Determination of the absolute luminescence efficiency in electrogenerated chemiluminescence. 9,10-Diphenylanthracene-thianthrene and other systems

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corresponds to approximately 2 mg/dl in a 10-μl sample. Because this sample is diluted to more than 1 ml in the analysis, this detection limit is actually less than 1 ppm of the total analysis volume. The analysis time is generally less than 10 minutes.

A unique feature of the method is the pH jump. This technique allows the enzyme to catalyze the reaction of glucose at a favorable pH for a known length of time. The sudden change of pH to a level favorable to CL emission serves as a timing device for the enzyme reaction. Because of this, the method seems particularly amenable to automation; this aspect is currently under consideration. (Concurrent with this research, Bostick and Hercules (*17*) have independently developed an automated method for CL glucose analysis employing similar chemical techniques.) In addition, the extension of this technique to other oxidase enzyme systems is anticipated. The method would seem to be applicable to any substrate that yields hydrogen peroxide when it undergoes enzyme catalysis in neutral solution.

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Electrogenerated Chemiluminescence: Determination of the Absolute Luminescence Efficiency in Electrogenerated Chemiluminescence; 9,10-Diphenylanthracene–Thianthrene and Other Systems

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The efficiency of electrogenerated chemiluminescence (ECL) (ϕ_{ecl}) of several systems is reported using both potassium ferrioxalate actinometry and calibrated-photodiode measurements. Experimental methods and necessary corrections in ϕ_{ecl}-determinations are discussed and ECL in mixed solvent systems (*e.g.*, acetonitrile (ACN)–benzene–toluene) is described. The following ϕ_{ecl} values were found: 9,10-diphenylanthracene (DPA) (7.8m*M*), thianthrene (TH) (11.1m*M*) (in mixed solvent): 20% peak efficiency, 5% for several hours; DPA (7.7m*M*, in mixed solvent) 4%; DPA (2.20m*M*, in mixed solvent) 8%; rubrene (in benzonitrile) 1.9%. Good agreement between pulsed stationary electrode and rotating ring-disk electrode measurements and between actinometric and photodiode determinations was found.

Electrogenerated chemiluminescence (ECL) involves the production of excited states, and ultimately light, by the electron transfer reaction between electrogenerated species, most frequently radical ions; a typical reaction sequence is:

$$A + e \longrightarrow A^{\cdot -} \quad (1)$$

$$D - e \longrightarrow D^{\cdot +} \quad (2)$$

$$A^{\cdot -} + D^{\cdot +} \longrightarrow D + A^{*} \quad (3)$$

The application of ECL to analytical determinations (*1–3*) and display devices has been considered. An important parameter in these and other applications, as well as in consideration of the fundamental aspects of ECL, is the ECL efficiency, ϕ_{ecl}, which represents the number of photons emitted per electron transfer reaction. We have previously discussed problems in the definition of efficiency in ECL systems and reviewed previous measurements (*4*). The fact that previously reported efficiency values have shown a wide variation even for the same system under similar conditions [see for example values given for the rubrene system which vary from 0.01 to 8.7% (*4–9*)] testifies to the difficulties in the measurement, the differences in assumptions made in the calculations, and variations in the nature of the environment in which the radical ion electron-transfer reaction occurs. We report here the ECL of the 9,10-diphenylanthracene (DPA)–thianthrene (TH) system; the high intensity found with this system allowed the first, di-

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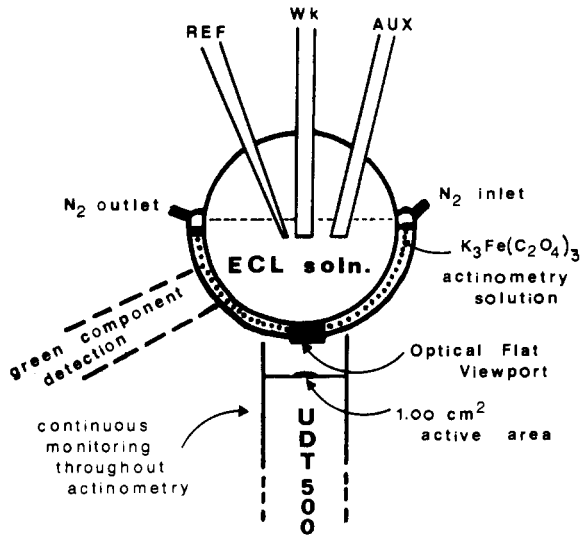

Figure 1. Apparatus used to determine ECL efficiency by actinometry

rect actinometric determination of ϕ_{ecl}. A simple system for direct luminescence measurements employing a calibrated PIN photodiode system is also described and ϕ_{ecl}-values of several other systems determined with this apparatus are given.

EXPERIMENTAL

Chemicals. 9,10-Diphenylanthracene (DPA) samples were obtained from City Chemical Corporation and Aldrich Chemical Co. Thianthrene (TH) and rubrene were obtained from Aldrich Chemical Co. Purification of DPA, TH, and rubrene were by previously published methods (*10*). Tetra-*n*-butylammonium perchlorate (TBAP) and tetra-*n*-butylammonium fluoborate ($TBABF_4$), both polarographic grade, obtained from Southwestern Analytical Chemical Co., were dried for 48 hr in a vacuum oven at 90 °C and stored in a desiccator over anhydrone that was dried previously in the same manner.

Acetonitrile (ACN), spectroscopy grade, Matheson Coleman and Bell Co., was purified using various methods based on the report of Osa and Kuwana (*11*). The first method, described by Bowman (*12*), consists of passing ACN over a column of activated alumina (Fisher Adsorption Grade, 80–200 mesh) several times, and storing it in an evacuable flask. The modified drying techniques involved vapor transfer of some of this dry ACN into a smaller evacuated flask containing freshly activated alumina or P_2O_5, allowing contact for only a few hours, and subsequent vapor transfer of this ACN to the ECL cell under a temperature gradient on the vacuum line. Omitting passing the ACN through the alumina column but letting it stand over activated alumina for at least 12 hours also gives satisfactory results.

Benzene, Matheson Coleman and Bell, spectroquality was degassed by freeze–pump–thaw (F-P-T) cycles prior to vapor transfer to clean dry sodium, where it was maintained for at least 24 hours prior to use in experiments. If the evolution of hydrogen was initially rather copious, the benzene was subjected to F-P-T cycles over the sodium. The amount necessary for experiments was vapor-transferred from the sodium flask directly into the ECL cell (or preparation vessel for RRDE studies). Toluene, Matheson Coleman and Bell, purif. grade, was treated by the same procedure as benzene.

Propylene carbonate (PC), Jefferson Chemical Co., Houston, Texas, solvent grade, was dried for 48 hours over activated Type 4A Molecular Sieves and distilled on the vacuum line discarding the first 20%. It was dried again in the same manner, distilled again at 90 °C discarding the first 10%, and stored under helium.

Benzonitrile (BZN), Matheson Coleman and Bell, spectroscopy grade, was purified by two methods. The first method involved passing the BZN over a column of activated alumina in a dry box (*12*). The second method used dry, freshly activated molecular sieves as the drying agent; first freeze–pump–thawed BZN was transferred by gravity in a closed evacuated system to activated molecular sieves. After 24 hours, it was transferred on the vacuum line, under gravity, into a solution preparation vessel (*9*), and eventually into the ECL cell. This second method was used in the preparation of the rubrene BZN solution that was used in the quantum efficiency measurements. We found no evidence by electrochemistry or fluorescence measurements that metal ions were leached from the sieves.

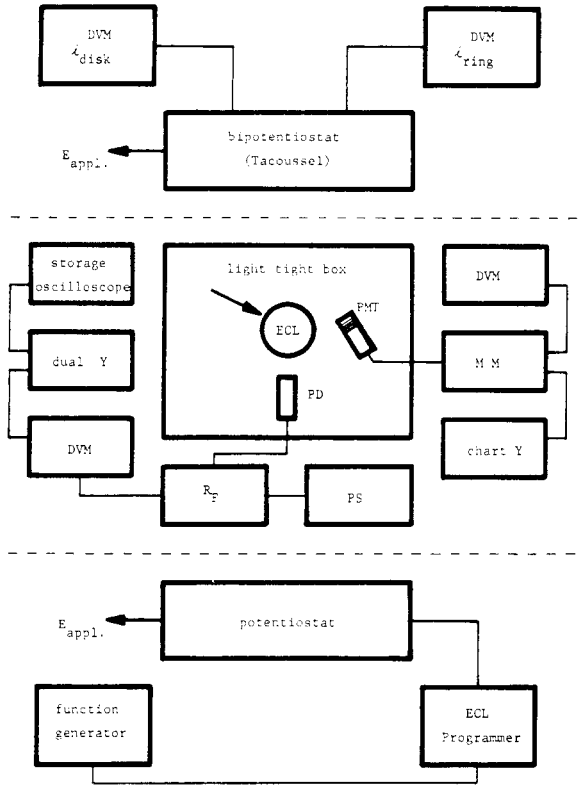

Figure 2. Instrumental set-ups employed in ECL efficiency measurements

Abbreviations are: WT, Wavetek 114 function generator; TX, Tektronix 465 storage oscilloscope equipped with Polaroid camera; PS, variable dc power source, used to supply ±15 V to PD operational amplifier; PD, UDT(UV)-500 photodiode; ECL, the cell with or without actinometry bath in which ECL is generated; R_F, the box containing the PD circuitry, including 21 precision feedback resistors for the PD operational amplifier (values: 100Ω, 201Ω, 499Ω, 997Ω, 1.94 kΩ, 5.00 kΩ, 9.98 kΩ, 20.0 kΩ, 50.0 kΩ, 99.9 kΩ, 151 kΩ, 199 kΩ, 299 kΩ, 401 kΩ, 498 kΩ, 1.024 MΩ, 2.02 MΩ, 2.98 MΩ, 5.07 MΩ, 7.63 MΩ, 10.06 MΩ); MM, the Aminco-Bowman photomultiplier microphotometer unit; PMT, RCA 1P 21 photomultiplier tube; DVM, digital voltmeter; Y, recorders

Apparatus. Three basic ECL cells were used in this study; the one employing a platinum rotating ring-disk (RRDE) has been described previously by Maloy and Bard (*9*), while pulsed ECL experiments were carried out either in a cell similar to the coulometry cell described by Childs *et al.* (*13*) (Cell 1) or in the ECL cell previously discussed [Figure 1*a* in (*14*) (Cell 2)]. Cell 1 was modified in this application to have only one solution chamber, the auxiliary electrode being housed in a small fritted compartment introduced at the top through a standard taper joint. The working electrode for this cell was a commercial platinum disk electrode (Beckman Instruments), provided with a male standard taper fitting, and the cell bottom was made of optical flat glass.

Preparation techniques of the ECL solutions, including freeze–pump–thaw (F-P-T) cycles for degassing, have been described in previous papers (*9, 10, 15, 16*). Chemical actinometry measurements, either by the RRDE or pulsed ECL techniques, used the cell shown in Figure 1 in conjunction with potassium ferrioxalate as the light sensitive compound; details and precautions relating to these measurements can be found in the literature (*9, 15–18*). ECL efficiency measurements were also made with a PIN photodiode with an integral operational amplifier (UDT-500UV; United Detector Technology, Inc., Santa Monica, Calif.) of fixed area and calibrated sensitivity, placed at an exactly measured distance from the working electrode.

Transient electrochemical experiments (cyclic voltammetry, cyclic double potential steps) were performed with a Princeton Ap-

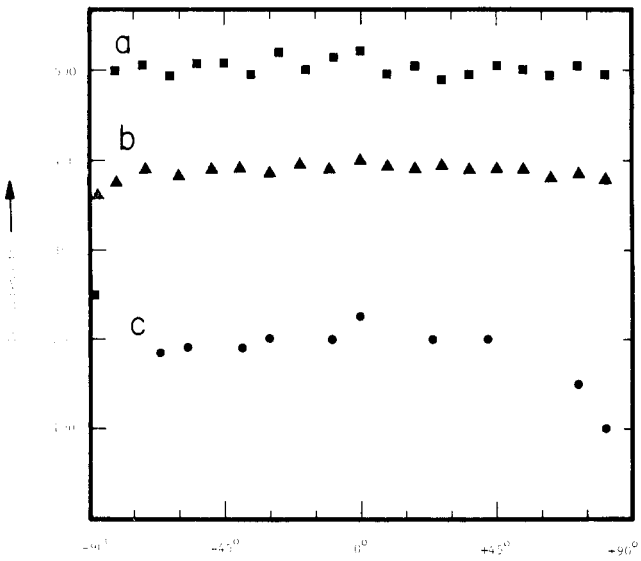

Figure 3. Solid angle dependence of ECL emission at plane platinum disk electrodes

(*a*) 7.8m*M* DPA, 11.1m*M* TH, and 0.1*M* TBAP in ACN:benzene:toluene under pulsed ECL (60 Hz); (*b*) solution as in (*a*), except at RRDE; (*c*) 0.1m*M* tris(bipyridyl)ruthenium(II), 0.1*M* TBAP in ACN:benzene at RRDE

plied Research Corporation Model 170 Electrochemical System (PAR-170), or with a PAR-173 linked to a Wavetek 114 function generator. Fluorescence and ECL spectra were taken with an Aminco-Bowman spectrophotofluorometer (SPF) housing a Hamamatsu TV R-456 photomultiplier tube having UV-improved S-20 spectral response. Fast transient current and light measurements were made with a Tektronix 564 storage oscilloscope equipped with a Model C-12 oscilloscope camera, while slow transient signals were recorded with X-Y or strip-chart recorders.

RRDE measurements utilized a bipotentiostat (Model BIPAD 2:, Tascussel Electronique, Villeurbanne, France), linked with a Wavetek 114 when a potential sweep was involved. Block diagrams of the different instrumental configurations employed are shown in Figure 2. Details of the experimental techniques and procedures are available (*15*).

Factors in Determination of ϕ_{ecl}. The determination of the average efficiency, $\bar{\phi}_{ecl}$, requires measurement of the total number of photons emitted for a known number of electron transfer reactions (*i.e.*, radical ion annihilations). One can also determine the instantaneous efficiency, ϕ_{ecl}, which is the rate of photon emission per rate of reaction (*4*). The measured quantities are the intensity or power of emitted radiation and the electrolysis current. A number of factors and assumptions must be considered before ϕ_{ecl} can be obtained from those quantities.

Determination of Emitted Photons. The photons emitted from the system can be determined either by actinometry or with a calibrated photodetector. The principles of actinometric measurements are well-known (*9, 15–19*); in its application to ECL systems correction for photons not absorbed by the actinometric solution, especially important for emission above 450 nm, must be made. In the previous actinometric ECL experiments, however (*9*), the total light output of the ECL system itself was insufficient to determine it directly with good precision, and a surrogate light source was necessary, thus causing additional calibration difficulties and errors (see "Geometric Considerations").

The application of photodiodes requires absolute calibration of the detector at a given wavelength and correction for its response at different wavelengths (or the use of a quantum counter (*20*). The PIN photodiode used in this study has a flat response (in terms of incident power) over a spectral region of 200 to 1100 nm. Conversion of the power (P), in watts, to intensity, I, in photons/sec, at a given wavelength, λ, is accomplished using the equations:

$$\epsilon(\text{eV}) = 1239.8/\lambda(\text{nm}) \quad (4)$$

$$I(\text{photons/sec}) = P(\text{watts})(6.241 \times 10^{18})/\epsilon(\text{eV}) \quad (5)$$

The photodiode was calibrated using a He–Ne laser, the beam of which was passed through a 0.99% neutral density filter before impinging onto the photodiode. The laser in turn was calibrated using an Eppley thermopile or a Spectraphysics Model 401C laser meter; both yielded a power of 1.85 ± 0.04 mW for the laser, corresponding to a photon flux of 5.89×10^{15} photons/sec at 6328 Å. The sensitivity of the photodiode was 2.5 μV/pW at the specified operating conditions, as compared to the manufacturer's nominal sensitivity figure of 5 μV/pW. The laser beam was directed to different portions of the photodetector surface to verify that the response was uniform across the total 1.00 cm^2 area of the detector. Once calibrated for a specified value of feedback resistor, R_F, in the current follower of the operational amplifier associated with the photodetector (*e.g.*, at 6328 Å, R_F = 500 Kohm and $I = 5.83 \times 10^{13}$ photons/sec yielded a 2.30-V response), the detector could be employed for other light levels simply by changing R_F, and for different wavelengths, by using a correction based on Equation 4.

Geometric Considerations. Since the detector only directly intercepts a small fraction of the total light emitted, some provision must be made for collecting all of the light emitted from the electrode or calculating what fraction is collected. Integrating spheres (*20*) or boxes (*6*) or a box composed of five solar cells (*5*), calibrated with a standard light source, have been used for ECL measurements. A possible difficulty with this arrangement is that the calibration may depend upon wavelength, and ECL solution and cell geometry, because the light passes many times through the ECL cell during multiple reflections. Alternately, if the distribution of light emission from the electrode is known, a geometric correction can be applied. One would expect the light distribution from ECL to be uniform in all directions. This was indeed demonstrated by measurements with the photodiode set at various angles to the axis of a RRDE or planar platinum disk electrode producing ECL employing either the TH/DPA or the tris-bipyridyl ruthenium(II) (*21*) systems (Figure 3). A uniform response is observed within ±90° from a line normal to the electrode surface; above this angle, the light is cut off by the electrode itself. Thus, the fraction of the total emitted light intercepted by the photodiode of active surface 1.00 cm^2 at r cm from the working electrode is $1/2\ \pi r^2$. For example, an $I = 1.00 \times 10^{12}$ photons/sec reading of the photodiode at 3.00 cm from the electrode corresponds to a total photon flux of 5.65×10^{13} photons/sec.

These geometrical factors can be of importance when calibrating an apparatus with a standard source whose intensity distribution may be different from that of an electrode during ECL. For example, using the photodiode, we discovered that the light distribution from the RRDE surrogate source utilized for calibration of previous apparatus (*9*) actually was more directed in a direction normal to its surface. This led to a considerable change (a factor of about 13) in the reported values of ϕ_{ecl}-values compared to those originally reported (corrected values are listed in (*4*)).

Reflectivity Corrections. Since ECL is emitted in a random direction throughout the lower hemisphere, it is reasonable to assume that emission occurs equally into the upper hemisphere toward the electrode. To account for the number of photons emitted in this direction, and detected by the photodetector, some assumptions must be made about the reflectivity of the electrode. If the reflectivity were 100%, all emitted photons would be accounted for by considering only those in the lower hemisphere. On the other hand, if the electrode behaved as a black body, so that the reflectivity was 0, a correction factor of two would have to be applied to the observed intensity, I_{obsd}, to account for all of the photons emitted in the ECL reaction which were lost. In general then the corrected intensity, I_{corr}, which is given by $I = 2\,I_{obsd}/(1 + R)$ where R is the reflectivity of the electrode, and is a function of the nature of the metal and solution, the wavelength, and the electrode potential (*22, 23*). The reflectance would also depend upon the condition of the metal electrode surface and losses at Teflon or glass insulators surrounding the electrode (*e.g.*, in the RRDE). In the absence of definitive data under the conditions of our experiments, we have assumed a reflectance of 0.45 at wavelengths of the DPA/TH system, and 0.55 for those of the rubrene system, estimated from previous studies under different conditions (*22, 23*).

Solution Absorbance Corrections. The light emitted at the electrode surface passes through a layer of solution before detection. Photons will be lost by absorption by species such as radical ions or products which do not fluoresce. Moreover, the parent component in the solution will absorb the higher energy photons of the emission and, depending upon the spectral distribution and the fluorescence yield, ϕ_f, re-emit some of these in random directions at longer wavelengths. This effect, an inner filter effect of the second kind (*24*), also occurs in fluorescence measurements; it is of greater importance and more difficult to treat in ECL where high

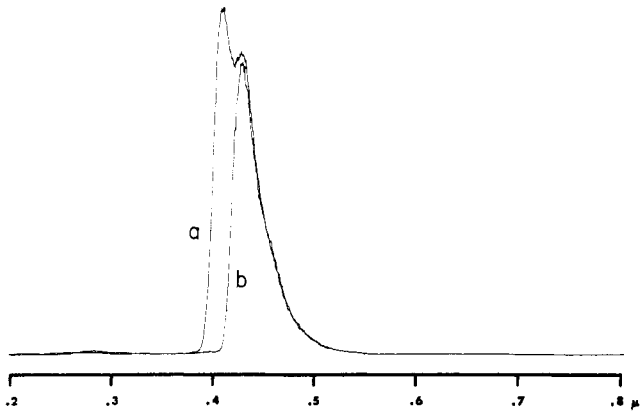

Figure 4(*a*). Solution filter effect in DPA solutions.

Fluorescence of (*a*) 0.02m*M* DPA in ACN:benzene:toluene containing 0.1*M* TBAP; (*b*) the same solution viewed through a 7.8m*M* DPA and 11.1m*M* TH solution with the same electrolyte and solvent in a cell 1.00 cm deep

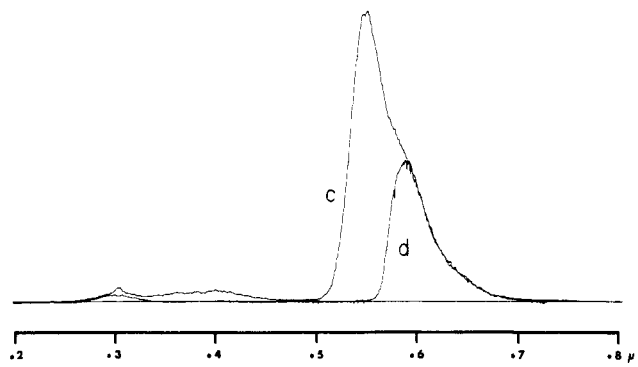

Figure 4 (*b*). Solution filter effect in rubrene solutions

Fluorescence of (*c*) 0.02m*M* rubrene in benzonitrile–0.1*M* TBAP; (*d*) the same solution viewed through a 2m*M* rubrene solution with the same electrolyte and solvent in a 1.00-cm cell

concentrations are employed and a reflecting electrode surface is present. Consider the spectra in Figure 4*a* showing the fluorescence of a 0.02m*M* DPA solution, which approximates the actual, unfiltered, ECL emission, and that of the same solution observed through a 7.77m*M* DPA–11.1m*M* TH (or 7.77m*M* DPA) solution. The loss that results when the shorter wavelengths are absorbed and remitted at longer wavelengths depends upon ϕ_f. For DPA, ϕ_f has been reported to be between 0.76 and 1.0 (*25*), although Berlman (*26*) uses it as a reference for obtaining fluorescence efficiencies and takes $\phi_f = 1.0$. Rubrene (Figure 4*b*) is usually taken to have a fluorescence efficiency of 1.0. For thianthrene ϕ_f is only 0.036 (*11*), but there is essentially no overlap between the fluorescence excitation and emission spectra of TH and, for this reason, the ARF correction was foregone in case of the systems referred to in Tables I and II. Consider the processes which occur following emission of ECL in a moderately concentrated solution of parent compound during multiple absorption–refluorescence (ARF) cycles. Let us assume that the absorption spectrum of the parent compound is such that one-half of the emission spectrum overlaps it, so that half of the total emitted photons (the high energy ones) can be absorbed by parent molecules. The number of these absorbed and re-emitted follow Beer's law and hence depend upon the molar absorptivities (ϵ) for absorption at the different wavelengths and the concentration of parent species. Most ECL solutions contain relatively high concentrations of species with high molar absorptivities. For example, for DPA in the region where the absorption spectrum overlaps the one for emission (390–420 nm), the ϵ-values at 410, 400, and 390 nm are approximately 1000, 8000, and 9000 l./mole-cm, respectively (*26*); for a 7.8 m*M* solution of DPA, such as that used in these experiments, essentially total absorbance occurs in this wavelength region within a distance of 1 mm. Upon one ARF-cycle then, 0.5 of the incident photons are absorbed, 0.5 $(1 - \phi_f)$ of them are lost, 0.25 ϕ_f are converted to the low energy (non-overlapped) ones which are not absorbable, and 0.25 ϕ_f are re-emitted in the high energy (overlapped) region. After a number of these cycles the high energy region of the spectrum will have disappeared and the fraction of the total lost will be given by:

$$\text{fraction of photons lost} \cong (1 - \phi_f)\sum_{n=1}^{\infty} l^n \phi_f^{n-1} \qquad (6)$$

where $l \cong$ fraction of the emission spectrum overlapped by the absorption spectrum (assumed one-half in the example above). For $\phi_f = 1$, no photons are lost, they are simply converted to lower energy ones (total output energy is decreased, however). For the case where $\phi_f = 0.84$ and $l = 0.5$, about 14% of the emission will be lost.

The above calculation does not take into consideration the fact that upon an ARF-cycle, the radiation is re-emitted in a random manner. This requires an additional reflectivity correction (beyond that discussed in the previous section) and implies that even when $\phi_f = 1$, the ARF effect of parent compound will cause loss in output photons when the electrode is not 100% reflective. While the quantitative treatment of this net ARF–reflection effect is difficult to carry out in general, its net result is to cause a redistribution of the spectrum toward longer wavelengths at an even shorter distance from the electrode. The total loss caused by this ARF–reflection effect for a species with $\phi_f = 1$, assuming a reflectance of 0.6 and $l = 0.5$ is about 30% of the emitted photons (compared to a 20% loss if only the reflectance effect is taken into account). In concentrated solutions (*e.g.*, 7.8m*M* DPA), this effect probably occurs within the 2–3 mm from the electrode surface. If the electrode diameter is small compared to this distance, additional losses due to non-reflected scatter may occur. While these effects can be minimized by working with low concentrations of parent species, this condition is usually not compatible with high accuracy photometric and electrochemical measurements in ECL.

Table I. ECL Efficiency Measurements of DPA/TH System Using Chemical Actinometry[a]

Method	Experiment duration, sec	$\bar{i}$, mA	$\bar{I}_{obsd}$, photons/sec	$\bar{\phi}_{ecl}$, %
RRDE[b]	975	1.6	4.18×10^{14}	4.2[d]
Pulsed[c]	4500	1.65	1.44×10^{14}	2.8[d]

[a] The solvent was 50% ACN:33% benzene:17% toluene (by volume) and contained 0.10*M* TBAP, 7.8m*M* DPA, and 11.1m*M* TH. [b] E_D = +1.40 V *vs.* SCE, E_R = −2.10 V *vs.* SCE. Rotation rate was 37 rev./sec. Because of rapid fall of ECL intensity, the experiment was stopped every 2 minutes for 30 seconds (not counted in 975-sec duration). [c] Electrode pulsed between +1.40 and −2.10 V *vs.* SCE at a frequency of 60 Hz; $\bar{i}$ (mA) based on the cathodic pulse. [d] Peak ECL intensities initially observed are higher than these averaged values by at least a factor of two (*e.g.*, a 335-mV reading on the PD during actinometry, in conjunction with peak efficiency value about 12%). Correction factors included the actinometric blindspot where the photodiode monitor was placed; both RRDE and pulsed measurements were corrected for reflectivity (R = 0.45). A unit efficiency was assumed for the actinometric process itself, consequently the $\bar{\phi}_{ecl}$ values may be 10% too high.

Table II. ECL Efficiency Measurements of DPA/TH System Using Calibrated Photodiode at Stationary Electrode[a]

Solution	$\bar{I}_{obsd}$, photons/sec	$\bar{i}$, mA	Pulse frequency, Hz	$\bar{\phi}_{ecl}$, %	Remarks
1	1.64×10^{14}	1.65	60	4.4	steady state-16 hr
1	2.50×10^{14}	3.38	300	3.3	steady state- 2 hr
2	2.23×10^{14}	1.60	60	6.2	steady state-14 hr
2	8.17×10^{14}	1.60	60	~20	peak intensity

[a] The solution was 7.8m*M* DPA, 11.1m*M* TH, and 0.1*M* TBAP in 50% ACN:33% benzene:17% toluene (by volume). The platinum electrode was pulsed between +1.50 and −2.10 V *vs.* Ag RE. To obtain $\bar{\phi}_{ecl}$, I_{obsd} was corrected for electrode reflectivity (R = 0.45). Solution 1 was subjected to some exploratory work involving extreme potentials of electrogeneration; the lower $\bar{\phi}_{ecl}$ values obtained with it may be caused by quenchers generated at the background potentials.

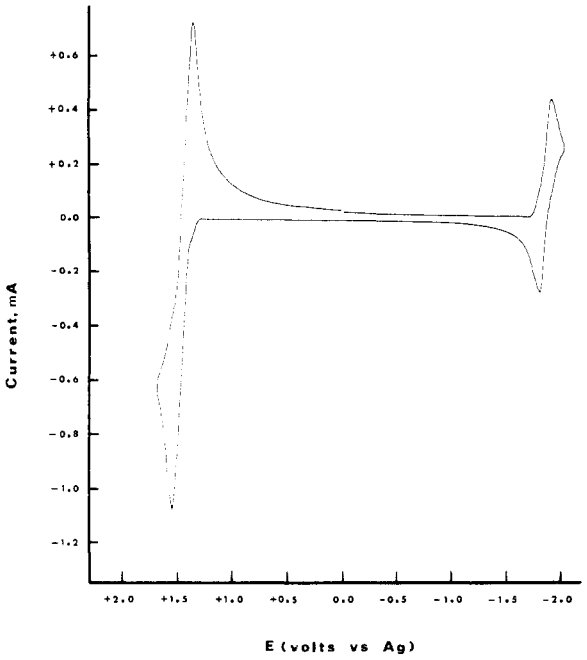

Figure 5. Cyclic voltammogram of the DPA/TH system in the mixed solvent (50% ACN:33% benzene:17% toluene) containing 0.1*M* TBAP

DPA was 7.77m*M*, TH, 11.11m*M*; scan rate was 100 mV/sec

Electrical Measurements. To determine the instantaneous ϕ_{ecl}, one can determine the total current, which must then be corrected for the nonfaradaic (charging) and the residual current. In determination of the average ϕ_{ecl} ($\bar{\phi}_{ecl}$) in transient measurements, one must determine the total number of faradaic coulombs per pulse which produce radical ion species. In the pulse experiments described here, the integration of the current–time curves (and also the intensity–time curves) was performed by tracing the oscilloscope photographs onto a special paper with a known and constant weight-area factor (31.2 mg/cm^2), cutting out the curves, and weighing these. From the area of the curves and oscilloscope settings, the photon flux and average current could be calculated. In case of the DPA/TH solutions, in which the number of radical cations generated per pulse (from the 11.1 m*M* TH + 7.8 m*M* DPA oxidizable species) was significantly greater than the number of radical anions generated per pulse (from only the 7.8 m*M* DPA), the average current (*i.e.*, electron flux, coulombs per second) was based on the cathodic pulse. In both cases, it should be remembered that the basic definition of ϕ_{ecl} is photons emitted per radical ion annihilation, and not per Faradaic electron, *i.e.*, even in case of "infinitely stable" ions, the number of radical ion annihilations will be half of the total (anodic and cathodic) Faradaic electrons per second. The correction for the nonfaradaic and background current was obtained by stepping between the limiting plateau of one wave (*e.g.*, that for generation of radical anion) and the foot of the other (*i.e.*, for generation of radical cation). For example, in the DPA/TH system ECL is obtained on stepping between +1.50 V (TH·$^+$and DPA·$^+$ formation) and −2.10 V (DPA·$^-$ formation), while the correction was obtained by stepping briefly to +1.50 and then to −1.40 V. This method gives a slight undercorrection for the charging and background currents. Determination of the Faradaic coulombs is also possible by a chronocoulometric technique using the integrated Cottrell equation for linear diffusion (*8*). For a large unshielded disk electrode such as that employed in these studies, appreciable non-linearity of diffusion can occur, especially at short times. For example, when low pulsing frequencies (*e.g.*, 1 Hz) are employed, the ECL results in a fairly uniform glow over the disk; at higher frequencies (*e.g.*, 500 Hz), the ECL takes the form of a ring on the outside edge of the disk. Finally, to obtain ϕ_{ecl}, the current must be used to calculate N, the number of redox events per second; this depends upon the relative concentration of the parent compound species and the stability of the radical ions (*4, 8*). Because of the stability of the radical ions in our solvents, we assumed that all Faradaic electrons contributed to the light producing reactions (*i.e.*, $N \cong 1$); this makes the ϕ_{ecl} values reported here conservative ones.

Table III. Typical Values for $i_p/v^{1/2}$ for the Oxidation of DPA and TH in Cyclic Voltammetry in an ACN–Benzene–Toluene Solvent[a]

Scan rate, v, mV/sec	Total peak current, i_p, μA	$i_p/v^{1/2}$
20	29.9	3.34
50	46.2	3.26
100	63.0	3.15
200	87	3.06

[a] The concentrations and solvent composition are given in the legend for Figure 5; a platinum disk working electrode was employed.

The electrical measurements are somewhat more straightforward with the RRDE since, under the condition that the flux of the disk-generated species governs the number of redox-events (*9*), the value of disk current gives N directly and the steady state intensity divided by the disk current gives $\bar{\phi}_{ecl}$. A difficulty with the RRDE, aside for the somewhat more complicated apparatus required, is that rather large currents are passed, so that solution decomposition with concomitant changes in ECL behavior may occur after short electrolysis times. Whereas we have observed steady ECL intensities under pulsed conditions, in RRDE experiments a rapid decay of ECL intensity was the common observation.

RESULTS

Electrochemistry and ECL of DPA/TH System. The electrochemistry and ECL of DPA alone (*9, 12, 15*) and TH (*27*) in ACN–TBAP solutions has been described. In dry ACN, cyclic voltammetry shows reversible oxidation of DPA to DPA·$^+$ (E_{p_a} = +1.35 V *vs.* SCE) and reversible reduction of DPA to DPA·$^-$ (E_{p_c} = −1.89 V. *vs.* SCE); DPA ECL shows an emission maximum at 428 nm. TH oxidizes at a platinum electrode to a stable cation radical with E_{p_a} = +1.25 V. *vs.* SCE; the relevant cyclic voltammetric criteria $E_p - E_{p/2}$, $E_{p_a} - E_{p_c}$ and i_{p_a}/i_{p_c}, are characteristic of a Nernstian oxidation to a stable cation. TH is not reducible in ACN–TBAP at a platinum electrode at potentials less negative than −2.4 V *vs.* SCE. The ECL emission of TH in the ACN–TBAP medium (produced on reaction of TH·$^+$ with PPD·$^-$), or in mixed solvents is characterized by a maximum at 430 nm (*27*). The addition of TH to a DPA (ACN–TBAP) solution with pulsing of the electrode to generate TH$^+$ and DPA$^-$, produces a substantial increase in ECL intensity over that observed for a DPA solution alone. The enthalpy of the electron transfer reaction between DPA·$^-$ and TH·$^+$, as calculated from the peak potential values and assuming $T\Delta S°$ = 0.1 eV (*28*) is −2.98 eV, slightly smaller than the singlet energy, E_s, of DPA (*ca.* 3.05 eV), but larger than that of TH ($E_s \simeq$ 2.84 eV) (*27*). Because of the proximity of the ECL peaks (428 nm *vs.* 430 nm), the ECL spectrum observed for DPA/TH does not identify whether the emitter is the excited singlet of DPA or TH.

The intensity of ECL emission is, in many cases, proportional to the concentration of the radical ion precursors (*1, 2*), and is limited in ACN by the low solubility (*ca.* 1 m*M*) of DPA and other fluorescent hydrocarbons. In a mixture of ACN and benzene, however, higher concentrations are possible (*e.g.*, 15m*M* DPA in 1:1 ACN:benzene by volume) while satisfactory electrochemical properties of the solution are preserved; the effect of the added benzene is simply to increase the solution resistance somewhat. A cyclic voltammogram of a solution containing 7.8m*M* DPA, 11.1m*M* TH and 0.1*M* TBAP in a solvent of 50% ACN:33% benzene:17% toluene (by volume) at a scan rate, V, of 100 mV/sec is shown in Figure 5. At these high concentrations (and currents), some effect of uncompensated resistance

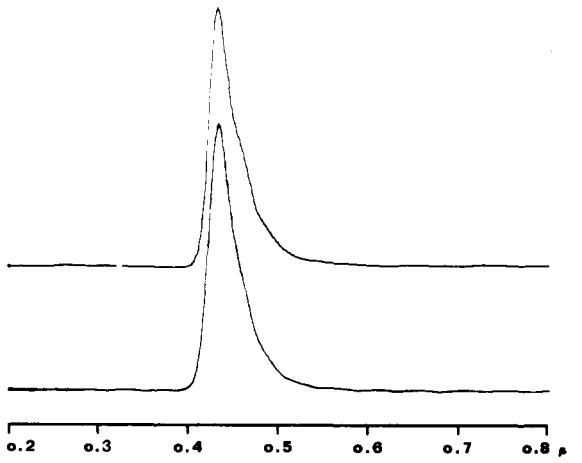

Figure 6. DPA and DPA/TH ECL in a mixed solvent consisting of 50% ACN:50% benzene

The solutions contained 0.1*M* TBAP and (*a*) 15m*M* DPA, 10m*M* TH; (*b*) 15m*M* DPA. Potential was cycled between −2.05V and +1.40 V (*vs.* Ag RE) at f = 60 Hz

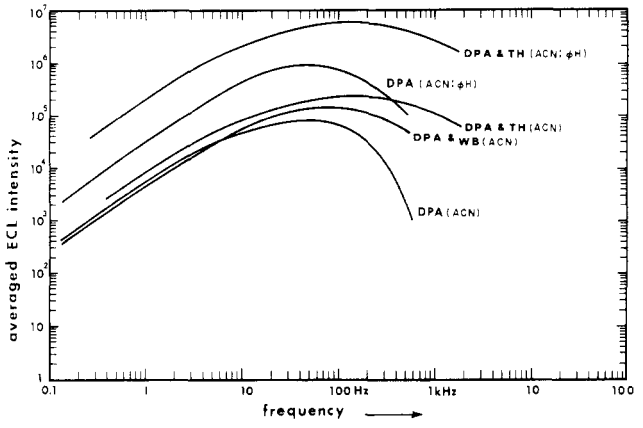

Figure 7. Frequency dependence of ECL from solutions of DPA and DPA/TH in ACN or 50% ACN:50% benzene

All solutions contained 0.10*M* TBAP and (from top downward) (*a*) 15m*M* DPA, 10m*M* TH; (*b*) 10m*M* DPA; (*c*) 0.5m*M* DPA, 0.5m*M* TH; (*d*) 1.5m*M* DPA, 1m*M* tetra-*N*-methyl-*p*-phenylenediamine(WB); (*e*) 0.5m*M* DPA. ECL generated by cycling between diffusion plateaus at indicated frequency

between working and reference electrode is seen (even when positive feedback iR compensation is employed) although $i_p/v^{1/2}$-values for the oxidation and reduction waves are quite constant with scan rate (Table III). When the concentrations of DPA and TH are reduced to about 1m*M*, the peak potentials in this mixed solvent are the same as those found in acetonitrile, and the oxidation peak of TH ($E_{p(R/R^+)}$ = +1.25 V *vs.* Ag RE) and of DPA (E_{pR/R^+} = 1.35 V *vs.* Ag RE) become individually identifiable. The reversible reduction of DPA is at $E_{p(R/R^-)}$ = −1.89 V *vs.* Ag RE (corrected to SCE). ECL of these DPA/TH solutions in mixed solvents could be obtained both by pulsing at a single electrode or at an RRDE; a typical ECL spectrum of the DPA/TH system compared with that of DPA alone in ACN:benzene is shown in Figure 6. The relative intensity of several systems containing DPA in ACN and ACN:benzene at several concentrations as a function of pulsing frequency is shown in Figure 7. In order to optimize the light output from the system, different ratios of acetonitrile, benzene, and toluene were tried, and the concentrations of DPA and TH were varied; a suitable system, which produced a luminescence of 3 mW/cm^2 of working electrode area consisted of a solution of 7.8m*M* DPA, 11.1m*M* TH, and 0.10*M* TBAP, in a solvent being a mixture of 50% (by volume) ACN, 33% benzene, and 17% toluene. Changing solvent composition or substrate or electrolyte concentration had essentially no effect on the ECL spectrum. This optimized system showed no change in emission intensity with time for several hours. We should emphasize that our optimization was with respect to ECL intensity rather than ϕ_{ecl}, and indeed Figure 7 as well as Table IV suggest that the maximum efficiency of the DPA/TH system may be higher than the values obtained in the 7.8m*M* DPA/11.1m*M* TH solutions.

Table IV. ECL Efficiency Measurements of the DPA System Using Calibrated Photodiode at RRDE

[DPA], m*M*	V *vs.* SCE, E_D	V *vs.* SCE, E_R	Rotation rate, rev/sec	i_d, μA	I_{obsd}, photons/sec	$\bar{\phi}_{ecl}$, %[c]
2.2[a]	+1.50	−2.15	23	240	7.60 × 10^{13}	7.6
2.2[a]	+1.50	−2.15	37	260	8.42 × 10^{13}	7.8
2.2[a]	−2.15	+1.50	23	296	7.60 × 10^{13}	6.2
2.2[a]	−2.15	+1.50	37	324	7.60 × 10^{13}	5.6
7.8[a]	+1.50	−2.20	23	790	1.14 × 10^{14}	3.5
7.8[a]	+1.50	−2.20	37	895	1.40 × 10^{14}	3.8
7.8[b]	+1.40	−1.95	37	288	6.76 × 10^{13}	5.7
7.8[b]	−1.95	+1.40	37	268	5.66 × 10^{13}	5.1
7.8[b]	−1.90	+1.40	23	196	4.57 × 10^{13}	5.6

[a] Solvent was 50% ACN:33% benzene:17% toluene containing 0.1*M* TBAP. [b] Solvent was 50% propylene carbonate:50% toluene containing 0.1*M* TBAP. [c] Correction of I_{obsd} to obtain I_{corr} involved Equation 6 (ϕ_f = 0.84 and l = 0.37) followed by a reflectivity correction (R = 0.45).

Efficiency Measurements. The ϕ_{ecl}-values for the DPA, DPA/TH, and rubrene systems under different conditions (pulsed or RRDE) were determined by several different methods.

Actinometry of DPA/TH System. The high intensity and good stability of the ECL of the DPA/TH system in mixed solvents allowed direct actinometric determination of the total number of photons emitted. The apparatus of Figure 1 was employed. The ECL was monitored continuously through a 1-in. diameter optically flat window in the bottom of the cell using the photodiode during a determination; the total emitted photons into the actinometric bath were corrected for those lost through this 5.07 cm^2 area viewing port (the electrode was 3.00 cm from the bottom of the cell (h) and the cell radius was 3.60 cm (r), leading to a total area at the surface of the actinometry solution of $2\pi rh$ = 67.8$_6$ cm^2 less the area of the viewing port). It was also found, by comparing the photodiode reading at the viewing port with that taken through the actinometry solution, that 29% of the emitted ECL light (primarily in the longer wavelength or green region of the emission) is transmitted through the 0.15*M* $K_3Fe(C_2O_4)_3$. The results were also corrected for this loss. Photodiode measurements showed that less than 1% of the light escaped above the plane of the electrode. The determined efficiencies at both a pulsed stationary electrode and RRDE are given in Table I.

Photodiode Measurements of DPA and DPA/TH Systems. A number of other ϕ_{ecl} measurements were made using the calibrated photodiode and the corrections described previously at a pulsed stationary electrode and an RRDE. These results are summarized in Tables II and IV. We include in Table IV some measurements made with propylene carbonate as the solvent. The ECL at an RRDE in this solvent was remarkably constant with time with radical cation generated at either disk or ring, in contrast to the filming behavior observed in the mixed solvent or ACN alone (*9*).

Table V. Variation of ECL Intensity (I) and $\bar{\phi}_{ecl}$ with Frequency (f) in the Rubrene System[a]

f, Hz	mV	$\frac{I_{ecl}}{f^{1/2}}$[b]	$\bar{\phi}_{ecl}$, %[c]
10	23	7.23	1.8
20	33	7.35	1.8
30	42	7.63	1.9
40	49	7.72	1.9
50	54	7.61	1.9
60	57	7.34	1.8
70	59	7.02	1.8
80	59	6.55	1.6
90	60	6.29	1.6
100	60	6.00	1.5

[a] The solution contained 2.00mM rubrene and 0.10M TBAP in benzonitrile. The platinum disk electrode was pulsed between + 1.10 and −1.60 V *vs.* Ag RE. [b] Photodiode output voltage read with DVM, R_F = 2 Megohms. [c] In applying a reflectivity corrections (R = 0.55), it was assumed that the ARF red-shift is complete prior to reflection.

Photodiode Measurement of the Rubrene System. Because a number of measurements have been reported for rubrene (*4–9*), we include here our results for ϕ_{ecl} of rubrene in a benzonitrile–0.1M TBAP solution. As previously reported by others, the cyclic voltammetry of rubrene under these conditions shows Nernstian reduction (E_{p_c} = −1.47 V *vs.* Ag RE) and oxidation (E_{p_a} = +1.00 V *vs.* Ag RE) with ΔE_p of 57 mV for both waves and high stability of both radical ions. The results of ECL measurements at a stationary electrode at frequencies (f) between 10 and 100 Hz are shown in Table V. The ECL was quite steady and $I/f^{1/2}$ was constant between 10 and 60 Hz. Above this frequency, a drop in $I/f^{1/2}$ is observed; this may be attributed to both difficulty in obtaining complete compensation of the uncompensated resistance (which is important in this medium) and loss of uniform current density at the unshielded disk electrode at higher frequencies. The light level in this system was constant for at least 16 hours (at which time the experiment was discontinued).

DISCUSSION

The quite good agreement between ϕ_{ecl} determined by direct actinometry and by calibrated photodiode in the DPA/TH system lends some confidence to these results. The largest uncertainty in these results arises not from the experimental measurements of photon flux or Faradaic current, but rather from estimations of electrode reflectance and corrections for ϕ_f and absorption–refluorescence effects. These considerations do not arise in determination of the luminance of an electrode undergoing ECL or ϕ_{prac} (*4*).

The results also suggest that addition of benzene and toluene to the acetonitrile cause an increase in ϕ_{ecl} (in addition to allowing higher intensities because of higher solubility) for the DPA and DPA/TH systems. Similar solvent effects in a mixed solvent system were observed by Pighin (*5*) in a comparison of rubrene in DMF *vs.* DMF–benzene. The effect of adding benzene is to decrease the dielectric constant of the solvent. In certain cases, when the enthalpy of the electron transfer reaction (*4*) is less than that needed to produce the excited singlet state directly, we have suggested that a greater difference in half-wave potentials (and hence greater $\Delta G°$) in lower dielectric constant solvents or at lower supporting electrolyte concentrations provides more efficient excited state formation (compared to ground state) or the greater production of singlet excited states compared to triplet states in the electron transfer reaction (*4, 29, 30*). For the case of DPA or the DPA/TH systems, however, the peak potentials are essentially the same in ACN alone or the mixed solvent, and the reaction enthalpy is sufficient to produce excited singlet states directly. Thus, the explanation of greater efficiency probably lies in changes in the nature of the steps during or following electron transfer. One possibility is the effect of solvent on the dissociation of the "encounter complex," or excimer or exciplex formed upon reaction of the radical ions into either excited states or ground states (*15, 31*). The formation of an "encounter complex" or excimer seems unlikely with molecules such as DPA where large steric hinderances might be expected; exciplexes involving DPA have been reported, however (*32*). Pighin (*5*) suggested that increased solvation of the excited state species (triplet rubrene) by benzene might decrease its rate of quenching by radical ions; this explanation is less likely for the short-lived excited singlet DPA or TH.

Finally, we would like to suggest the potential usefulness of mixed solvent systems, such as ACN–benzene, ACN–benzene–toluene, DMF–benzene, etc., in electroanalytical and electropreparative studies. The dielectric constants of the mixtures are large enough that supporting electrolytes such as TBAP can be dissolved in them to produce solutions of reasonable conductivity. The much greater solubility of organic substrates in it and the possibility of continuous variation of the dielectric constant between that of the polar component and that of the nonpolar one suggest several applications.

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Computerized Kinetic Luminescence Spectrometry: Time-Resolved and Component-Resolved Phosphorescence Spectrometry

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A computer-controlled laser phosphorimeter is described. The form of data acquisition utilized by this system is unique in that the phosphorescence spectra are recorded on magnetic tape as signal-averaged, families of decay curves. The utility of this data format is illustrated in the analysis of phosphorescence spectra of samples exhibiting nonexponential decay. An extremely flexible and simple procedure for the generation of time-resolved spectra is described. The technique of component-resolved spectrometry is discussed in detail and illustrated by the resolution of the phosphorescence spectra of the constituents from the emission of a binary mixture. The system described is extremely versatile in that the decay of phosphorescence spectra can be analyzed in terms of any one of a wide variety of kinetic models. The results of this kinetic analysis may be displayed in the form of calculated time-resolved and component-resolved spectra for comparison with observed time-resolved spectra and spectra of pure components.

Phosphorescence spectra obtained by conventional means are frequently rendered difficult to interpret because of the superposition of emission from two or more excited species. Most efforts have been devoted to the simplification of these complex emission spectra through either tedious purification schemes (*1*) or application of elaborate mechanical (*2*) and electronic devices (*3–7*). It has only been recently that serious attempts have been made to study this phenomenon. It now appears that there are several situations that can give rise to the formation of more than one excited species and, thus, to complex emission spectra. Perhaps the most common situation is that in which the components of a mixture of substances are emitting independently in the same spectral region (*7–10*). In certain instances, a single pure substance can afford complex emission spectra. The following explanations for this type of behavior have been offered, but in many cases have not been confirmed experimentally. Simultaneous emission from both n,π^* and π,π^* states has been demonstrated in some cases (*11*) and suggested for others (*12*). (For a summary of the complex emission behavior of aryl carbonyls, see Reference *12*.) Emission from different states of aggregation has been demonstrated (*13*). Emission from a single substance in different conformations (*14, 15*) or different solvent or matrix environments (*12*) might account for complex emission. Finally, at very low temperatures emission has been observed from the three sub-levels of the triplet state (*16, 17*).

Workers in this area have relied heavily upon kinetic information which was acquired by recording the relative emission intensity as a function of time at one or, at most, a few different wavelengths. While the analysis of decay data of this kind can provide one with an estimate of the number of emitting species and the manner in which they undergo change, kinetic analysis alone provides little information concerning the nature of the species involved. To make judgements obtaining to chemical structure, one also requires spectrometric information in which the relative emission intensity is recorded as a function of wavelength. Conventional time-resolved luminescence spectrometry combines this type of kinetic and spectrometric data in a very qualitative fashion; rigorous kinetic analysis of conventional time-resolved spectrometric data is not possible. Consequently, quantitative kinetic and spectrometric information are acquired in two independent sets of measurements. We have assembled a computerized kinetic luminescence spectrometry system which unifies kinetic and spectrometric analysis in a novel and rigorous fashion.

In principle, the kinetic spectrometry system described here might be used to study any sample exhibiting complex emission behavior. However, it was felt that the only way to evaluate the capabilities of the approach used in this system was to apply the technique to a known mixture of emitting substances. For this purpose we have selected a mixture of anthrone (*ca.* $8.8 \times 10^{-4} M$) and benzophenone (*ca.* $3.8 \times 10^{-4} M$) to illustrate in detail the technique of kinetic spectrometry.

THE DATA ACQUISITION SYSTEM

The unification of kinetic and spectrometric information requires the recording of relative luminescence intensity as a function of *both* time and wavelength *simultaneously*. This can be accomplished by taking advantage of the high speed data acquisition capability of an on-line computer to permanently record a complete family of emission decay curves taken at small wavelength intervals over the entire spectrum range. It then becomes possible by again employing a computer to reassemble these decay data into a com-