

AN EXAMINATION OF THE UTILITY OF ELECTROGENERATED
CHEMILUMINESCENCE FOR THE DETERMINATION OF
AROMATIC HYDROCARBONS AND RELATED COMPOUNDS

A Thesis submitted for the Degree of
Doctor of Philosophy of the University of London

by

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August 1970

ABSTRACT

The phenomenon of electrogenerated chemiluminescence has been examined as a potential analytical technique for the determination of trace amounts of aromatic polycyclic hydrocarbons and related compounds. An apparatus has been constructed to establish the optimum excitation conditions for the observation of ecl emission from such compounds, and to obtain analytical data at high sensitivity.

Long-wavelength ecl emission peaks arising from decomposition products and excited dimer formation have been examined, and related to parameters of the applied signal.

An attempt has been made to utilise ecl for the analysis of aromatic polycyclic hydrocarbons separated from tobacco residues by preparative scale gas chromatography.

ACKNOWLEDGEMENTS

I would like to thank my supervisors, Dr. G. F. Kirkbright and Dr. B. Fleet, for their help and encouragement during the preparation of this thesis, and Professor T. S. West, for his valuable advice.

I would also like to thank the Science Research Council for their financial support, and also the Tobacco Research Council and the British-American Tobacco Company for the loan of equipment, and for providing samples.

Finally, I would like to thank my fiancée, Anne, for typing this thesis, and for correcting the English wherever necessary!

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CHAPTER I

1.1 Historical Observations

Chemical reactions may sometimes provide sufficient energy for one of the products or reactants to be raised to an excited state, from which light emission may be observed. Familiar examples of this process, which is known as chemiluminescence, are the oxidation of luminol or lucigenin with hydrogen peroxide, producing light of sufficient intensity to be seen even in diffuse daylight.

If a chemiluminescent reaction occurs in the region surrounding an electrode during electrolysis, then the process is often termed electrochemiluminescence, or more simply, 'ecl'.

Historically, the first report of this phenomenon seems to be that of Sluginov¹, who reported that light was emitted when water was electrolysed with a platinum electrode. In 1914, Bancroft and Weiser² observed light emission at a mercury anode when aqueous solutions of halogen salts such as potassium bromide were electrolysed. Other similar observations^{3,4} have since been made for the electrolysis of a number of other metal salts in water. A recent spectroscopic study of this type of electrode luminescence by Edkie and Mande⁵ showed that the emission obtained from the cathode consisted of atomic lines from the electrode and electrolyte materials, superimposed on some band emission, whereas that from the anode

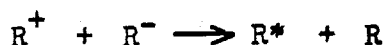
consisted of atomic lines from the electrolyte metal superimposed on a continuum. It was postulated that the emission occurred as a result of corona discharge effects across a thin film of gas formed at the electrode surface.

The electrolysis of certain Grignard reagents in ether solution has been reported⁶ to emit light, although the conditions in the original experiments were not very well defined, and they do not appear to have been pursued further. Shlyapintokh et al⁷ have found that alkaline solutions of eosin and fluorescein emit light when subjected to square wave or d.c. electrolysis at 30 V; 10^4 photons/second were emitted from a 1 cm^2 platinum anode when a current of 14 milliamps was passed. The authors postulated that the light emission occurred as the result of the combination of active cathodic and anodic intermediates.

Harvey^{8,9} found that the chemiluminescent substances luminol and luciferin emit light when they are electrolysed in alkaline solution, due to their reaction with electrolytically formed oxygen or hydrogen peroxide. This has since been reported by many other workers, and has recently been studied in detail by Epstein and Kuwana¹⁰ in an attempt to elucidate the mechanism and species responsible for the electrogenerated chemiluminescence in the presence of oxygen and base. This phenomenon has since been used^{11,12} to study problems of mass transfer in fluids, as a visual indicator of solution flow.

In 1964, Hercules¹³ and Visco and Chandross¹⁴ reported a new kind of ecl process, produced by the a.c. electrolysis of solutions of aromatic hydrocarbons in aprotic solvents such as dimethylformamide (DMF) containing a supporting electrolyte.

Hercules examined visually the light emitted at platinum electrodes from a number of compounds such as anthracene, perylene, and rubrene, and compared it (in terms of colour) to that obtained by normal solution fluorescence methods. To explain the observations, he considered that the most obvious explanation, that is, the reaction of electrogenerated anions and cations of the hydrocarbon concerned to give the excited singlet state of the molecule



was not wholly consistent with all of his observations. In particular, light was most intense when anionic species were being generated, and were reacting in the bulk of the solution with cationic species formed during the previous half-cycle of the voltage in the case of a.c. electrolysis, or at the other electrode when two adjacent electrodes with a d.c. signal source were used. Because of the greater stability of hydrocarbon anions than cations in solvents such as DMF, he postulated that if simple anion-cation annihilation was the reaction responsible for light emission, then light should be most intense during the generation of cations, and their subsequent reaction with the more stable anions in the bulk of the

solution. As a possible way out of the dilemma, he postulated the formation of a complexed aromatic positive radical ion such as Ar_2^+ , of sufficient stability to reach the cathode.

Visco and Chandross examined the effect of experimental parameters upon the ecl emission of 9,10-diphenylanthracene (DPA), which was chosen as a model system, and a number of other polycyclic aromatic hydrocarbons. The emission was generated by a sine or square wave a.c. signal, and monitored with a monochromator and photometer. Cyclic voltammetric measurements indicated that, in DMF, the reactants giving rise to the singlet excited state were the hydrocarbon anion, and an oxidised product which was not the cation. In acetonitrile (AN), the reactants were the hydrocarbon anion and cation. The particular reaction mechanism suggested by the authors originally relates¹⁵ to chemiluminescence reactions studied by them, involving removal of an electron from the DPA anion (produced chemically using sodium metal) with a chemical oxidising agent such as benzoyl peroxide.

Since these original publications, many others have appeared relating to some aspect of the phenomenon. Theoretical studies have been concerned largely with the degree of involvement of triplet species, and processes leading to their formation. However, because of the instability of radical cations in DMF, this solvent has largely been dropped from use in theoretical studies of simple

systems, to be replaced by benzonitrile. However DMF still appears to be the best solvent from the points of view of intensity of emission and field of application.

In addition to polycyclic aromatic hydrocarbons, several other classes of organic compounds have been reported to show fairly intense ecl emission under similar conditions to those used by Hercules¹³, and Visco and Chandross¹⁴. Zweig, Maurer and Roberts¹⁶ have examined the ecl of an extensive series of donor-substituted aromatic hydrocarbons, and have shown a correlation between the stability of the ion radicals formed, and the ecl emission efficiency. They have also examined¹⁷ the ecl characteristics of a series of aryl-substituted isobenzofurans, isoindoles and related compounds, and have found several compounds, such as 1,3,4,7-tetraphenyl-isobenzofuran, which show ecl emission comparable in intensity, but superior in stability, to aromatic hydrocarbons.

Simple heterocyclic systems such as carbazole¹⁸ also show ecl under some conditions, although the emission spectrum does not correspond to that of the singlet excited state of the heterocycle itself. A more recent study¹⁹ of this system suggests that the emitting species may be a protonated carbazole anion, or an excited dimeric species.

Signore et al^{20,21,22,23} have studied the shape of the light pulse obtained when alternating positive and negative pulses are

applied to an electrode in simple hydrocarbon systems. They have developed a relationship between parameters of the applied signal and the pulse shape, which agrees with experimental results they have obtained, and have also studied electron transfer between anions of one hydrocarbon and cations of another, formed at the electrode surface.

Cruser and Bard²⁴ have reported an extension of Feldberg's^{25,26} theoretical treatment of ecl, using a digital simulation technique, in order to determine experimentally the rate constants of decomposition of the radical cations of a number of hydrocarbons. They further suggest²⁷ that ecl might be employed as a tool in electro-organic chemistry for measuring the rates and elucidating the mechanisms of fast chemical reactions, following the electron transfer step.

Weller and Zachariasse²⁸ have studied a chemiluminescence phenomenon which arises when solutions of hydrocarbon radical anions are mixed with a suspension of the perchlorate salt of Wurster's Blue (W.B., or N,N,N',N'-tetramethyl-p-phenylene diamine). This substance exists as a stable salt, containing the oxidised cationic radical. Emission very similar in most respects to ecl emission is seen in many cases, arising from electron transfer from the hydrocarbon anion. Although some charge transfer emission was anticipated by the authors, light emission in the expected region (18 kK) was only seen for biphenyl and naphthalene.

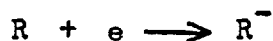
Maloy, Prater and Bard²⁹ have generated the cation of W.B. electrochemically from N,N,N',N'-tetramethyl-p-phenylenediamine itself, using a ring-disc electrode system, and have allowed it to react with pyrene anions formed at the other electrode. This, the authors claim, gave a more intense and stable emission from pyrene than they were able to generate using a.c. electrolysis of pyrene alone, which they state was too weak to measure.

W.B. cation has also been used by Faulkner and Bard³⁰ in an experiment designed to study the effect of magnetic fields upon ecl processes. As before, the cation was generated electrochemically, and reacted with DPA^- , and the effects of magnetic fields up to 8 kG upon the ecl emission observed using a simple two-electrode cell powered from a 10 Hz square wave generator. The photomultiplier tube was removed 90 cm from the magnet to prevent the possibility of interaction between the two.

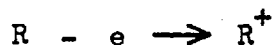
1.2 Theory of ecl Processes

Electrode Processes and the Generation of Excited States

Most aromatic hydrocarbons are readily reduced at a platinum or mercury electrode to the corresponding anionic radical:-



During the anodic cycle of the alternating potential applied to the electrode, a cationic radical is generated:-



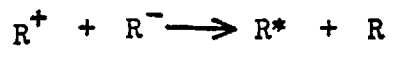
or,



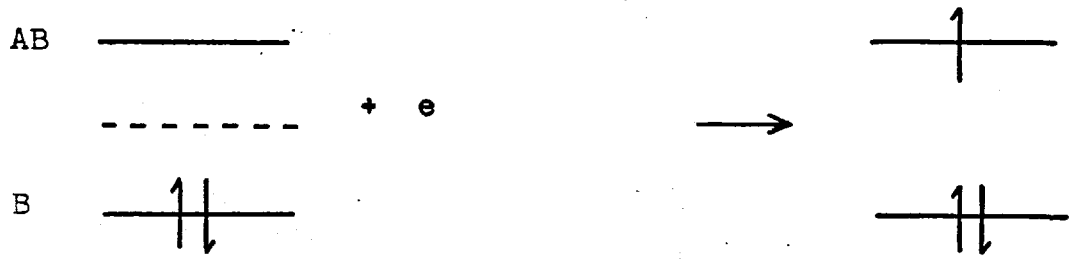
For most aromatic hydrocarbons, the anion radical is stable for a considerable time in solution, whereas the cationic radical is much less stable. The rubrene cation, for example, only exists for about ten seconds under the conditions used by Maricle et al³¹, and this is one of the more stable aromatic hydrocarbon cations known. However, for most aromatic hydrocarbons, the lifetimes of the anion and cation will be long compared to the period of time during which they are actually generated (typically, 50 or 60 Hz signals are used), hence very little of R^+ or R^- will have decayed spontaneously before reaction has taken place.

Radicals being generated at the electrode surface diffuse (or are stirred) into the layer of solution immediately surrounding the

electrode, where reaction with those formed during the previous half-cycle can take place:-



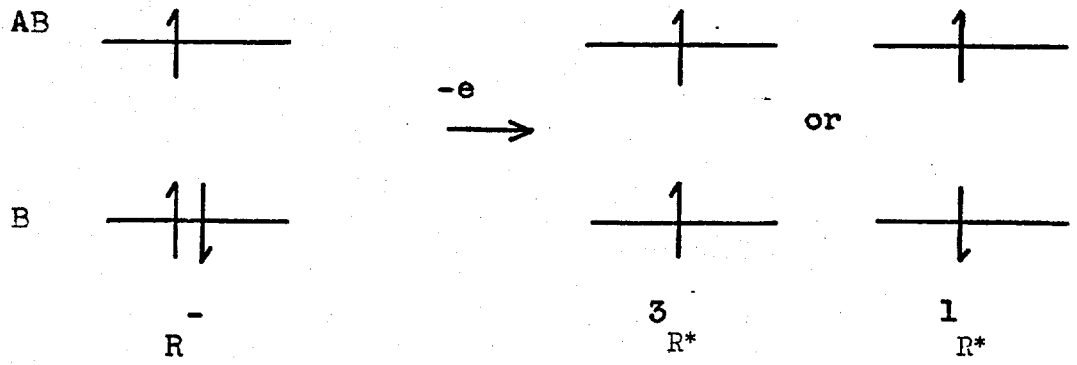
where R^* is an excited singlet or triplet state of the parent molecule. In terms of simple molecular orbitals, it can be pictured as:-



R (Ground State.)

R^- (Anionic Radical.)

then;



Excited triplet or singlet state.

From 18.

R^* may also be formed by the oxidation of R^- by species other than R^+ . In fact, the oxidant may be bromine when a tetra-alkylammonium bromide is used as the supporting electrolyte³². Also, Rauhut et al³³ have reacted DPA^- with chemical oxidants such as lead tetraacetate and ceric ammonium sulphate to obtain the same light emission. There is also some evidence that oxygen may be involved directly^{34,35}.

R^* may also be produced by the reduction of R^+ . Hercules et al³⁶ have obtained light emission from the generation of the rubrene cation alone in DMF, although the intensity of the emission was much reduced compared to the cation-anion annihilation ecl. The fact that no emission was observed in acetonitrile when just the cation was generated, except when impurities such as DMF, triethylamine or n-butylamine had been added, led the authors to suppose that the reductant was DMF itself, or some product derived from it.

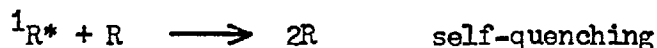
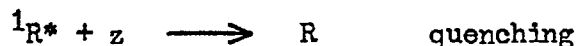
$^3R^*$ and $^1R^*$ may decay in a number of ways, some of which involve radiative and some non-radiative transitions. In the simplest of all the proposed mechanisms, which has frequently been suggested by many workers, cation-anion annihilation leads to the formation of $^1R^*$, followed by normal singlet emission:-



Since the singlet energy level involved is similar in all respects

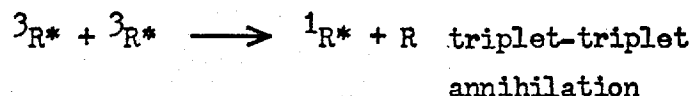
to that giving rise to the normal fluorescence, the ecl and solution fluorescence emission spectra would be expected to be similar.

Alternative transition pathways for $^1R^*$ are:²⁶



Involvement of Triplet Species

If cation-anion annihilation leads to the formation of $^3R^*$, then the following series of reactions can also be considered²⁵, provided, of course, the energy level of $^3R^*$ above the ground state is more than half that of $^1R^*$:-



Triplet-triplet annihilation has been invoked in several cases^{33,37} to explain the inadequacy of the cation-anion annihilation reaction to provide sufficient energy to populate $^1R^*$ directly. For example¹⁸, the annihilation of the anthracene cation and anion will yield about 3.2 eV ($E_{R,R^-} = -2.0$ V, $E_{R^+,R} = +1.2$ V) and the energy of the lowest singlet state of anthracene is about 3.2 eV. Clearly, sufficient energy ought to be available here from the annihilation reaction of R^+ and R^- . However³⁸, when DPA^- is formed at a mercury

electrode ($E_{R,R^-} = -1.9$ V) and the potential switched to values more positive than + 0.51 V, light emission from the excited singlet state of DPA is seen, even though the energy provided by the annihilation reaction is less than that for singlet formation. Here, clearly, is a case for the alternative mechanism.

To distinguish between the two methods of populating $^1R^*$, Feldberg^{25,26} has developed a relationship comparing the quantitative aspects of direct singlet, and triplet-triplet annihilation singlet formation, using a double-step, controlled potential technique, viz:-

$$\log \frac{fPF}{\pi^{\frac{1}{2}} \phi i_f} = -1.45(t_r/t_f)^{\frac{1}{2}} + 0.71$$

where t_r , t_f are the durations of the first and second potential pulses, P is the signal from the photomultiplier, f a correction factor to convert P to moles photons per second, ϕ the ecl quantum efficiency, and i_f the cell current at the end of the time of the generation of the radical anion (t_f). One of the assumptions made by Feldberg in deriving this relationship was that the rate constant for the formation of $^1R^*$ from R^- and R^+ should be high.

Hence a plot of $\log Pt_f^{\frac{1}{2}}$ vs. $(t_r/t_f)^{\frac{1}{2}}$ should show a linear slope of -1.45. This value has been obtained by Lansbury³⁹, but values as high as -2.9 have been obtained by other workers^{37,40}. To explain this difference, Feldberg has extended his relationship to cover triplet-triplet annihilation, and has shown that a difference between

the two mechanisms only becomes apparent when significant triplet quenching occurs, which will change the gradient of the relationship plotted from experimental data up to the limiting value of -2.90.

Ecl emission at a long wavelength has been observed for phenanthrene⁴¹, which the authors attributed to phosphorescence emission from the triplet state, produced by oxidation of R^- . However, this has been discounted by Parker and Short⁴² on the grounds that the ecl emission observed showed no structure, whereas the room temperature phosphorescence excited by optical means was structured. In addition, the postulated mechanism for the formation of the triplet state involved heterogeneous electron transfer at the electrode surface, which they have also invoked to explain some of their results⁴³ obtained for the ecl of rubrene in DMF.

However, the feasibility of such processes has been doubted by Chandross and Visco⁴⁴, and Marcus⁴⁵, who have concluded that, at potentials sufficient to form ${}^3R^*$ from R^+ or R^- at the electrode directly, ${}^3R^*$ would be quenched by electron exchange with the electrode itself.

The exact nature of ecl processes where there is insufficient energy from the reaction of R^+ and R^- to form ${}^1R^*$ has been the subject of considerable controversy, resulting in few irrefutable conclusions. The whole process seems further complicated by the formation of decomposition products in the systems studied, as a result of reactions between e.g. R^- and water, to produce RH^{-31} , followed by formation of

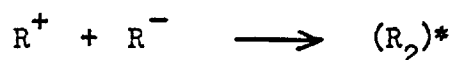
RH^+ and subsequent reaction with R^- to give ${}^1R^*$. Processes where light emission occurs at potentials less than those required for the formation of R^- or R^+ , due to the presence of impurities, have often been described as 'pre-annihilative'.

Some evidence for triplet-triplet annihilation as a contributor to ecl emission has come from the magnetic field studies of Faulkner and Bard³⁰. They observed that magnetic fields had a pronounced effect upon ecl emission intensity in cases where there was insufficient energy from the cation-anion annihilation to provide direct population of the singlet state, indicating that some paramagnetic species (e.g. a triplet species) was involved in a rate determining step leading to ecl emission. Where there was sufficient energy from the reaction of R^+ and R^- (e.g. DPA^+ and DPA^-) to lead to direct population of the singlet state, no effect was observed in the presence of the magnetic field, implying that triplet species were not involved in any rate determining step involved in this ecl emission.

Excimer Emission

The formation of excimer species $(R_2)^*$ in conventional solution fluorescence is a well established phenomenon⁴⁶, resulting in broad structureless emission from concentrated solutions of hydrocarbons such as pyrene, at a longer wavelength than the normal singlet emission spectra. It was originally reported by Chandross et al⁴⁷ that many

hydrocarbons showed ecl peaks at long wavelengths, which they attributed to excimer emission; in some cases such as anthracene, they reported ecl excimers where no corresponding solution fluorescence excimer had been observed under the same conditions. They suggested the formation of the excimer state via the reaction:-



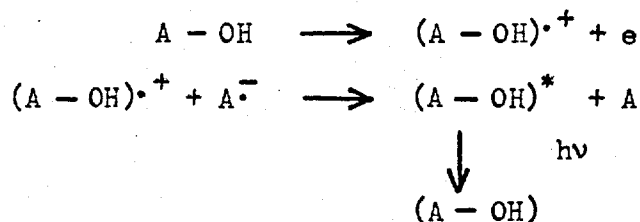
They ascribed the non-formation of ecl excimers in the case of molecules such as DPA and rubrene as being due to steric hindrance.

Parker and Short⁴⁸ have made an extensive study of the ecl emission from 9,10-dimethylantracene, which contains an excimer emission band first reported by Chandross et al⁴⁷. They measured the ratio of dimer to monomer emission intensities under various conditions, and compared it to that obtained in prompt and delayed fluorescence processes. They concluded that there were two types of process contributing to the ecl emission, one leading to the direct population of the excited monomer state, and the other to direct population of the excited dimer. They discounted triplet-triplet annihilation as a major contributor to ecl emission in this system, except at high temperatures, and where large applied potentials were used.

More recent publications have indicated that some of the long wavelength emission observed for various compounds may be due to

emission from cation decomposition products. Faulkner and Bard⁴⁹ concluded that the long wavelength band observed for anthracene was due to emission from anthronol, produced by the decomposition of the cation radical of anthracene, and probably excited by energy transfer.

A recent study by Werner, Chang and Hercules⁵⁰ has indicated that a number of other products, as well as 9-anthronol may be involved in the ecl of anthracene. Using a highly sensitive image-intensifier spectrograph, they have examined the single-pulse spectra of anthracene and dimethylantracene, and have concluded that emission from anthronol may arise from energy transfer, or by mixed annihilation reactions, i.e.:-



They also report less excimer emission in 9,10-dimethylantracene ecl spectra than was observed by Parker and Short⁴⁸.

In a thermodynamic treatment of ecl, Hoytink⁵¹ has shown that only a small proportion of cation-anion encounters will lead to the formation of excimers, due to the fact that, at the nearest distance of approach for R^+ and R^- (ca. 10 Å), the interaction between the excited and ground state molecules will be much smaller than kT at room temperature.

1.3 Instrumental Techniques used to study ecl

Electrodes

Much of the qualitative, and all of the quantitative work that has been reported in the literature, has used pairs of simple platinum or gold electrodes, connected to a step-down line transformer (50 or 60 Hz), or to a simple square wave generator. These are generally the same as, or are sophistications of, the electrode assemblies employed by Hercules¹³ and Visco and Chandross¹⁴.

The simplest electrode configuration, that of parallel platinum foils, has been used for both simple qualitative work¹³, and also, more quantitatively based, theoretical aspects of ecl⁴⁸. A platinum rod, surrounded by a platinum gauze cylinder has been used¹³, similar in principle to concentric helices, which have also been used¹⁴. Bard¹⁸ has used two wire helices sealed into the side of a standard taper joint for experiments where spectroscopic measurements have been made, and similarly, Zweig et al^{16,52,53} have used wire gauzes set apart from each other.

In controlled potential experiments, a platinum wire or mercury drop working electrode is often used, with an isolated counter and reference electrode (usually saturated aqueous calomel)¹⁸. Hercules³⁶ has used a similar cell arrangement, but with a tin oxide working electrode, constructed from Corning tin oxide glass. A recent publication⁴⁰ has used a platinum disc as the working electrode,

viewed by the photomultiplier through an annular hole in the counter electrode.

Some preliminary studies have been reported²⁹ using a concentric ring-disc electrode pair, connected to a dual channel potentiostat. Most of the more recent publications^{40,31,37} use operational amplifier potentiostats, in conjunction with pulse and signal generators, to provide the necessary signal at the electrode in qualitative experiments.

Light Measurements

Observations of the emitted light from the electrode have been made visually,¹³ and with a variety of spectroscopic devices. In some cases^{32,40}, the cell has simply been placed in a black box containing a photomultiplier tube. Zweig et al have used a spectral brightness meter⁵³, or a fast Raman spectrograph⁴¹ for many of their observations, although most workers have used a conventional spectrofluorimeter assembly, connected directly to an electronic amplifier and meter, (e.g. Aminco-Bowman photometer) or to an oscilloscope where high time resolution is required. One of the more novel recent methods⁵⁰ uses an image intensifier spectrograph, sufficiently sensitive that spectra at high resolution may be obtained from single light pulses.

1.4 Quantitative Aspects of ecl

A Russian group has examined the ecl emission from a number of biological anti-oxidants such as ascorbic acid and α -tocopherol, and has used the phenomenon to determine these compounds in methanol or acetone-chloroform solvent mixtures down to concentrations of 10^{-5} M^{54,55}.

Bobr et al⁵⁶ have measured the amounts of aromatic hydrocarbons such as anthracene and methylcholanthrene accumulating in the liver lipids of mice as a function of time after injection, using an ecl method.

The effect of solute concentration on the ecl emission of several substituted isobenzofurans has been observed¹⁷, using simple platinum electrodes, with the emitted light monitored directly, without the use of a monochromator. The curve that was obtained for the compound 1,3,4,7-tetraphenylisobenzofuran between 1 and 5.5 mM was linear, although the precision was not good. The compound 1,3-di-p-anisyl-4,7-diphenylisobenzofuran gave a relationship exhibiting marked concentration quenching.

Cruser and Bard⁵⁷ have examined the ecl intensity of diphenylanthracene in DMF as a function of concentration over the range 0.3 to 1.0 mM, using a cell consisting of two parallel platinum spirals connected to a step-down line voltage transformer, placed in the cell compartment of an Aminco-Bowman spectrofluorimeter. The cell voltage

that was used was in the order of 100 V. At this voltage, the emission rapidly reached a peak, and then decayed exponentially with time. The peak intensity showed a linear relationship to concentration. This work was later extended²⁴ to the compounds rubrene, anthracene and 1,3,6,8-tetraphenylpyrene in addition to DPA, and linear relationships between 0.001 and 0.50 mM, 0.67 and 10.70 mM, and 0.026 and 0.157 mM respectively obtained for the compounds, using the cell and detector assembly employed before. With the exception of anthracene, the precision of the results was quite good. The authors report that no self-quenching was observed at all, even for anthracene above 1 mM, as opposed to the normal solution fluorescence behaviour observed for this compound.

CHAPTER II

Experimental Section

2.1 Preliminary Experiments

In order to qualitatively examine the eel characteristics of a large number of compounds, a simple electrode assembly was employed. This consisted of two 1 cm^2 platinum foils 5 mm apart, placed in a 2 cm diameter cylindrical cell. The compound to be examined was dissolved in DMF to produce a 10^{-3} M solution, and then sufficient 1 M tetrabutylammonium perchlorate or bromide was added to make the solution 10^{-2} M with respect to the supporting electrolyte. After degassing with nitrogen, visual observation was made of the electrodes when a variable low-voltage (0 - 30 V) was applied from a step-down mains transformer. Solvents other than DMF were examined, but with the exception of acetonitrile and methylene chloride, none of those investigated was found to be as effective as DMF with respect to the intensity and stability of the emission produced. Acetonitrile was satisfactory in very dilute solution, but 10^{-3} M solutions of hydrocarbons in this solvent discoloured rapidly when a current was passed, and the emission decayed rapidly. Methylene chloride was useful for some hydrocarbons at high concentrations, and gave a more stable emission than DMF (hydrocarbon cation radicals are reported to be

fairly stable in this solvent⁵⁸). However, ecl emission from methylene chloride solutions appeared to be rather weak compared to DMF at lower concentration levels than 10^{-3} M.

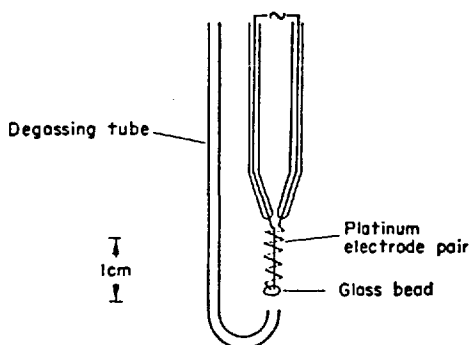
In the majority of cases, the light emission was most intense when the solution was stirred continuously, appearing as a brief, bright pulse over the whole area of the electrode, which rapidly dimmed to a fairly steady emission from the edges.

Most aromatic hydrocarbons gave visible light emission, even those not normally fluorescent, e.g. triptycene. However, the emission was often weak and transient, the generation of which required large applied potentials. Because of the low intensity of the emitted radiation, a cell and detector assembly was constructed which permitted efficient collection of the emitted radiation by a sensitive photomultiplier tube (EMI 9601 B) connected to a microammeter (RCA type WV-84C).

The electrode assembly (Fig. 2.1B) consisted of two fine platinum grids wound one over the other on a machined teflon support. When a potential was applied to the electrode connections, ecl appeared as a bright flickering effect in the region immediately next to the platinum wires.

Using this arrangement, a great many compounds were examined. In addition to the hydrocarbons found to show ecl visually with the earlier experimental arrangement, other classes of compounds were also

(a) Spiral type:



(b) Grid type

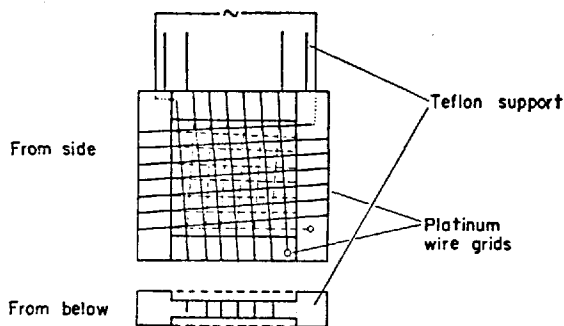
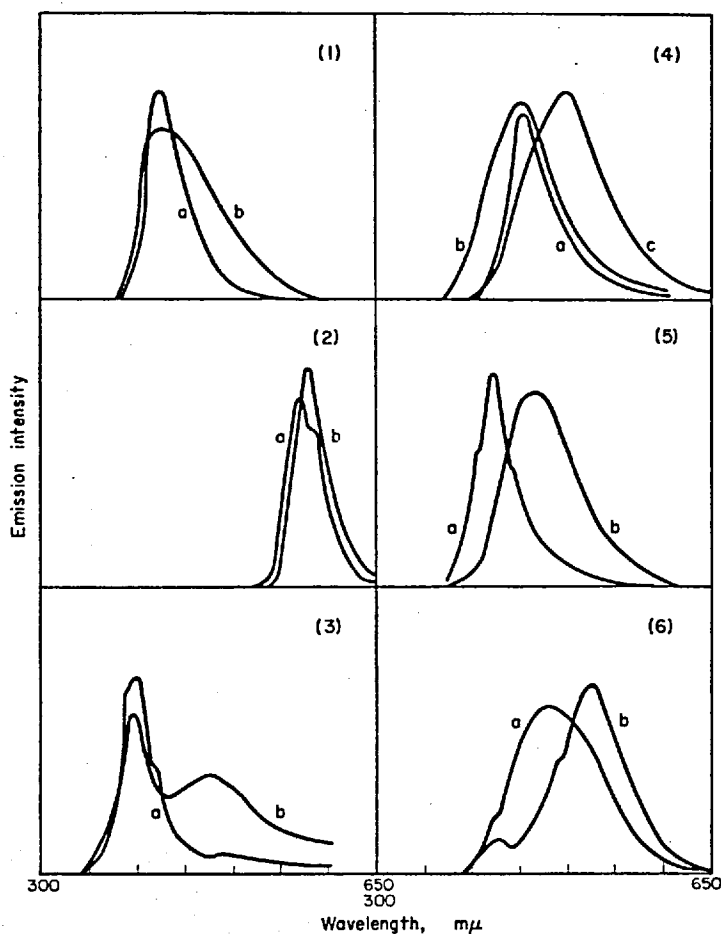


Fig. 2.1

found to exhibit the phenomenon. Some heterocycles, azo dyes, alkaloids, and metal complexes gave light emission, although in the case of metal complexes (e.g. aluminium oxinate) it was very weak indeed. Some compounds such as $\text{Cr}(\text{acac})_3$ depressed the weak background emission that was usually obtained for the solvent-electrolyte alone if a large enough signal was applied. Compounds containing free $-\text{OH}$, $-\text{NH}_2$ and



Electroluminescence and fluorescence spectra obtained.

- (1) 9-Phenylanthracene, $10^{-3}M$ in DMF. *a*—Fluorescence emission spectrum (excitation at $320\text{ m}\mu$); *b*—electroluminescence (E.L.) emission spectrum, tetrabutylammonium perchlorate electrolyte ($10^{-2}M$), 3 V a.c., continuous stirring.
- (2) Rubrene, $5 \times 10^{-3}M$ in DMF. *a*—E.L. emission spectrum, tetrabutylammonium perchlorate ($10^{-2}M$), 3 V a.c., continuous stirring; *b*—fluorescence emission spectrum (excitation at $430\text{ m}\mu$).
- (3) Pyrene, $10^{-3}M$ in DMF. *a*—Fluorescence emission spectrum (excitation at $355\text{ m}\mu$); *b*—E.L. emission spectrum, tetrabutylammonium bromide electrolyte, 6 V a.c., continuous stirring.
- (4) Coronene, $10^{-3}M$ in DMF. *a*—Fluorescence emission spectrum (excitation at $365\text{ m}\mu$); *b*—E.L. emission spectrum, tetrabutylammonium perchlorate electrolyte, 3 V a.c., continuous stirring; *c*—as *b* but without stirring.
- (5) Anthracene, $10^{-3}M$ in DMF. *a*—Fluorescence emission spectrum (excitation at $365\text{ m}\mu$); *b*—E.L. emission spectrum, tetrabutylammonium perchlorate, 3 V a.c., continuous stirring.
- (6) Anthracene, $10^{-3}M$ in DMF. *a*—E.L. emission spectrum in tetramethylammonium chloride electrolyte, 3 V a.c., continuous stirring; *b*—E.L. emission spectrum, lithium chloride electrolyte ($10^{-2}M$), 3 V a.c., continuous stirring.

Fig. 2.2

similar substituent groups showed almost negligible ecl, although if methylation using methyl sulphate was carried out, the ecl was much stronger. Some substituent groups such as $-\text{COOH}$ and $-\text{SO}_3\text{H}$ also depressed the ecl, but to a lesser extent. The presence of alkyl and aryl groups generally had a similar effect to that observed in solution fluorescence, e.g. the ecl intensity of anthracene, 9-phenylanthracene, 9,10-diphenylanthracene showed a steady increase in the order given.

To study the emission spectra obtained by ecl, and to compare them to solution fluorescence spectra, an Aminco-Bowman spectrofluorimeter was used. A simple electrode assembly (Fig. 2.1a) was arranged on a vertical rail so that it could be lowered reproducibly into the centre of a 1 cm^2 spectrofluorimeter cell in the cell compartment of the instrument. The electrode pair consisted of a 10 mm length of platinum wire (0.004" diameter), surrounded by a coaxial helix 4 mm in diameter, constructed from the same material. Ecl emission spectra were measured by scanning the emission monochromator soon after applying the a.c. voltage to the electrode pair. Fluorescence spectra were measured in the normal way, either before or after electrolysis, after the electrodes had been raised from the focal point of the cell. Generally, the widest slits were used in the emission monochromator, which gave a spectral half-intensity bandpass of 20 nm.

Fig. 2.2 shows the ecl and fluorescence spectra obtained under the stated conditions for a number of compounds. As can be seen, the ecl and fluorescence emission spectra are not the same in most cases,

and, with anthracene, the ecl spectrum varied greatly by alteration of parameters such as the electrolyte, stirring etc.

In order to study the phenomenon for its possible analytical utility, a far more sensitive and selective arrangement was obviously necessary. To generate light most efficiently around an electrode, a potentiostat used in conjunction with a square wave source was required. This would give some possibility of selectivity in generating ecl from a mixture of compounds.

In addition, a conventional prism or grating monochromator would involve too great a light loss, thus a simple variable wavelength interference filter system seemed to be the best alternative. Although the spectral bandpass of such systems may be larger than that of conventional monochromators, the effective aperture and transmission are very much higher.

2.2 Final Experimental Assembly

A block diagram of the apparatus which was employed is shown in Fig. 2.3. A signal from a function generator was applied to the working electrode of the cell by means of an operational amplifier potentiostat. The light emitted in the vicinity of the electrode was viewed by a photomultiplier tube after passage through a variable wavelength metal dielectric interference filter. The photosignal was displayed either on the oscilloscope, or on a potentiometric recorder. The current passing through the cell was shown on the oscilloscope as a conventional cyclic voltammogram.

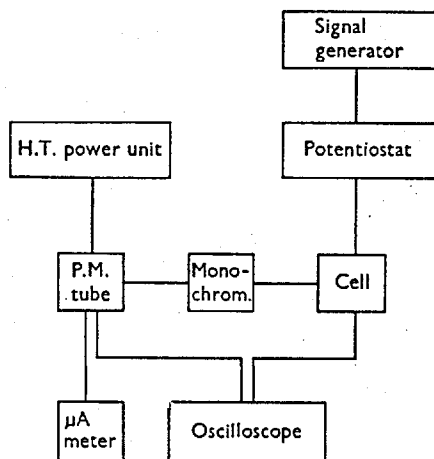
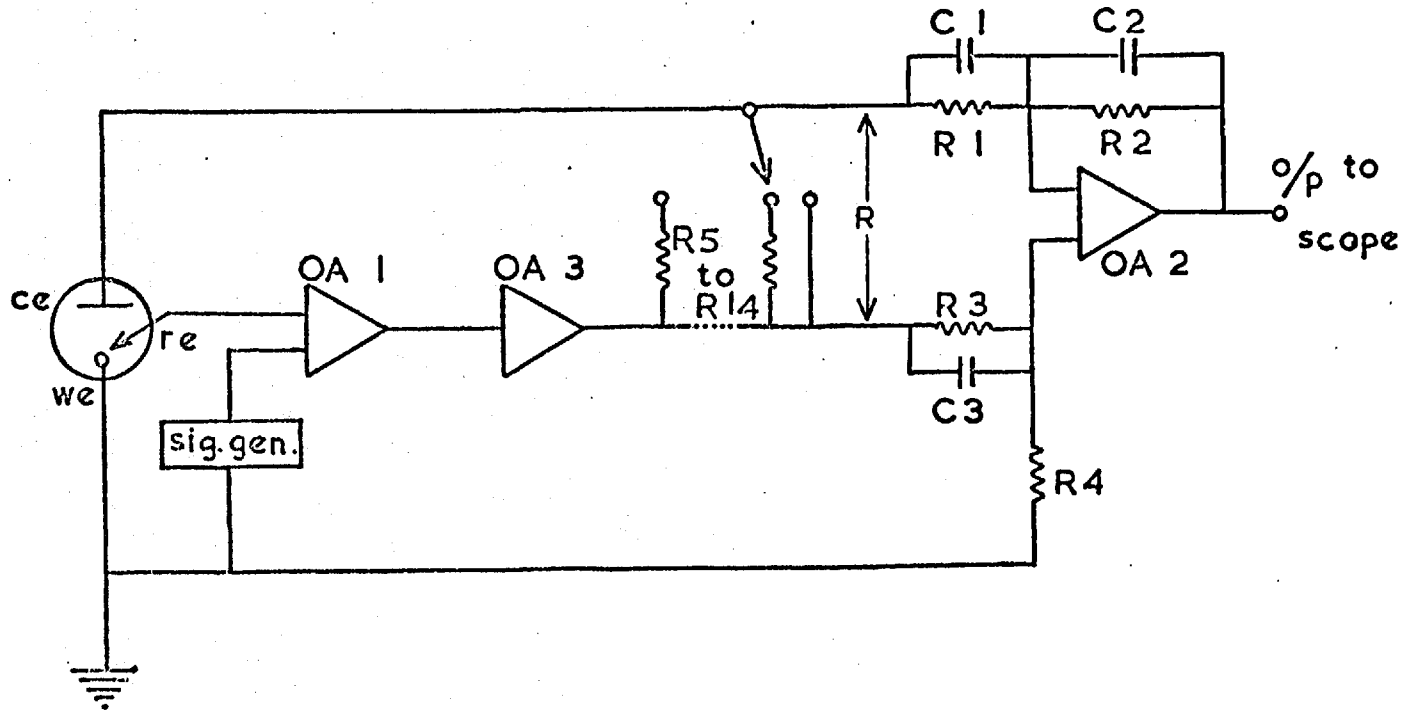


Fig. 2.3

The signal generator was a Hewlett-Packard 3300 A function generator, with a 3302 A trigger/phase lock plug-in. This provided a sine, triangular or square wave signal between 0.01 and 100,000 Hz, with two outputs at the same frequency, but not necessarily with the same waveform. With the plug-in in operation, single sweeps could be obtained, or the electrode held at one voltage for a length of time, and then pulsed at any desired frequency or waveform to another voltage.

The amplitude of the outputs was variable from 300 mV to 25 V peak to peak. In order to vary the position of the centre of the voltage sweep, a variable d.c. voltage level between + 2.5 V and -2.5 V was applied between the circuit ground and the output ground of the signal generator. This d.c. level was provided by connecting a 1 k Ω multi-turn potentiometer ("Helipot", Beckmann Instruments Ltd.) in series with two 2.5 k Ω metal oxide resistors ('Hystabs', R.S.), and this was used to drop the potential of the \pm 15.0 volt outputs of the low voltage power supply employed with the operational amplifiers, to the desired level.

The potentiostat circuit (Fig. 2.4) was based on a single operational amplifier, using the configuration described by Schwarz and Shain in Fig. 4b. ⁵⁹ Low cost, epoxy encapsulated operational amplifiers were used for OA1 and OA3 (Philbrick PF85AU). These had built-in overload protection on the output and input, and were found to be satisfactory in use. OA2 was a booster amplifier (Philbrick P66A)



OA 1, OA 3 = PF 85AU
 OA 2 = P 66A
 C1, C2, C3 = 47 pf.
 R1, R2, R3, R4 = 470k Ω

R5 to R14 = 0,50,100, 500, 1k, 5k, 10k ,
 50k, 100k, 500k Ω .

Fig. 2.4

to increase the maximum output current of OA1 from 2.2 mA to 100 mA. OA3 was used to measure the voltage developed across the switched resistance value R as a result of the passage of the cell current between the counter electrode and working electrode. Values of R between 50 and 500,000 ohms were used, with one switch position corresponding to a direct short. This gave satisfactory voltage levels for display on the oscilloscope with cell currents in the range 1 μ A to 100 mA.

The low voltage power supply used was supplied by Coutant Ltd., and was arranged to give +15, 0, -15 d.c. voltage levels. These were adjusted initially, using a digital voltmeter (Hewlett-Packard 3439 A), to the desired values.

When in use, the potentiostat showed no observable distortion or 'ringing', even when fairly considerable currents were being drawn from it. With a 5 kHz square wave between + 2.0 V and -2.0 V applied to a 10^{-3} M solution of diphenylanthracene and 10^{-1} M tetrabutylammonium perchlorate, the observed rise time was 8 μ sec.

No noticeable increase in performance was observed when a voltage follower was inserted between the reference electrode and the negative input of OA.1.

The electrode assembly which was employed is shown in Fig. 2.5. The sample cell was a fused silica spectrophotometer cell (10 x 10 x 40 mm), with a machined teflon stopper, through which the three

electrodes and the nitrogen inlet and outlet tubes were inserted.

The normal sample volume was 2.0 ml.

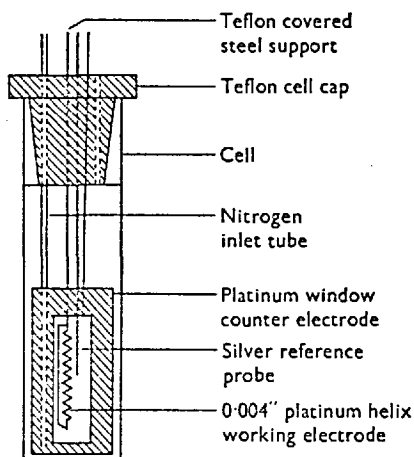


Fig. 2.5

The working electrode was a helix of 0.004 inches diameter platinum wire, with ten 1.5 mm diameter turns, 1mm apart. This was supported on a teflon-coated, stainless steel bracket, which provided the connection to the potentiostat.

The counter electrode was a sheet of platinum (0.9 x 2.0 cm) with an aperture (0.3 x 1.2 cm) through which the light reaching the photomultiplier tube passed. The counter electrode was bent around the working electrode slightly, to provide more uniform current density,

and hence light output, from the working electrode. Visual tests in a darkened room using concentrated hydrocarbon solutions showed that no light from the counter electrode reached the photomultiplier tube. A length of 1/16 inch platinum rod was spot-welded to the top of the counter electrode, and acted as a support and connection to the potentiostat.

The reference probe was a length of silver wire, projecting into the solution just behind the working electrode. The gas inlet tube was drawn out to a fine jet, and placed just behind, and to one side of, the working electrode. When nitrogen was being passed through the solution, very rapid and efficient stirring took place in the region of the working electrode.

The cell assembly described was essentially a compromise between one of maximum suitability for practical analytical measurements and that required to permit a theoretical interpretation of the processes involved. From a practical analytical viewpoint, the requirements include a large area working electrode to produce maximum light emission, and the absence of external fluid connections which would make the optical sealing of the cell difficult, and ease of sample changing without contamination. From a fundamental theoretical viewpoint, a very small area working electrode, a counter electrode isolated by a salt bridge to prevent the electrode products from reaching the working electrode, and an aqueous calomel electrode, isolated from the solution by a salt bridge, are all desirable features.

In practice, the compromise seemed to work reasonably well. Cyclic voltammograms were obtained which showed a well-defined wave shape, identical to that obtained using a working electrode of smaller area.

The silver wire has been reported¹⁸ to act as a pseudo-reference electrode in these solvent-electrolyte conditions and to maintain a potential relative to an aqueous saturated calomel electrode that can be measured at the end of an experiment. Measurement of the potential between the silver wire and an aqueous S.C.E. in 10^{-1} M TBAP using a high resistance digital voltmeter (Hewlett-Packard 3439 A, $10\text{ M}\Omega$ input impedance) established the correction curve shown in Fig. 2.6. This was reproducible except when water, oxygen or some other impurity was present, which caused slight curvature of the graph beyond -0.5 V on the x-axis.

It was difficult to assess the effects caused by non-isolation of the counter electrode: moving the counter and working electrodes much further apart caused little effect, however, except at very low sweep rates in stirred solution.

The oscilloscope which was used throughout was a Hewlett-Packard 175 A, with 1752 A and 1780 A plug-ins. This had a vertical sensitivity of 0.005 V/cm , and a horizontal sensitivity, when an external signal source was used, of 0.1 V/cm . When current/voltage, and light intensity/voltage curves were displayed, the horizontal amplifier was connected

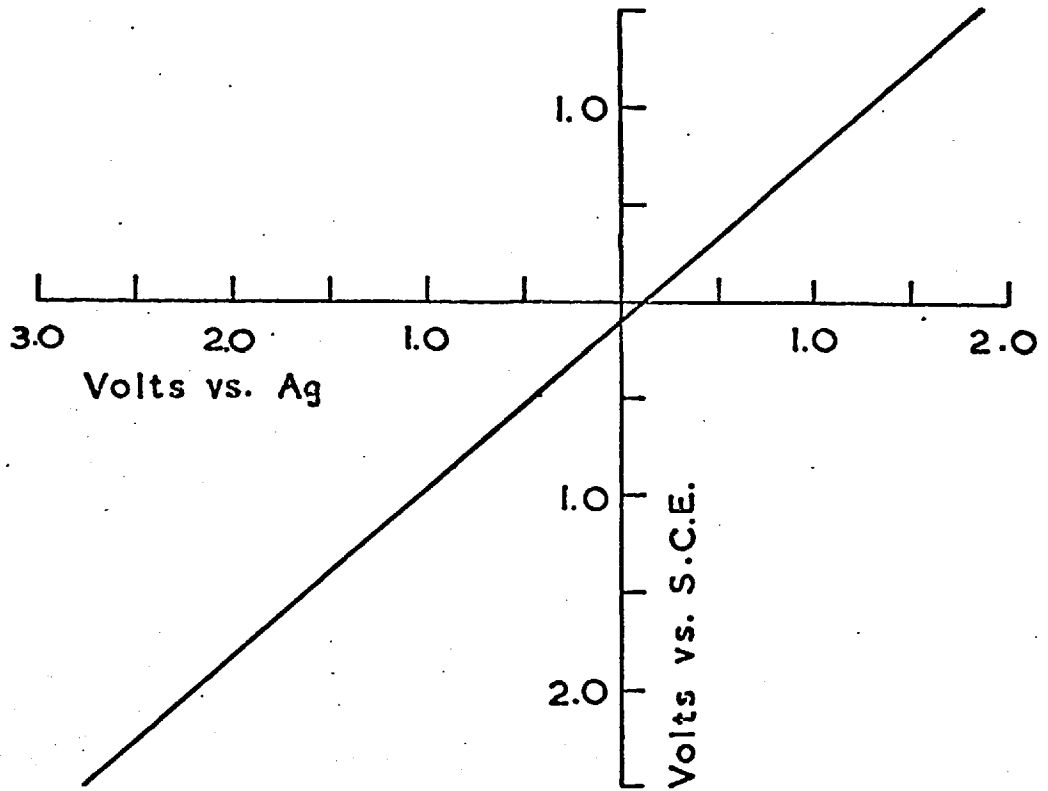


Fig. 2.6

directly to one output channel of the signal generator, switched to a triangular waveform.

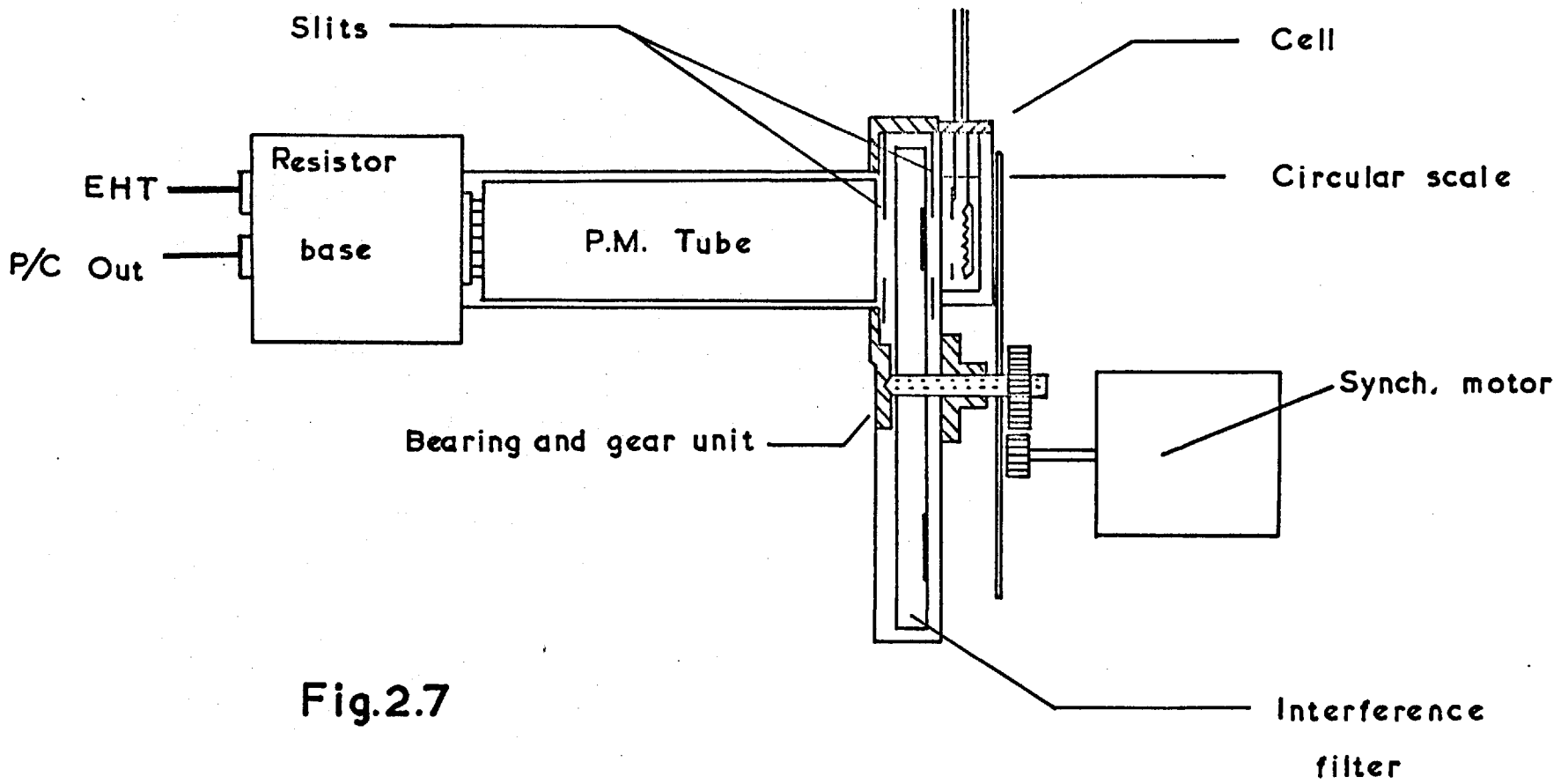


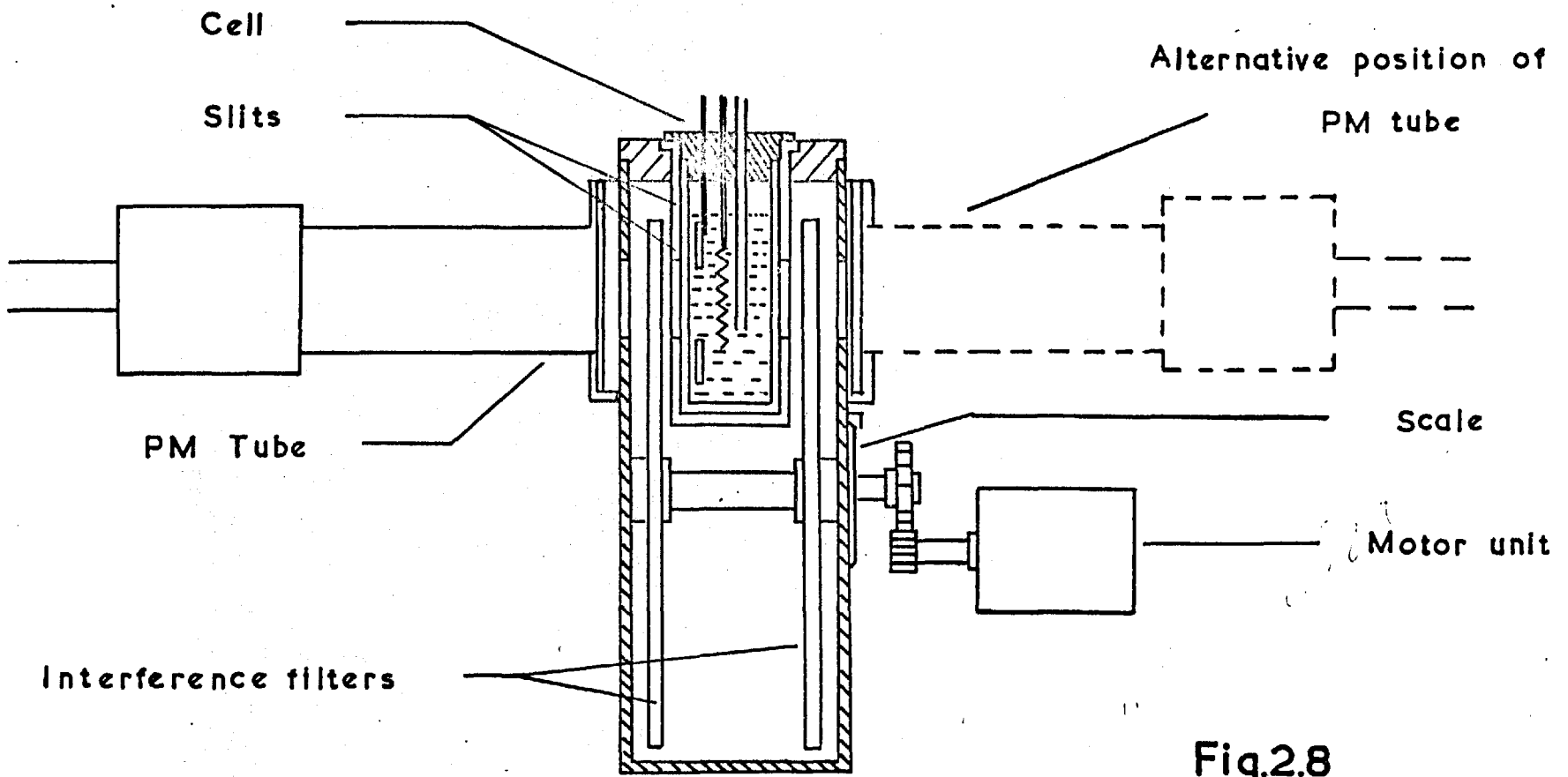
Fig.2.7

The 1780 A single-sweep plug-in was used where a photograph of a single sweep was desired. Photographs were obtained on a fast 35 mm film (Ilford HP3), using a single-lens reflex camera (Practica VF) fitted with close-up extension rings.

The potentiometric recorder which was used (Smiths RE.511) had an input sensitivity of 0.1 mV/cm. When it was connected directly to the output from the photomultiplier tube, a 15 k ohm resistor and an 8 μ F capacitor were connected across the inputs.

Monochromator Assembly

This is shown in Fig. 2.7. The cell faced directly towards the end window photomultiplier tube (EMI 9601 B) and was as close to it as possible (2 cm). Light emitted from the working electrode passed through the window in the counter electrode, then a 1.5 mm slit, and finally through the variable wavelength interference filter (Barr and Stroud Ltd.) and a 1.5 mm slit, to reach the photomultiplier. The circular interference filter was mounted on a lubricated shaft which could be rotated at several preselected speeds by the synchronous motor. The wavelength at which the filter was set was read off from a circular scale attached to the bearing shaft, that had been calibrated using a chart supplied by the manufacturer. This was checked by using light from spectral discharge lamps (Na, Cd and Hg) reflected down a glass rod placed in the position normally occupied by the working electrode.



The filter which was used covered the spectral range 400 - 700 nm, with an average transmission of 40%, and a half-intensity bandpass of ca. 20 nm at the slit width chosen.

In order to examine the spectral region below 400 nm, a filter covering the range 320 - 420 nm (Barr and Stroud Ltd.) was also obtained. This was mounted on the same bearing shaft as before, but on the other side of the cell, as in Fig. 2.8. To record this portion of the emission spectrum between 320 and 420 nm, the cell was reversed and the photomultiplier placed in the alternative position shown, so that emitted light passed through the short wavelength filter before reaching it. The transmission characteristics of this filter were very irregular, however, so that even using the transmission curve supplied by the manufacturer, it was not found possible to obtain a meaningful spectrum in this range. However, had a filter been available which showed a less erratic transmission, it should have been possible to measure the emission between 320 - 420 nm, to extend the spectra below 400 nm.

When the high speed of rotation of the metal dielectric interference filter was used, the signal was displayed on the oscilloscope. Triggering of the time base was achieved by making a slit at the 400 nm end of the filter, which passed light of all wavelengths, and hence gave a high-voltage pulse.

2.3 Purification

Nitrogen

White-spot nitrogen (British Oxygen) was purified by passage through a 2% solution of the sodium salt of anthraquinone-2-sulphonic acid in 2 N sodium hydroxide solution, to which granulated zinc had been added. After this treatment to remove oxygen, the gas was then dried by passage first through concentrated sulphuric acid and then through magnesium perchlorate, and finally passed through the solvent (usually dimethylformamide) in order to produce a gas stream saturated with vapour, and thus prevent evaporation within the sample cell.

Solvents

Dimethylformamide (British Drug Houses Ltd. Laboratory Reagent grade) was dried overnight over anhydrous potassium carbonate, and then over a molecular sieve (Lind 5 A). The dried solvent was then distilled at 32°C and 1.5 mm pressure, using a vacuum still with automatic reflux ratio adjustment, set at 25:1. A 20 inch vertical reflux column packed with 1/8" glass beads was used. The still was supplied by Baird and Tatlock Ltd.

The first and the last 25% of the distillate were rejected, and the remaining 50% stored in teflon-sealed brown glass bottles for use. Gas chromatographic analysis showed a water level in the material so obtained of 4.5 µg/ml. The solvent as obtained from the manufacturer

typically contained 240 $\mu\text{g}/\text{ml}$.

Methylene chloride (BDH Ltd.) was dried over sodium wire, and then distilled under reduced pressure.

Other solvents (e.g. acetonitrile, benzonitrile and dimethylsulphoxide) were manufacturers' laboratory grade reagents dried by contact with molecular sieves.

Preparation and Purification of Supporting Electrolytes

Tetrabutylammonium perchlorate was prepared by addition of a slight excess of anhydrous perchloric acid (Hopkin and Williams, ANALAR), diluted with three times its volume of distilled water to a tetrabutylammonium hydroxide solution (BDH Laboratory Reagent grade 40%) with an equal volume of water added. The suspension of the precipitated salt was stirred for 30 minutes, and then filtered off under suction and washed with distilled water. After two recrystallisations from a 2:1 ethanol-water mixture, the salt was dried in a vacuum oven at 96°C for 24 hours.

Lithium chloride and lithium perchlorate (K and K) were dried and used directly. Tetrabutylammonium bromide, chloride and iodide (K and K) were recrystallised from ethanol and dried before use.

Other electrolyte materials were used as supplied, if of Analar grade, or recrystallised before use.

Purification of Aromatic Hydrocarbons etc.

Compounds that were obtained directly from the manufacturer were purified before use by either, (i) recrystallisation (ii) vacuum sublimation or (iii) preparative scale gas chromatography, (using the Perkin-Elmer F21 with a $\frac{1}{4}$ " x 5' 10% S.E. 52 on celite column), or a combination of several methods. It was generally found best to use gas chromatography for reasonably volatile materials, e.g. fluorene, whereas less volatile hydrocarbons such as 9,10-diphenylanthracene were best purified by vacuum sublimation.

A series of aromatic hydrocarbons were obtained directly from B.A.T. and T.R.C. These were already gas chromatographically pure, and were used as supplied.

The purification of the aromatic compound was frequently very critical. Many compounds showed ecl emission if the manufacturers' material was used directly, but subsequent purification produced samples that showed no ecl at all, or ecl at entirely different wavelengths. For example, 9-bromoanthracene (Koch-Light) showed moderate ecl emission at 435 nm if used directly; however, this emission had disappeared almost completely after several vacuum sublimation procedures. Materials where a marked change in ecl characteristics was noticed after purification included triphenylene, carbazole and fluorene.

To avoid confusion, the commonly used and accepted nomenclature for the compounds examined has been used throughout. Where the IUPAC letter designation is used, this is placed first to clarify tabulation.

Preparation of Solutions

Solutions were prepared just before use from deoxygenated solvent and fresh concentrated stock solutions of the electrolyte and aromatic hydrocarbons. Solutions of concentration less than 5×10^{-5} M were prepared in situ, using concentrated stock solutions and a 10 μ l or 50 μ l syringe (Hamilton).

In order to deoxygenate the solution before use, it was either placed in the cell and purified nitrogen bubbled rapidly for five minutes, or a vacuum freezing technique was used. The solution was placed in a 5 ml test tube (Quickfit), connected to a vacuum line, and frozen in liquid nitrogen. While the solution was warming up, the vacuum pump was connected. This procedure was repeated four times, and the solution then rapidly transferred to the sample cell, and nitrogen passed in the normal way.

CHAPTER III

Qualitative Observations of the ecl of some aromatic hydrocarbons and related compounds

Compounds that had been shown to give ecl emission by the initial screening procedure were examined further using the potentiostat-interference filter assembly. 10^{-3} M solutions of the compound in a solution of 10^{-1} M tetrabutylammonium perchlorate in DMF were prepared as described. Two ml aliquots of these were placed in the sample cell. The optimum excitation conditions for each compound were then established, with respect to the parameters of voltage, frequency, signal waveform and stirring.

For the great majority of aromatic hydrocarbons, the voltage limits that gave the most intense and stable emission corresponded to just greater than the voltages necessary to generate the radical anion and cation of the compound. The use of larger amplitude signals to generate the emission frequently gave a brief, bright pulse of light, which rapidly decayed to a low light level, accompanied by the appearance of light emission with peaks at wavelengths longer than those observed initially.

Where oxidation and reduction peaks were observed which were well defined, the peak potentials of these (converted to values vs. the S.C.E. using the correction curve Fig. 2.6) are reported. Usually, the maximum emission intensity was obtained when a square waveform

Table 3.1

<u>Compound.</u>	<u>Applied Potential.</u> (V vs Ag)	<u>Ecl Maxima.</u> (nm)	<u>Oxidn. Peaks.</u>	<u>Redn. Peaks.</u> (V vs S.C.E.)
Pyrene.	+1.5 to -2.5	<u>400, 470.	+1.08	-2.30
" , 1,2-benz	+1.5 " -2.2	<u>410</u> , 530.	+1.23	-2.01
" , 3,4-benz	+1.3 " -2.2	<u>495</u> , 560.	+0.95	-2.00
				-2.42
" , (a1)dibenz	+1.5 " -2.0	470, <u>500</u> ,	+1.18	-1.80
		550.		-2.10
" , (b1)dibenz	+1.5 " -2.5	423, 502,	+1.12	-2.24
		<u>535</u> , 570.		-2.61
" , (ah)dibenz	+1.4 " -1.6	470, <u>570</u> .	+1.06	-1.48
" , (ai)dibenz	+1.3 " -2.0	438, <u>461</u> .	+0.98	-1.80
			+1.21	-2.04

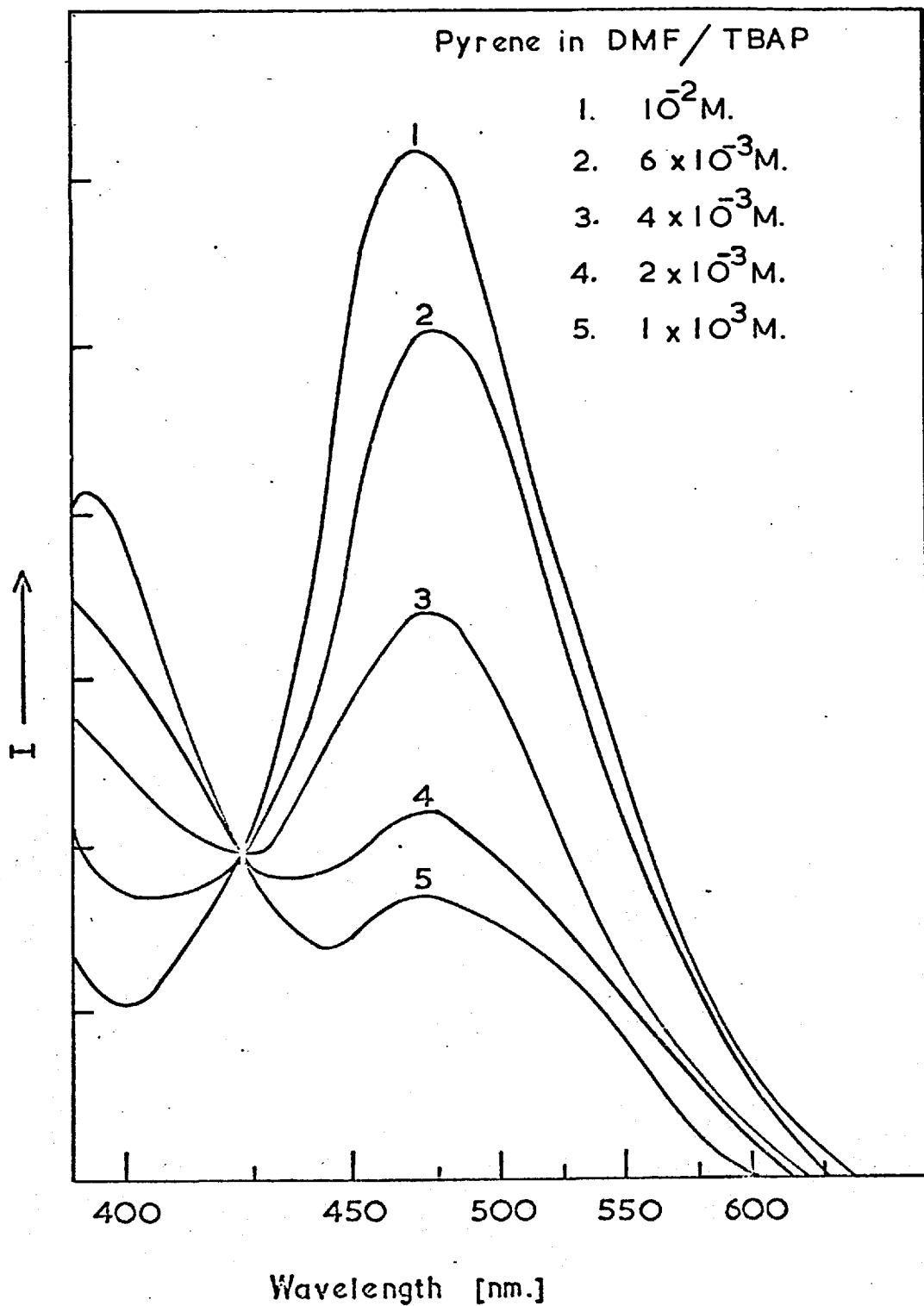
signal was used with a stirred solution. With the majority of aromatic hydrocarbons, the emission intensity was found to reach a maximum at about 30 Hz, and to remain constant until about 100 Hz, when it gradually declined, disappearing finally at about 3 kHz. In these cases, a 74 Hz signal was used, as this produced a steady signal of maximum intensity, which did not 'beat' with the d.c. to a.c. chopper in the amplifier of the potentiometric recorder.

3.1 Pyrene and Related Compounds

Table 3.1 lists the ecl spectral and electrochemical characteristics for the series of benz- and dibenz- substituted pyrenes studied. With the exception of (al)-dibenzpyrene (150 Hz), (bl)-dibenzpyrene (480 Hz) and (ah)-dibenzpyrene (30 Hz), the signal applied to the working electrode was a 74 Hz square wave signal.

Pyrene was found to show fairly intense ecl, with a principal maximum that occurred below 400 nm, i.e. beyond the range of the interference filter. The lifetime of the emission was rather short, and the emission spectra were obtained within two minutes of the potential being applied. If TBAB electrolyte was used instead of TBAP, the emission was more intense initially, but was rapidly replaced by a peak at 528 nm, accompanied by the appearance of a yellowish colouration of the solution, and a yellow fluorescence. The shape of the ecl spectrum changed markedly with concentration; Fig. 3.1

Fig. 3.1

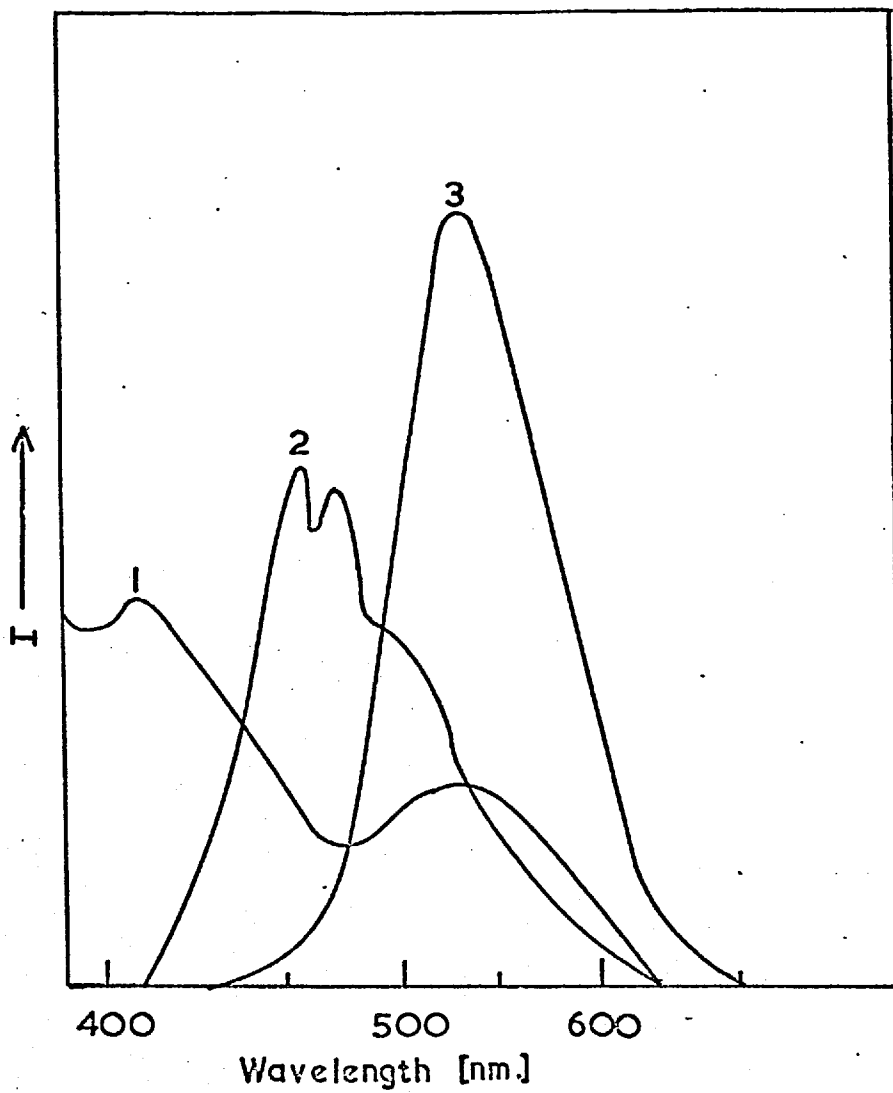


shows the ecl spectra obtained for pyrene solutions between 1×10^{-2} M and 1×10^{-3} M, measured at the optimum potential limits, and in stirred solution. The spectra were reproducible, and did not change significantly in the time taken for their measurement.

The ecl emission from 1,2-benzpyrene measured at the optimum potential conditions showed peaks at 410 and 530 nm. The latter peak, although present initially, increased slowly with time, and eventually predominated. Slight changes in the applied potential caused the emission spectrum to alter considerably. Fig. 3.2 shows the ecl spectra obtained for 10^{-3} M and 10^{-2} M solutions, at the potential limits indicated.

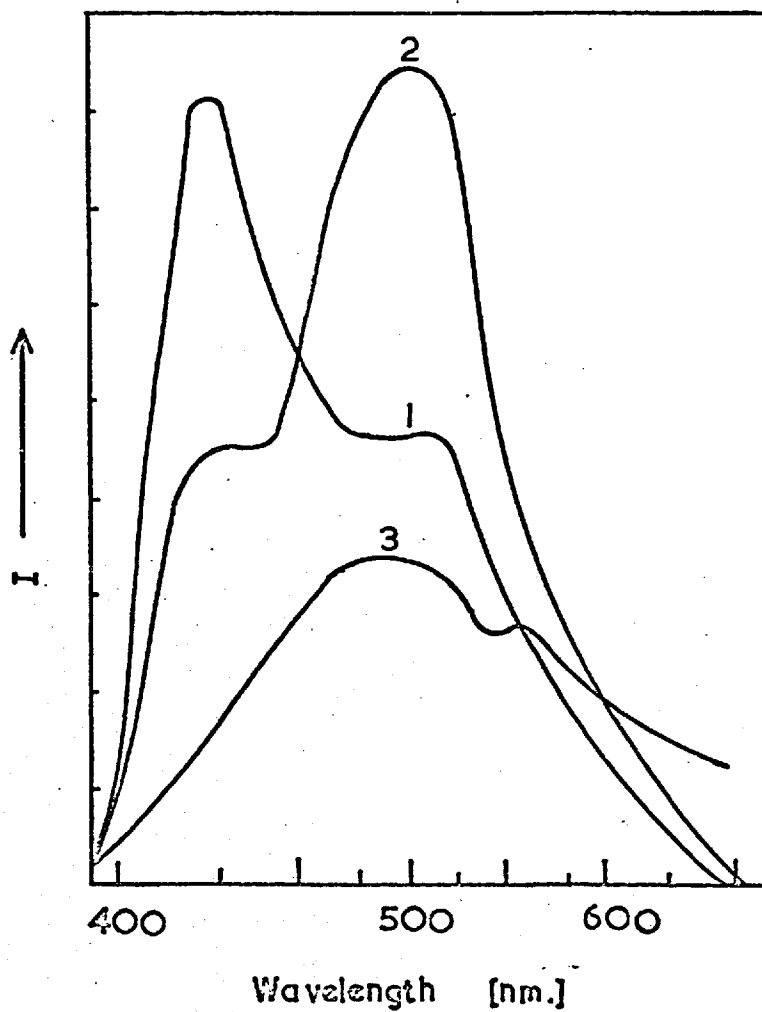
Excitation of ecl from a 10^{-3} M solution of 3,4-benzpyrene in the presence of 10^{-1} M TBAP produced a rather diffuse emission peak (max. 495 nm) that was reproducible only with difficulty (Fig. 3.3). However, the use of 10^{-1} M TBAB as electrolyte gave a much more stable and intense emission; this exhibited a shift in the spectral maximum with concentration (Fig. 3.3, 1 and 2) comparable to that obtained for pyrene. The potential limits that were used with TBAB (+ 1.8 \rightarrow -2.2 V vs. Ag) corresponded to the formation of the pyrene anion and bromine.

Fig. 3.4 shows the ecl emission spectra obtained for (ai), (al), (bl) and (ah) dibenzpyrenes, measured under the optimum conditions stated. The emission from (al)-dibenzpyrene was intense and stable, and showed no changes in spectral distribution with time, unlike that from



1. 10^{-3} M. +1.5 to -2.2V vs Ag.
2. " +0.7 to -2.0V "
3. 10^{-2} M. +0.7 to -2.0V "

Fig. 3.2



1. 10^{-3} M, TBAB. 3,4-benzpyrene.
2. 10^{-2} M, TBAB. "
3. 10^{-3} M, TBAP. "

Fig. 3.3

(bl)-dibenzpyrene which was rather weak, and decayed rapidly. 10^{-4} M solutions of the latter compound showed only extremely weak ecl with a principal maximum at 420 nm. The use of 10^{-1} M TBAB as electrolyte almost totally quenched the emission.

(ah) and (ai)-dibenzpyrenes both gave a stable and intense emission, like that of (al)-dibenzpyrene, with no long-wavelength peaks appearing during the course of the electrolysis. The spectra of all four compounds were unusually structured for ecl spectra. Experiments with more concentrated solutions were not possible because of the very limited amount of each compound that was available.

A comparison between the ecl spectral data obtained, and that reported^{60,61} for the solution fluorescence of the same compounds, is given in Table 3.2, which lists the ecl and fluorescence maxima, with the principal maximum underlined in each case: ecl peaks marked (*) are peaks which do not appear in the reported fluorescence spectra. The emission spectra are basically similar (within experimental limits) in most cases, but are modified by several factors.

- (1) Absorption of short-wavelength light is more pronounced in ecl, causing the principal ecl maximum to correspond to a fluorescence peak of longer wavelength than that which is the principal fluorescence peak. For example, (al)-dibenzpyrene has an intense fluorescence maximum at 470 nm, but self absorption has caused this to be a minor peak in the ecl spectrum.

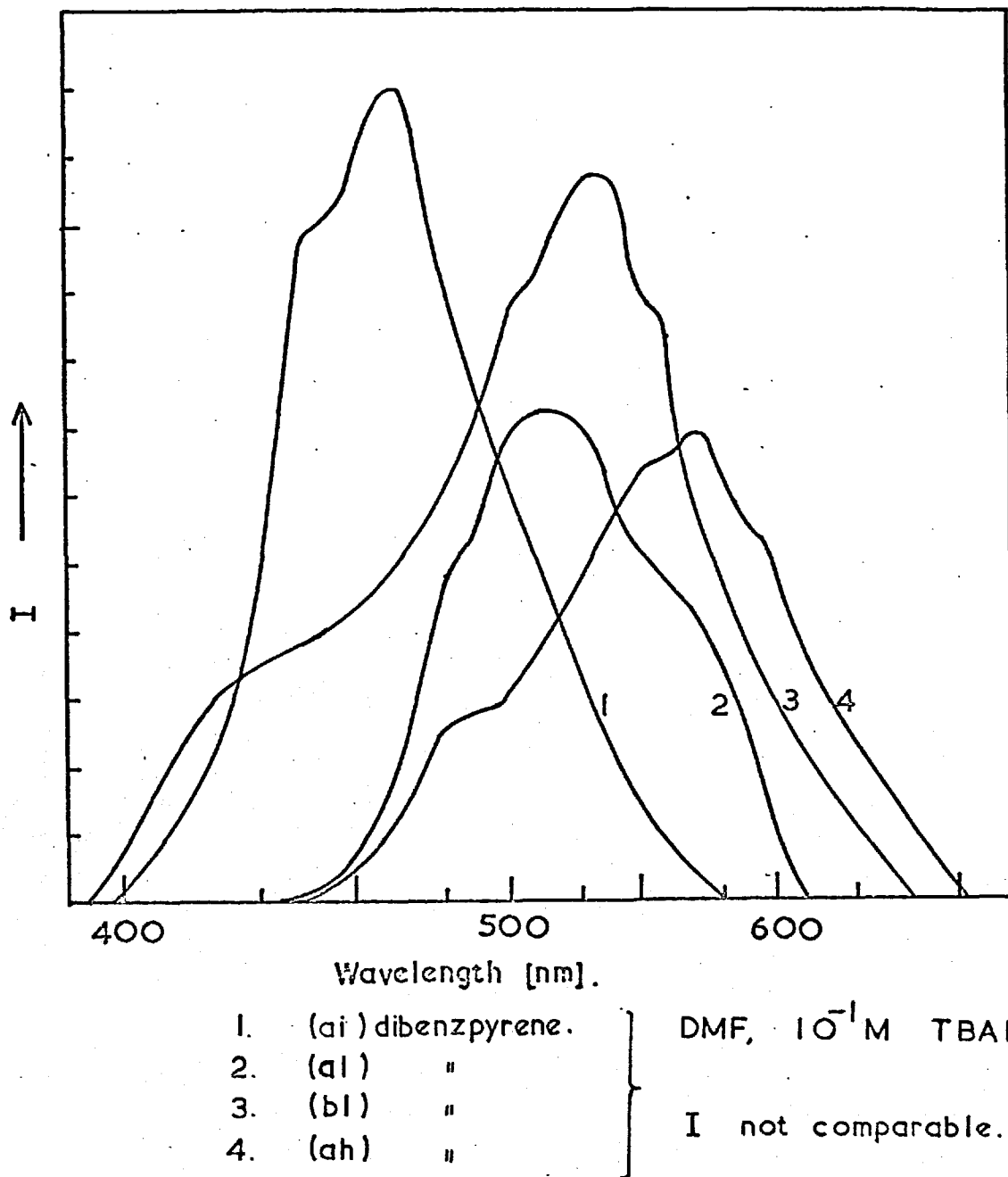


Fig. 3.4

Table 3.2.

<u>Compound.</u>	<u>Ecl Maxima.</u> (nm)	<u>Fluorescence Max.</u> (nm) 60,61
Pyrene.	<u>400</u> , 470.	385, 392, 430, 445. Excimer at 480.
" , 1,2-benz	<u>410</u> , 530*.	<u>389</u> , 399, 412. Excimer at 458.
" , 3,4-benz (TBAB)	<u>495*</u> , 560*. <u>420</u> , 505.	<u>406</u> , <u>426</u> , 453. Excimer at 510.
" ,(al)dibenz	470, <u>500</u> , 550.	<u>470</u> , <u>500</u> , 550.
" ,(ai)dibenz	438, <u>461</u> ,	<u>430</u> , 445, <u>460</u> , 477, 485.
" ,(ah)dibenz	470, <u>570*</u>	<u>449</u> , <u>485</u> , 515.
" ,(bl)dibenz	423, 502*, <u>535*</u> , 570*.	<u>397</u> , <u>420</u> , 448, 477.
-4 (10 M)	<u>420</u> .	

The radical ions themselves are often intensely coloured⁶², and all of the emitted radiation during the ecl process must pass through a 'filter' of these ions, as well as decomposition products and the parent hydrocarbon itself. As a result, strong absorption in certain spectral regions is to be expected.

- (2) Many of the ecl spectra have peaks at a long wavelength (i.e. 500 - 600 nm) that do not correspond to listed fluorescence peaks. In some cases, e.g. 3,4-benzpyrene, the principal peak may be of this category, although with most of the compounds, these peaks may appear after some period of electrolysis, particularly if the potential limits are in excess of those required to generate the radical ions. Because these peaks increase in intensity as discolouration of the solution (and the appearance of fluorescence peaks at the same wavelength) proceeds, it seems reasonable that they are due to emission from decomposition products formed during the ecl process. The existence of such compounds has been demonstrated recently for anthracene, and 9,10-dimethylanthracene^{49,50}, and several mechanisms postulated in order to explain the high emission efficiency for the impurities, considering the low levels at which they are formed.

Both pyrene (Fig. 3.1) and 3,4-benzpyrene (Fig. 3.3) show long wavelength peaks comparable to those in solution fluorescence measurements caused by excimer emission. In both cases, the decay rates of the long-wavelength peaks were identical to those of the normal monomer peak, and no additional long-wavelength peaks appeared under the conditions used. It seems likely, therefore, that the emission at long wavelengths originated from an excimer species which was either formed during or subsequent to the normal cation-anion annihilation process, as discussed in Chapter 1. Quantum efficiencies could not be measured as a function of concentration, using the method of Parker and Short⁴⁸, because of the absence of spectral data, and hence the amount of monomer emission, below 400 nm.

Table 3.3

<u>Compound.</u>	<u>Applied Potential.</u> (V vs. Ag.)	<u>Ecl Maxima.</u> (nm)	<u>Oxidn. Peaks.</u>	<u>Redn. Peaks</u> (V vs. S.C.E.)
Anthracene.	+1.4 to -2.1	<u>410</u> , <u>430</u> , <u>460</u> .	+1.10	-1.95 -2.48
" , 9-phenyl	+1.4 to -2.1	<u>430</u> .	+1.10	-1.94 -2.54
" , 9,10-diphenyl	+1.4 to -2.0	<u>432</u> .	+1.06	-1.88 -2.56
" , 9,10-dimethyl	+1.3 to -2.1	<u>430</u> , <u>440</u> , <u>468</u> . 550 exc.	+0.94	-1.94
" , 1,2-benz	+1.4 to -2.3	<u>412</u> . 520 exc.	+1.06	-2.04
" , 2,3-benz	+1.0 to -1.7	<u>480</u> , <u>510</u> , <u>560</u> .	+0.75	-1.56 -2.12
" , 1,2:3,4-dibenz	+2.0 to -2.6 0.0 to -2.6	< <u>400</u> , <u>408</u> . <u>570</u> .	+1.23	-1.87 -2.32
" , 1,2:5,6-dibenz	+1.7 to -2.3 +0.3 to -2.6	<u>422</u> , <u>440</u> . <u>530</u> , <u>570</u> .	+1.36	-2.13 -2.48
" , 1,2:7,8-dibenz	+1.7 to -2.4 +0.4 to -3.0	<u>417</u> . <u>530</u> .	+1.29	-2.22 -2.70
Anthrone.	0.0 to -3.5	<u>520</u> , <u>570</u> .		-1.22

3.2 Anthracene and Related Compounds

Table 3.3 lists the optimum excitation conditions, the ecl maxima, and well-defined oxidation and reduction peaks that were observed for a series of substituted anthracenes. A 74 Hz square wave signal, with stirring, was used in all cases except for 9,10-dimethylanthracene (10 Hz) and 2,3-benzanthracene (400 Hz). When a different signal amplitude caused a variation in the emission spectrum, both sets of values are given.

The ecl of anthracene itself is very complex, and two publications^{49, 50} have been devoted to the study of the different products formed during the ecl process and the emission that arises from them. Visual observation of the working electrode showed that a deep blue colouration appeared while reduction was occurring. Although the product generated during the oxidation cycle was not visible at the electrode itself, a red colouration appeared immediately above it at the surface of the solution. This rapidly changed to a yellow (green fluorescent) product, and then slowly faded to a colourless (blue fluorescent) product within ten minutes. The formation of a yellow product during the ecl of anthracene, and its slow conversion to a colourless (blue fluorescent) substance, has been attributed by Bard⁴⁹ to the formation of anthronol, and its tautomerisation to anthrone. The red compound (not previously reported) must therefore be an intermediate between the anthracene cation and anthronol. The shape of the anthracene ecl

spectrum (10^{-3} M solution) varied greatly between 400 and 460 nm, with the two peaks at 410 and 430 nm almost absent in some cases. The peak at 460 nm was often shifted to lower wavelengths (down to 445 nm), suggesting the possibility that it was an apparent peak caused by variable absorption of light in the region 400 - 460 nm.

The u.v. absorbance of a post-electrolysis anthracene solution showed a region of strong absorption between 392 and 426 nm, which was not present before electrolysis. The red intermediate might also be expected to absorb light in this region, although it was not possible to obtain its absorption spectrum owing to its short lifetime. Fluorescence measurements confirmed the observation of Bard⁴⁹ that new fluorescent products were formed during the electrolysis, with emission maxima at long wavelengths. As the solvent-electrolyte combination is involved in the formation of the anthracene break-down products responsible for emission⁵⁰, then alteration of the supporting electrolyte material should have some effect on the emission spectrum obtained. Table 3.4 shows the ecl maxima observed, using 10^{-3} M anthracene solutions in DMF, containing either 10^{-1} M or less of the different supporting electrolytes, depending on solubility. The optimum potentials were found to vary slightly from compound to compound.

9-phenylanthracene emitted intense ecl when the square wave potential was first applied to the working electrode. After several

Table 3.4

<u>Supporting Electrolyte.</u>	<u>Ecl Max.(nm)</u>
Tetrabutylammonium perchlorate.	<u>410</u> , <u>430</u> , <u>460</u> .
" bromide.	410, 430, <u>530</u> .
" iodide.	<u>450</u> , <u>550</u> .
" chloride.	<u>495</u> , 560.
Lithium chloride.	<u>510</u> .
Lithium perchlorate.	<u>455</u> .
Tetraphenylphosphonium bromide.	<u>410</u> , 430, 455.
Ammonium chloride.	<u>510</u> , 560.

minutes, however, the intensity dropped and the position of the emission maximum changed considerably. Examination of the current-voltage curve produced when a wide-range triangular sweep was applied, showed that an oxidation peak (+ 0.5 V vs Ag) rapidly appeared during the electrolysis. This ecl behaviour is rather similar to that of anthracene itself, although the emission is initially more intense, and decays more rapidly.

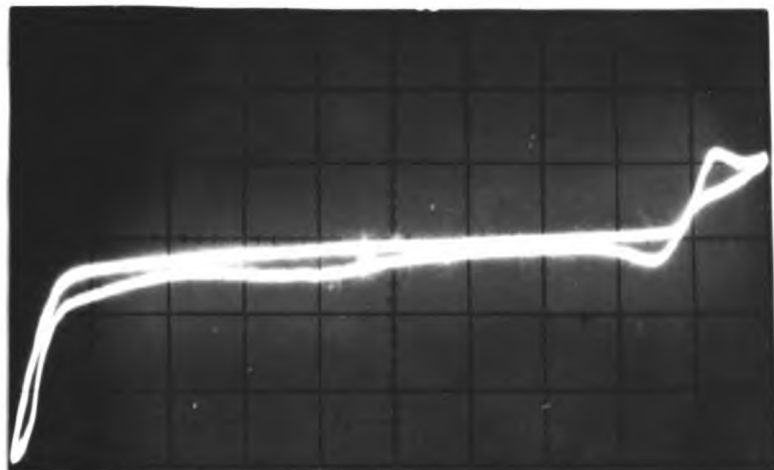
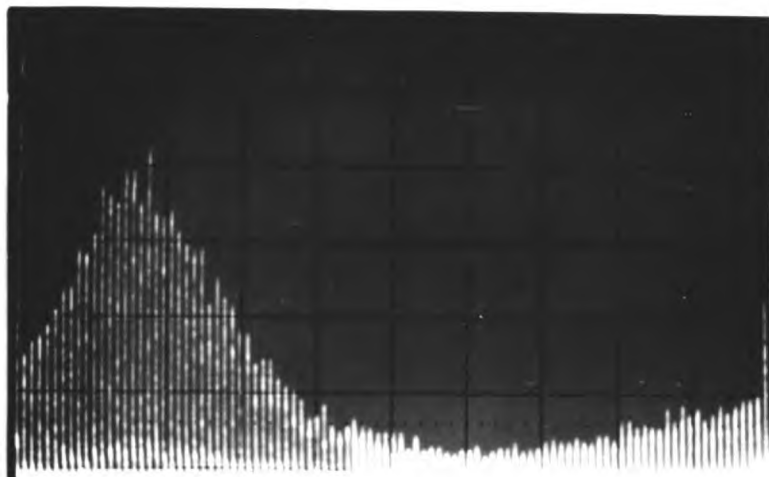
Fig. 3.5a shows the wide range cyclic voltammogram obtained initially, and the emission spectrum of this solution (recorded oscilloscopically) several seconds previously. Fig. 3.5b shows the emission spectrum and cyclic voltammogram recorded three minutes later. As can be seen, the initial emission peak at 430 nm has been replaced by peaks at 450 and 540 nm.

Cyclic voltammograms were recorded with a 1 Hz signal at a slightly greater amplitude than that required to produce both the anion and cation of the hydrocarbon, in order to show both peaks more clearly. At this sweep rate and amplitude, the positions of both peaks are distorted compared to the measured values in Table 3.3.

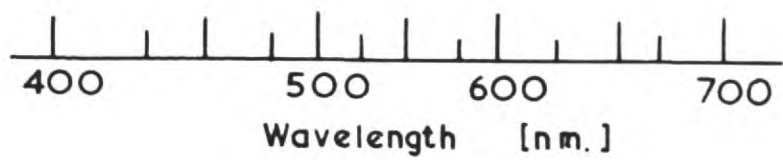
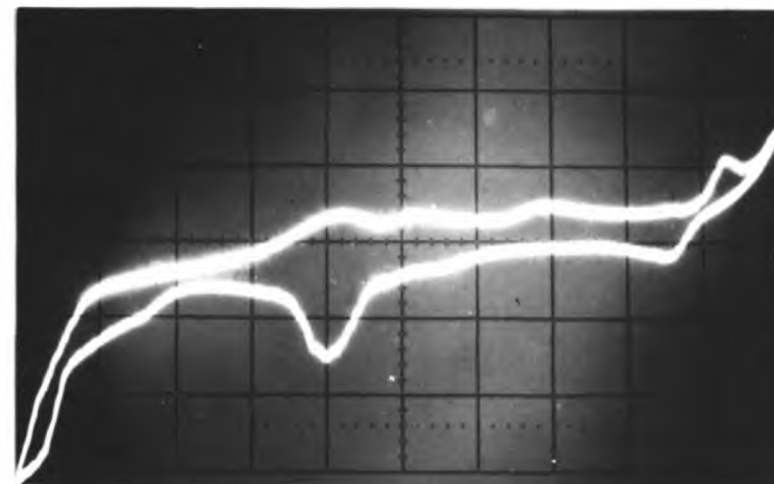
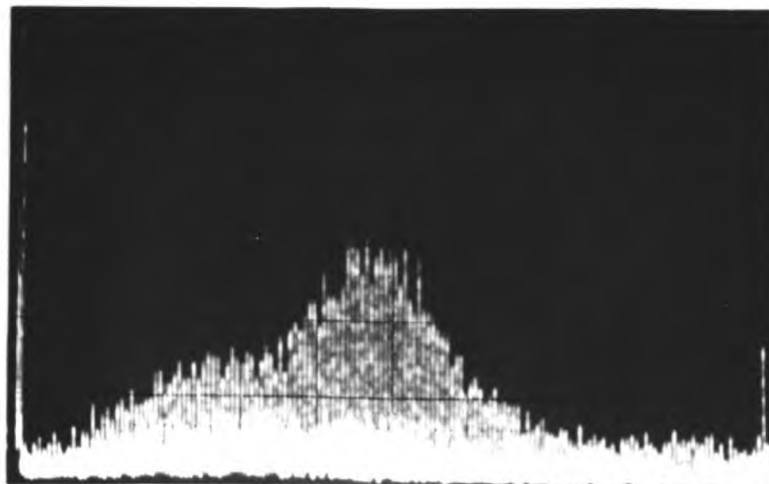
The emission from 9,10-diphenylanthracene was amongst the most intense and stable for any of the compounds examined. Self-absorption of short-wavelength components caused the ecl spectrum to lack the structure reported in its fluorescence spectrum⁶³. However, the ecl spectrum in methylene chloride was much less self-absorbed in this region, and a second peak at 410 nm could be distinguished (Fig. 3.6).

Fig 3.5

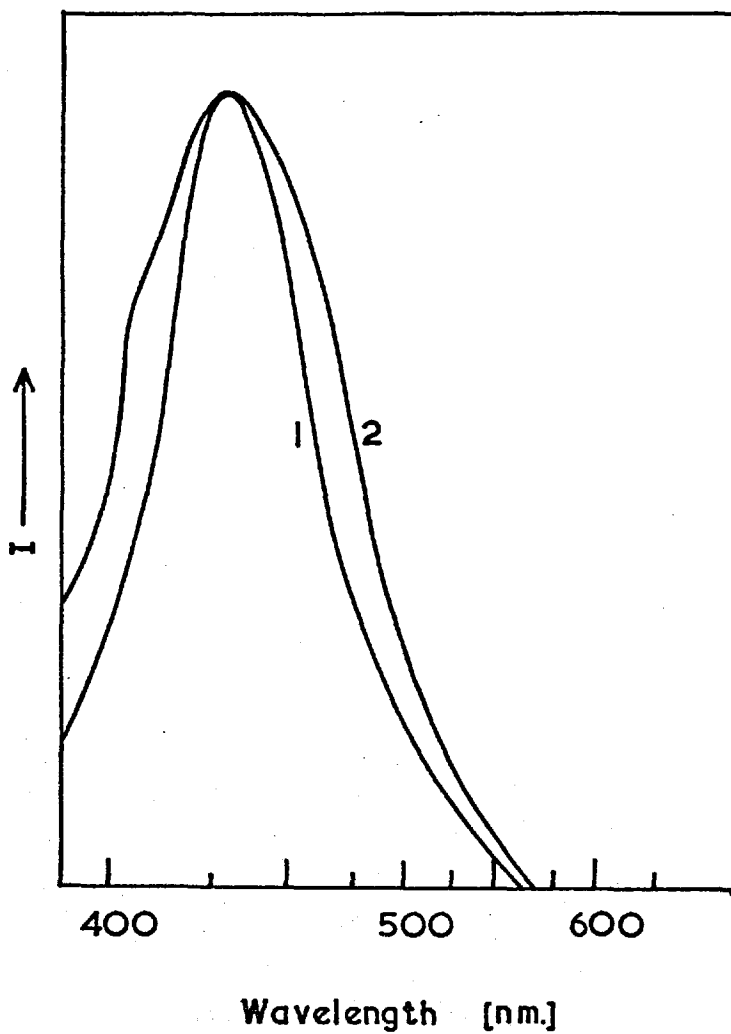
a



b



+ 1.5 to -2.4 V vs. Ag.



Spectra of DPA in

1. DMF + 10^{-1} M TBAP.

2. MeCl₂ " "

(Corrected to the maximum intensity of 1.)

9,10-dimethylanthracene (DMA) was examined primarily to see whether the observations of Parker and Short⁴⁸ concerning the excimer component of the ecl spectrum of this compound were valid, when a potentiostat was used, instead of the simple two electrode cell powered from a mains transformer that they had used. The emission that was obtained from a 10^{-3} M solution was very intense and stable if stirred, although it decreased rapidly in the absence of stirring. Spectra were measured for concentrations of DMA between 10^{-3} M and 3×10^{-2} M. Two sets of spectra were obtained: the first was measured at a constant applied potential (+ 1.3 \rightarrow -2.1 V vs Ag), and the second at the maximum output intensity, which corresponded to larger potential limits as the concentration of solute was increased. The spectra remained constant in intensity and shape during measurement.

The observation of Parker that the amount of excimer emission depends on the signal amplitude was confirmed for the potentiostat system; in addition, the spectral distribution did not depend upon the frequency of the square waveform signal applied. All of the spectra obtained were then treated by the procedure used by Parker; correction for photomultiplier and monochromator response was made, and the spectra converted to energy units (cm^{-1}) instead of wavelength (nm). In addition, all of the spectra were normalised at 460 nm, where self-absorption and excimer emission were assumed to be negligible.

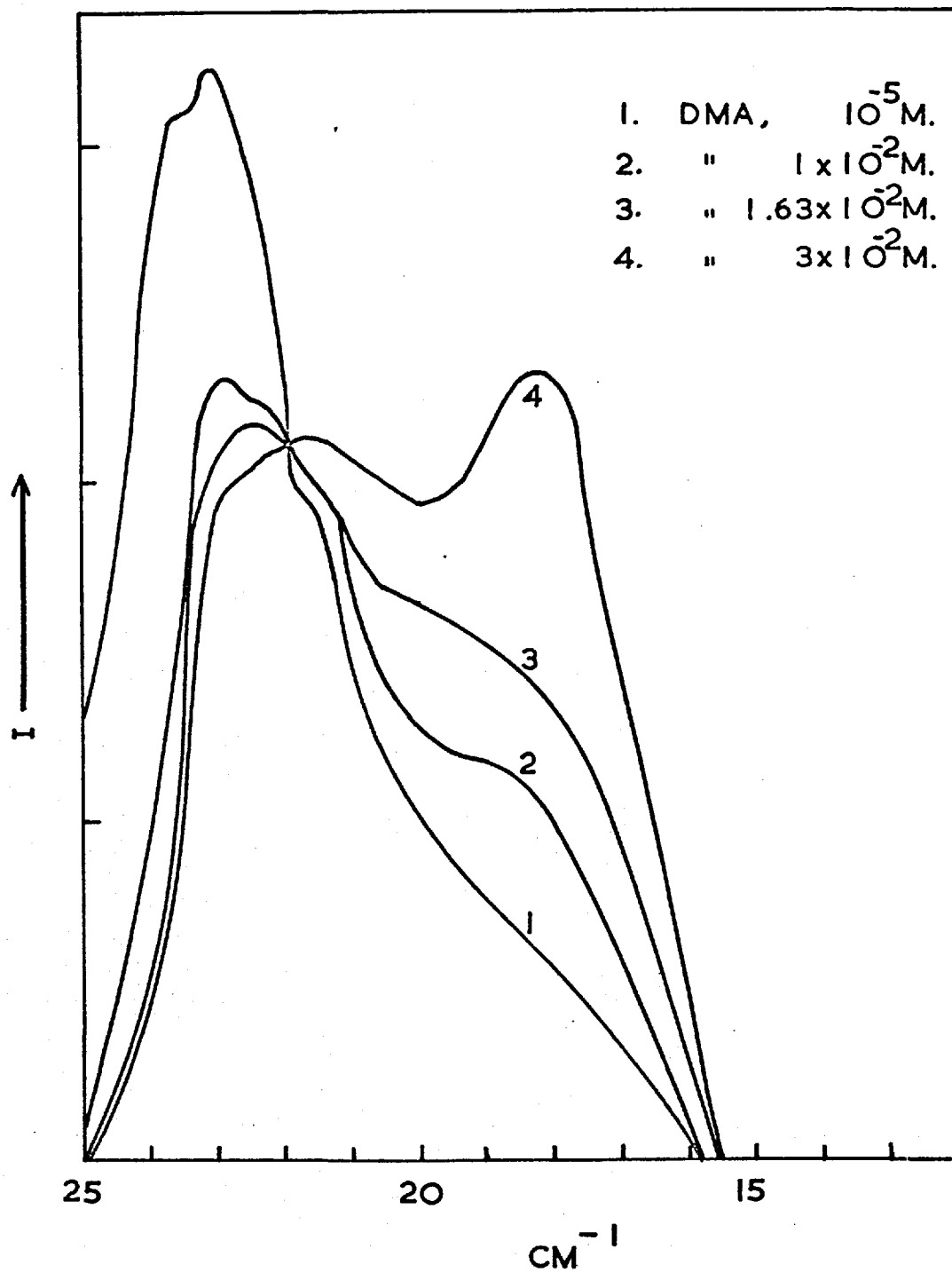


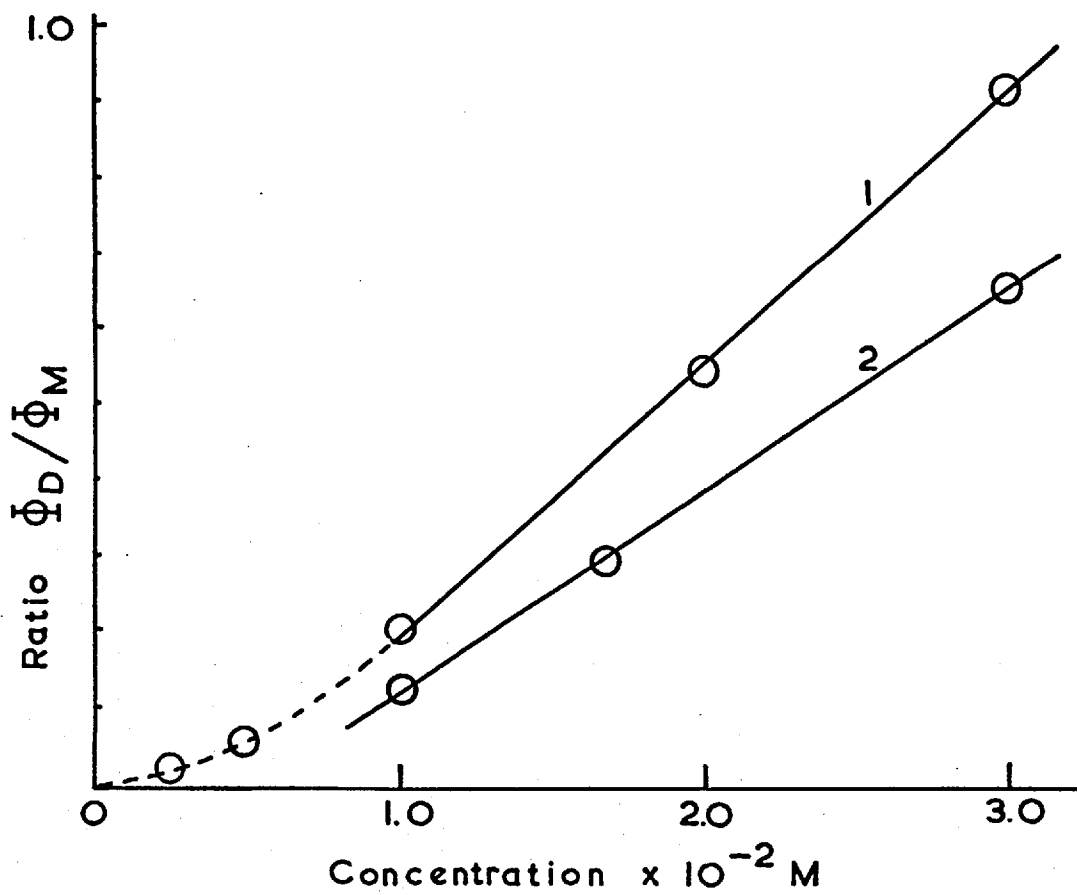
Fig. 3.7

The spectrum of a 10^{-5} M solution of DMA similarly treated was then subtracted from each of the spectra in turn, and the area under each peak ($\bar{\Phi}$ monomer and $\bar{\Phi}$ dimer) obtained by integration. Fig. 3.7 shows the corrected spectra obtained at the optimum signal amplitude for 10^{-5} , 1×10^{-2} , 1.63×10^{-2} and 3×10^{-2} M solutions of DMA. Values of $\bar{\Phi}_D/\bar{\Phi}_M$ were plotted against concentration, and are shown in Fig. 3.8.

The straight line portions of the curves obtained with the potentiostat system do not give a positive intercept for $\bar{\Phi}_D/\bar{\Phi}_M$ (cf. the results of Parker) and the amounts of dimer emission are, in general, much lower than with Parker's two-electrode system.

Values less than those of Parker have been confirmed by Hercules in a recent publication⁵⁰. However, the results do confirm the linear relationship between $\bar{\Phi}_D/\bar{\Phi}_M$ and concentration that Parker obtained, and that the ratio is dependent upon the applied potential.

A trivial explanation for the voltage dependence could result from Hoytink's observation⁵¹ that the approach of R^+ and R^- is not near enough to form the dimer directly. If this is so, then dimer formation could result from interaction of the excited singlet formed during the annihilation process with a ground state molecule. With the higher applied potential (and lower amount of excimer emission,) the electrode would be surrounded almost entirely by R^+ and R^- and the concentration of R itself would be low. However, at the lower potential, the formation of R^+ and R^- is less efficient, and many uncharged



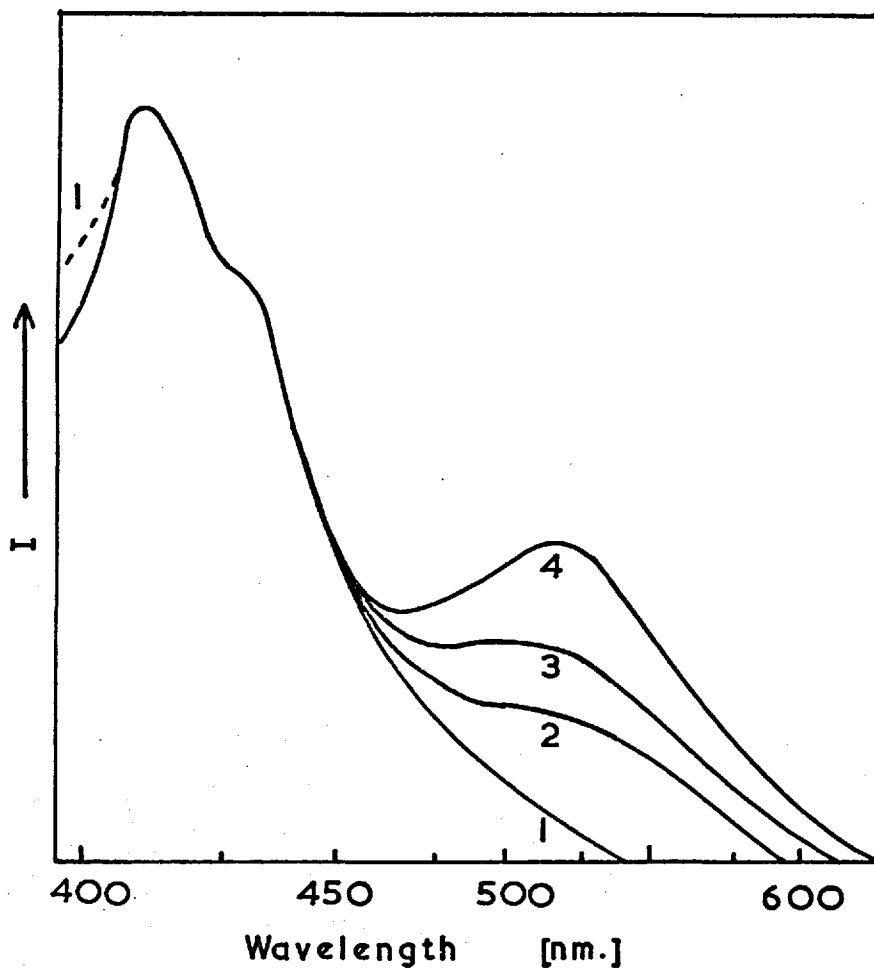
1. DMA, +1.3 to -2.1 V
2. " Optimum V [var.]

Fig. 3.8

hydrocarbon molecules must be present around the excited singlet molecules formed by annihilation. This would increase the amount of interaction between $^1R^*$ and R, and thus the amount of excimer emission. Of course, the situation may be greatly complicated by triplet involvement, as Parker suggests.

The compound 1,2-benzanthracene was also examined in some detail, because solution fluorescence measurements⁶⁴ show that excimer species are readily formed. However, like pyrene part of the ecl emission spectrum lies below 400 nm, and quantum efficiency measurements could not be made.

In unstirred solution the ecl emission at 412 nm remained intense, but a peak rapidly appeared at 560 nm; within minutes this peak increased in amplitude to about four times that of the peak at 412 nm. This time dependence strongly suggested that this was a peak arising from decomposition products. In stirred solution an emission peak at 520 nm was obtained which showed the same time dependence as the peak at 412 nm, and was markedly affected by concentration. Fig. 3.9 shows the ecl emission spectrum of 1,2-benzanthracene between concentrations of 2×10^{-3} and 10^{-2} M. The recorder sensitivity was adjusted so that the pen deflection at 412 nm for each solution was the same. As the peak at 520 nm displays a concentration dependence characteristic of an excimer peak, and agrees within experimental limits with the value of the solution fluorescence excimer peak (510 nm, from Birks and Christophorou⁶⁴), it most probably arises from an excimer species.



1.	1,2-benzanthracene.	2×10^{-3} M.
2.	"	4×10^{-3} M.
3.	"	6×10^{-3} M.
4.	"	1×10^{-2} M.

Fig. 3.9

2,3-benzanthracene gave a weak, but stable ecl emission, with a spectrum similar to that reported⁶³ for its solution fluorescence.

1,2:3,4-dibenzanthracene also gave weak ecl, with a principal emission maximum below 400 nm. The optimum voltage conditions corresponded to the second oxidation and reduction peaks: no ecl was seen if only the first oxidation and reduction products were generated. If a signal between 0 and -2.55 V was applied to the electrode, a low intensity peak appeared slowly at 570 nm.

1,2:5,6-dibenzanthracene gave a very intense emission at voltages corresponding to anion and cation formation. In addition to the peaks visible initially, a peak at 530 nm appeared during electrolysis. The use of the second voltage limits in the table gave very intense emission, with peaks at 530 and 570 nm.

1,2:7,8-dibenzanthracene showed very similar behaviour, with a principal ecl maximum at 417 nm, and a peak at 530 nm which grew rapidly during electrolysis. Very intense emission at 530 nm was generated by application of + 0.4 \rightarrow -3.0 V to the working electrode.

3.3 Fluorene and related compounds

Table 3.5 shows the optimum excitation conditions for fluorene and several allied aromatic compounds. Oxidation and reduction potentials were not in general well defined, and the potential limits used did not correspond to those required for anion or cation formation.

Table 3.5

<u>Compound.</u>	<u>Ecl Maxima.</u> (nm)	<u>Applied Potential.</u> (V vs. Ag.)
Fluorene.	<u>536.</u> then 575, 625.	-0.2 to -3.4
" ,2-methyl	<u>540.</u> then <u>570.</u>	-0.2 to -3.3
" ,1,2-benz	<u>550.</u>	-1.0 to -3.7
" ,2,3-benz	<u>550, 562.</u>	-1.1 to -3.6
	550, <u>562.</u>	-1.1 to -2.5
Fluorenone.	<u>540, 570.</u>	-0.3 to -3.3

The emission from fluorene was sufficiently intense to be easily visible in daylight. In stirred solution, the emission rose rapidly (ca. 2 seconds) to a peak intensity value, and remained at this for about twenty minutes, before decaying slowly. In unstirred solution, the emission rapidly passed through a peak (ca. 0.5seconds) and had decreased to practically zero within three minutes. The decrease in light intensity was accompanied by the appearance of a reddish colouration in the vicinity of the working electrode, which instantly turned yellow if stirring was resumed. In this case, light emission reappeared at the original intensity. Fig. 3.10 shows the time intensity behaviour for a 5×10^{-3} M fluorene solution at the optimum potentials. The emission obtained from an unstirred 1×10^{-3} M solution was more stable than the more concentrated solution, and changed noticeably with time. Fig. 3.11 shows the emission spectra at this concentration, after one, three and five minutes. Several new fluorescence peaks could be observed in the post-electrolysis solutions, with the following excitation and emission maxima.

(i) Pre-electrolysis (Fluorene)

Excitation	270 nm	Emission	310 nm
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(ii) Post-electrolysis, new peaks

Excitation	Emission
340 nm	<u>420</u> , 470 nm
<u>400</u> , 460 nm	530 nm

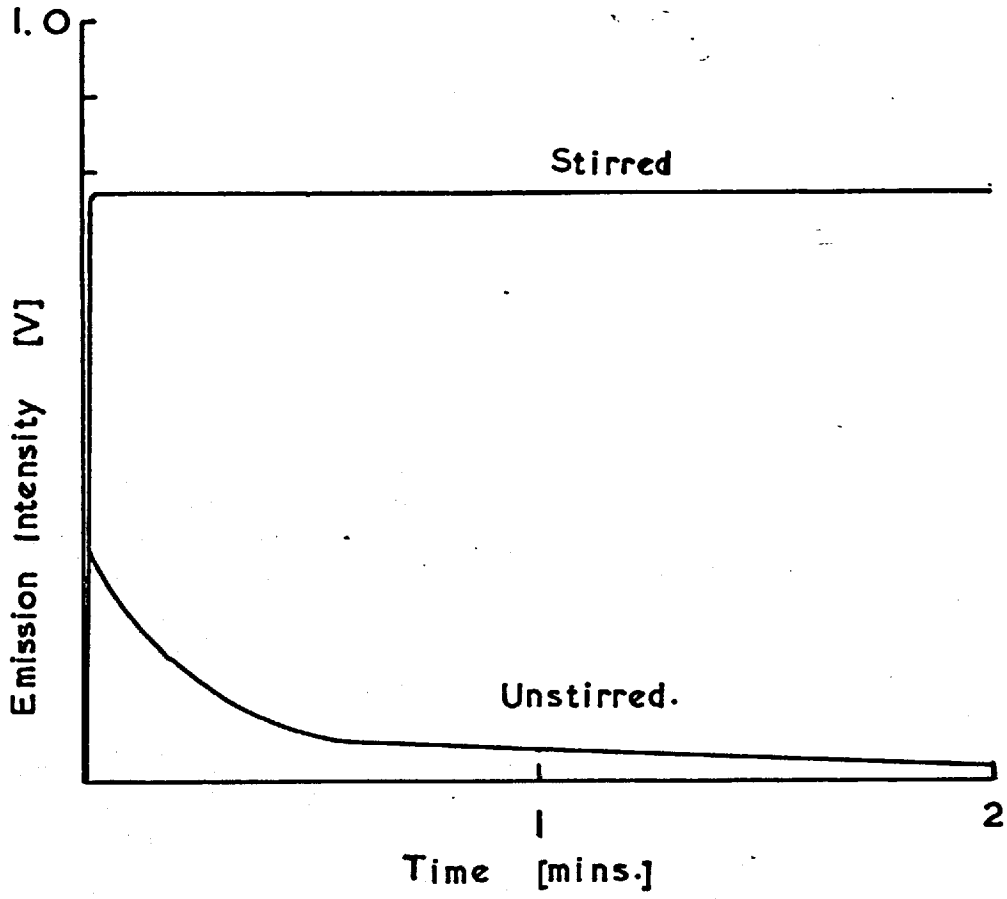


Fig. 3.10

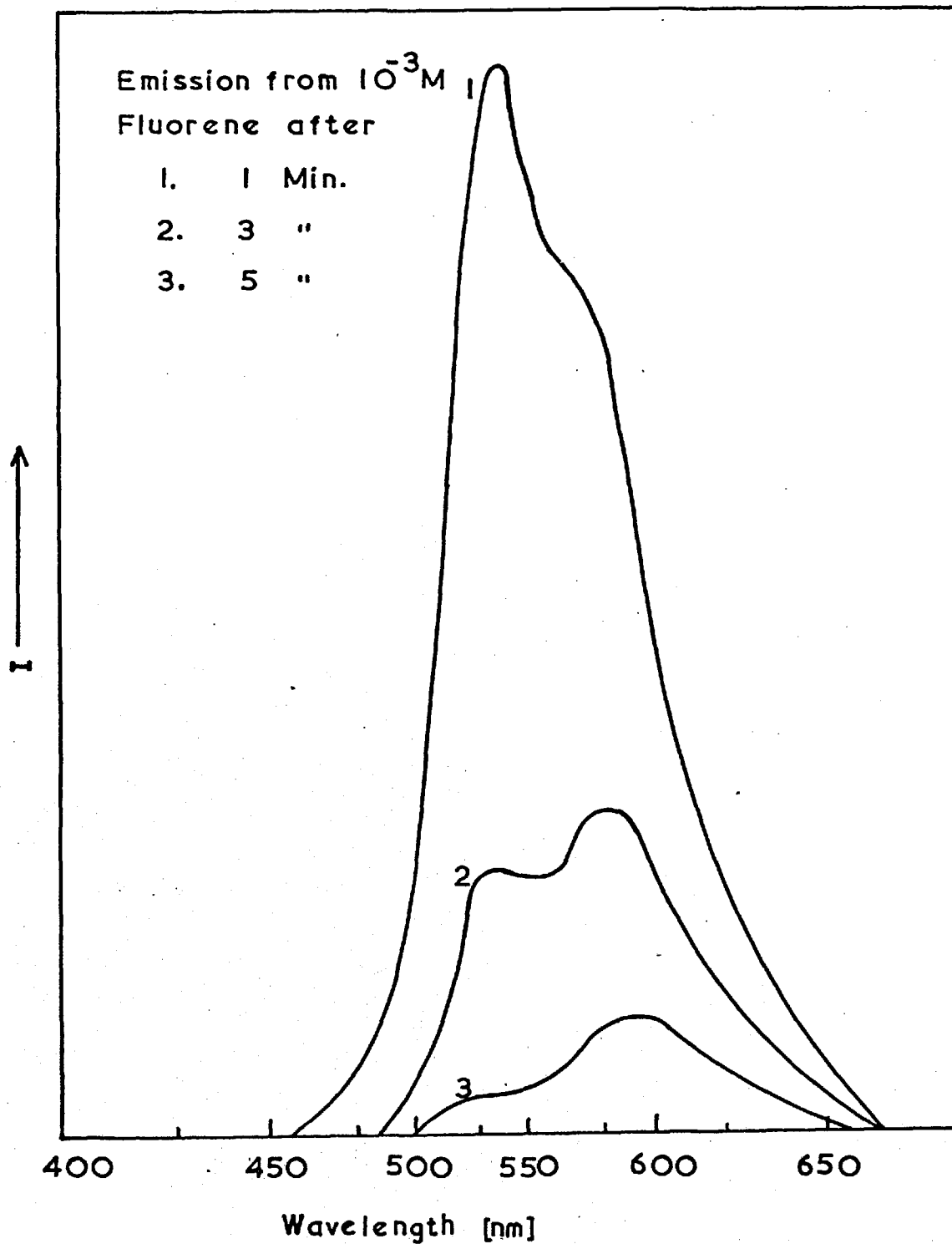


Fig. 3.11

In addition, the post-electrolysis solutions were mixed with water (10 ml) and then extracted with a large volume of cyclohexane (250 ml) and the extracts dried with anhydrous sodium sulphate and evaporated down to 1 ml. This gave four peaks when injected into the Perkin-Elmer F21 gas chromatograph (preparative column) with retention times of 1.9, 3.2, 5.7 and 7.0 minutes, in addition to several minor peaks. The peak at 3.2 minutes gave an identical melting point, retention time and u.v. absorption spectrum to pure fluorene itself. The peak at 5.7 minutes was identical in retention time, melting point and very similar in u.v. spectrum, to a sample of pure fluorenone. No identification of the other two peaks was achieved.

Fluorenone itself showed no ecl initially, although a weak emission with peaks at 540 nm and 570 nm appeared if the solution was reduced at -2.10 V (vs Ag) for several minutes before the square wave was applied.

The ecl from 2-methylfluorene was very similar to that from fluorene. When the emission was generated in unstirred solution, the original emission maximum at 540 nm rapidly decreased in intensity, and was replaced by one at 570 nm.

Both 1,2- and 2,3-benzfluorene gave intense and stable ecl emission when large negative potentials were applied. In the case of 2,3-benzfluorene, the shape of the emission spectrum was slightly altered when different potential limits were applied.

It is clear that the emission obtained from these compounds does not originate from the excited singlet state, as the normal fluorescence emission spectra of these compounds lie below 400 nm. The fact that very similar emission to that from fluorene could be obtained from the reduction product of fluorenone (probably fluorenol or some intermediate) suggests that the emitting species is probably phenolic in nature, as has been shown by Bard⁴⁹ to be the case for anthracene.

3.4 Fluoranthene and related Compounds

The ecl characteristics of a series of benz-substituted fluoranthenes are given in Table 3.6. 3-methylcholanthrene has been included because of its related structure, and somewhat similar ecl behaviour. All spectra were measured using a 74 Hz square wave applied potential, and in stirred solution. Although most of the compounds showed well-defined reduction peaks, the oxidation peaks under these conditions were not, in general, well characterised, and have mostly been omitted.

Fluoranthene showed intense ecl at potential limits corresponding to anion and cation formation, with an emission maximum that corresponded to the longest wavelength fluorescence maximum (468 nm, Van Duuren⁶¹). Both reduction peaks for this compound were well defined (Fig. 3.11). If larger potentials were applied to the working electrode, then the emission obtained was more intense, and at a long wavelength, not characteristic of the normal singlet emission spectrum.

Table 3.6

<u>Compound.</u>	<u>Applied Potential.</u> (V vs. Ag.)	<u>Ecl Maxima.</u> (nm)	<u>Oxidn. Peaks.</u>	<u>Redn. Peaks.</u> (V vs. S.C.E.)
Fluoranthene.	+1.5 to -2.0	<u>470.</u>	-	-1.84
	+2.0 to -3.2	470, 570.		-2.55
" , 2,3-benz	+1.6 to -2.0	415, <u>438.</u>	-	-1.86
	-1.0 to -2.0	<u>520.</u>		-2.48
" , 3,4-benz	+1.8 to -2.0	415, <u>440.</u>	-	-1.83
	+1.4 to -2.3	<u>515</u>		-2.46
" , 6,7-benz	+1.4 to -2.0	<u>475</u> , 520. then;	+1.10	-1.87
		425, <u>457</u> , 475, 570.		-2.40
3-methylchol-	+1.9 to -1.6	415, <u>438</u> , 470.	+0.94	-1.46
anthrene.	+1.3 to -2.5	438, <u>505</u> , 530.	+1.47	-2.31

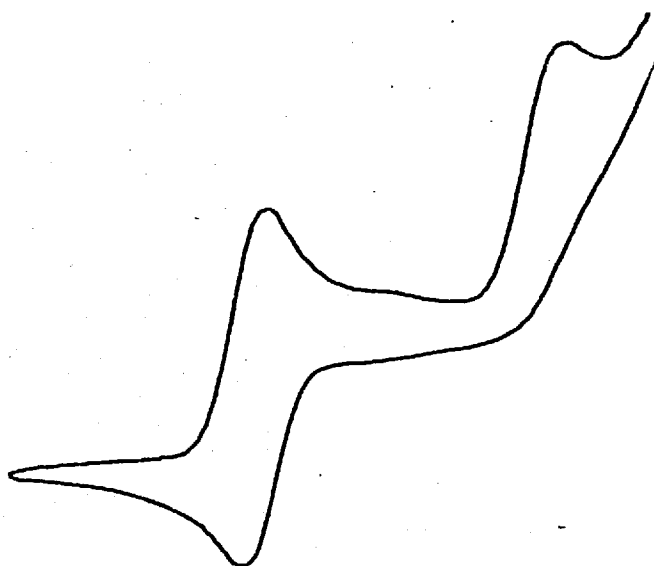
2,3-benz- and 3,4-benz- fluoranthene exhibited very similar ecl behaviour. At potential limits corresponding to anion and cation formation, the emission spectra were similar to the fluorescence emission spectra (measured using the Aminco-Bowman spectrofluorimeter). Both gave long wavelength peaks not found in the fluorescence spectra when other potential limits were applied, although the optimum potentials were different for the two compounds. The emission at 520 nm for 2,3-benzfluoranthene was very much more intense than the long-wavelength peak of 3,4-benzfluoranthene, although the latter increased greatly with concentration, and at 10^{-2} M gave a very intense emission, easily visible in daylight.

6,7-benzfluoranthene showed only weak ecl when the potential limits in Table 3.6 (corresponding to the formation of anion and cation) were first applied. However, the intensity rose slowly until after about five minutes, an intense spectrum with maxima at 425, 457, 475 and 570 nm was obtained (Fig. 3.12). With the exception of the peak at 570 nm, these correspond fairly well to the fluorescence emission maxima reported⁶⁵ for this compound at 418, 444, 472, 490 nm. No other compound was found where the initial ecl spectrum, which did not resemble the fluorescence spectrum, changed to one which did, rather than vice versa, which was usually the case.

Very little emission was observed with 3-methylcholanthrene when the anion-cation potential limits were applied. However weak emission appeared at the fluorescence emission maxima (Van Duuren⁶¹, 393, 415, 442, 470 nm) when potential limits corresponding to the formation of

the second cation and the first anion were used. If the cation and the second anion potential limits were used, very intense emission at a longer wavelength was obtained. Fig. 3.13 shows both spectra.

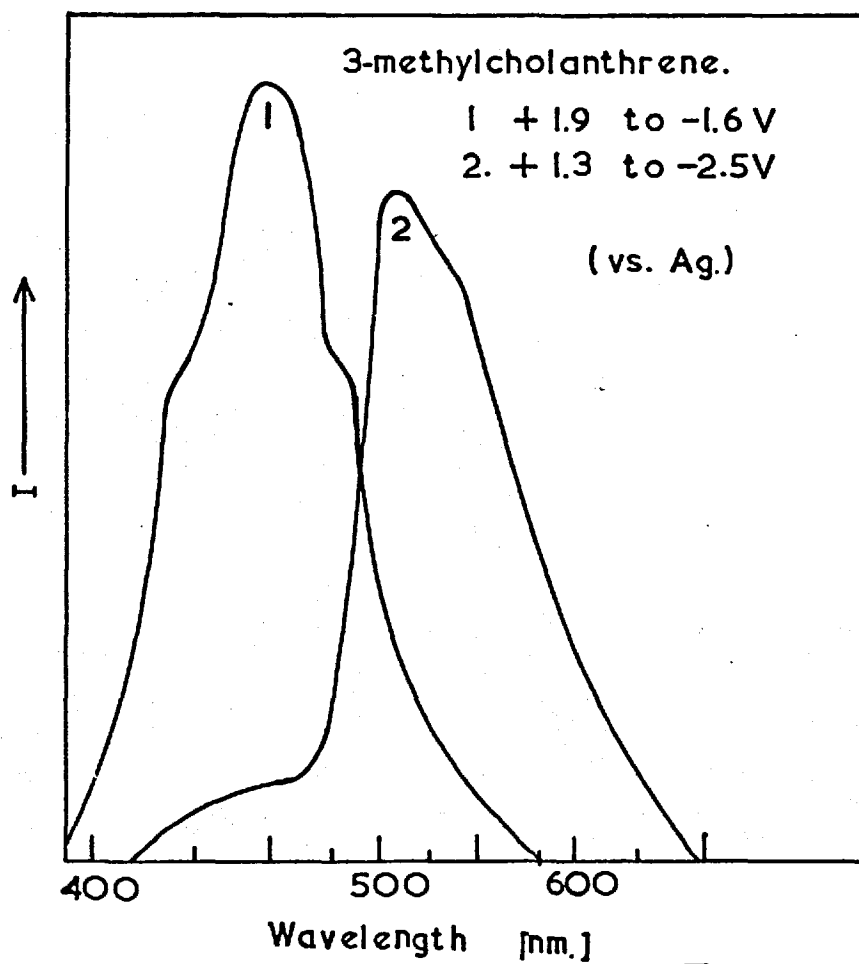
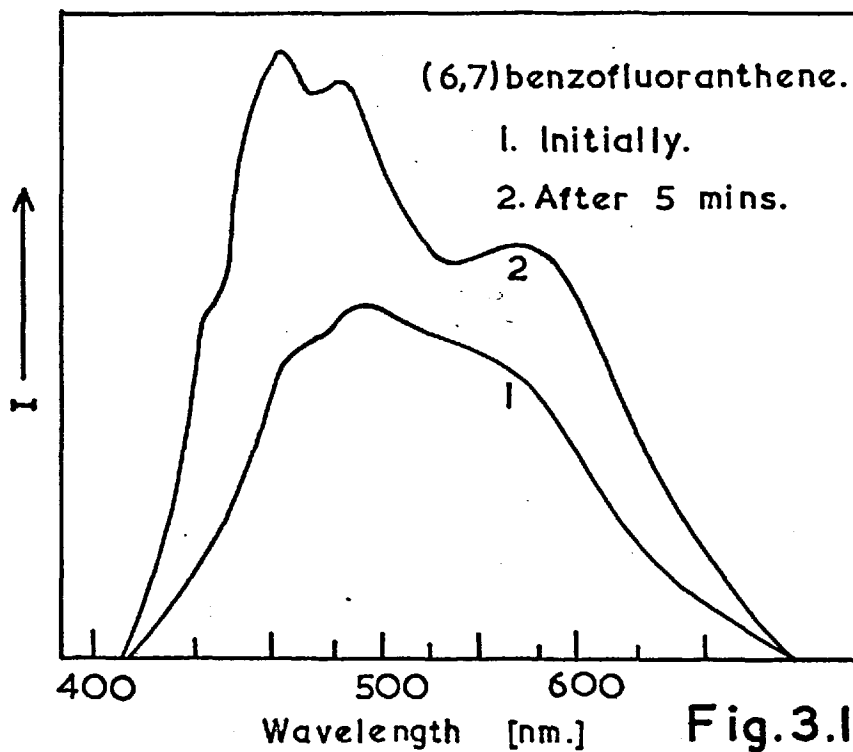
Most of the ecl spectra that were obtained for these compounds could be attributed to normal singlet emission or to decomposition products.



Fluoranthene, 10^{-3} M 0.05 Hz.

-1.25 to -2.75 V vs. S.C.E.

Fig. 3.11



3.5 Naphthalene and related compounds

Table 3.7 lists the ecl characteristics for a series of substituted naphthalenes. The radiation emitted in most cases was at considerably longer wavelengths than the fluorescence emission for the same compounds, and did not usually appear at potentials corresponding to the formation of anions and cations of the parent compound.

Both naphthalene and 2-fluoronaphthalene gave emission with a maximum below 400 nm, that rapidly (within 5 seconds) gave way to a weaker emission at longer wavelengths. With 2-fluoronaphthalene, this latter emission remained stable for about ten minutes, but with naphthalene itself, it decayed rapidly to diffuse and weak emission bands in the region 450 to 550 nm.

The light emission from 1-methylnaphthalene was intense, but not very stable, and occurred beyond ca. 0.5 V (vs. Ag), where a large, diffuse oxidation peak slowly appeared. Although the emission maximum remained at a constant wavelength, the intensity slowly reached a maximum and then decayed rapidly. The ecl behaviour of 2-phenylnaphthalene was very similar, although the emission intensity was rather more stable.

2-methoxy-, 2,3-dimethoxy- and 2-hydroxy-3-carboxynaphthalene gave weak but stable ecl emission that did not change appreciably with time. The addition of small amounts of aluminium bromide to solutions of 2,3-dihydroxy- or 2-hydroxy-3-carboxynaphthalene produced a noticeable increase in the ecl intensity of the solution, possibly due to the formation of an aluminium complex, and its subsequent ecl.

Table 3.7

<u>Compound.</u>	<u>Ecl Maxima.</u> (nm)	<u>Applied Potential.</u> (V vs. Ag.)
Naphthalene.	<400, 422. 470.	+1.4 to -2.9, 30 Hz, st. +0.3 to -2.9, "
" , 1-methyl	455.	+1.2 to -2.6, "
" , 2-phenyl	445.	+1.9 to -2.1, "
" , 2-fluoro	<400, 420, 433.	+1.6 to -3.2, 74 Hz, st.
" , 2-methoxy	490.	+0.8 to -3.4, " , unst.
" , 2,3-dimethoxy	470, 500, 530.	+0.7 to -3.1, 220 Hz, "
" , 2-hydroxy-3- carboxy	520.	+0.4 to -2.8, 74 Hz, "
2,2'-Binaphthylamine.	428, 555.	+0.8 to -3.3, " "
2,2'-Binaphthyl.	<400, 420.	+1.9 to -2.3, 30 Hz, st.
Acenaphthene.	432.	+1.6 to -3.2, 74 Hz, st.
Acenaphthylene.	550.	+1.2 to -3.6, " "
		All using square wave.

2,2'-binaphthyl gave intense ecl at potentials corresponding to anion and cation formation, with an emission maximum below 400 nm that gave an apparent peak in the spectrum plotted at 680 nm, due to harmonic transmission of the interference filter. The emission from 2,2'-binaphthylamine was weak, but stable, and was most intense in unstirred solution.

Acenaphthylene gave very weak ecl that faded rapidly, in contrast to that from acenaphthene, which was moderately intense.

With the exception of 2,2'-binaphthyl, the ecl emission from this group of compounds was not sufficiently stable or intense to permit quantitative measurements to be made. Most of the emission maxima (again, perhaps except for 2,2'-binaphthyl) do not correspond to reported fluorescence values⁶³ for these compounds, which lie in the region 320-340 nm and hence ecl emission probably originates from decomposition products.

3.6 Diphenyl, Stilbene and Related Compounds

This group of compounds is the only one found to emit ecl that did not possess fused-ring structures. It was not possible to determine all of the emission maxima, as these often occurred below 400 nm. However, because of the transmission properties of the interference filter, an 'apparent' peak was often seen in the spectral region 650 - 700 nm, due to harmonic transmission of radiation below

Table 3.8

<u>Compound.</u>	<u>Ecl Maxima.</u> (nm)	<u>Applied Potential.</u> (V vs. Ag.)
Diphenyl.	475, <u>525</u> .	+1.3 to -2.8
	475, <u>570</u> .	+1.6 to -3.6
Benzylidiphenyl.	<u>460</u> , 490.	+1.0 to -3.0
o-terphenyl.	<u>465</u> .	+1.1 to -2.9
m-terphenyl.	<u>490</u> , (700).	+1.2 to -3.2
p-terphenyl.	< <u>400</u> , (680).	+1.1 to -3.1
o-quaterphenyl.	<u>555</u> .	+1.2 to -3.6
t-stilbene.	< <u>400</u> .	+2.2 to -2.4
1,8-diphenyl-1,3,5,7 -octatetraene.	480, <u>555</u> .	+1.3 to -1.9

400 nm. Because the photomultiplier tube was not sensitive beyond 620 nm, radiation at wavelengths longer than this would not be detected.

Diphenyl itself was found to emit intense ecl, with emission maxima that were affected by the applied potential and stirring. At both sets of potential limits listed in Table 3.8, the emission rose rapidly (about twenty seconds) to a maximum, and remained stable at this value for several minutes. Both benzyldiphenyl and *o*-terphenyl displayed very similar ecl characteristics, although no change in emission spectrum with applied potential was evident for these compounds. *m*-terphenyl gave weak emission, with the principal maximum below 400 nm, and a low intensity peak at 490 nm. *p*-terphenyl and *t*-stilbene gave only very weak ecl, with maxima that were below 400 nm. The emission from *o*-quaterphenyl was very weak and transient.

The emission from 1,8-diphenyl-1,3,5,7-octatetraene was both stable and intense, and appeared immediately the potential was applied. This compound and diphenyl gave sufficiently intense and stable emission for calibration data to be obtained down to concentrations of 10^{-5} M.

3.7 Other Aromatic Hydrocarbons

Tables 3.9 and 3.10 list the ecl characteristics for a number of other aromatic hydrocarbons. A 74 Hz square-waveform signal was used in all cases; all of the solutions were stirred during the measurement

Table 3.9

<u>Compound.</u>	<u>Applied Potential.</u> (V vs. Ag.)	<u>Ecl Maxima.</u> (nm)	<u>Oxidn. Peaks.</u>	<u>Redn. Peaks.</u> (V vs. S.C.E.)
Pentacene.	+2.0 to -2.0	<u>590.</u>	-	-
Picene.	+2.0 to -2.4	< <u>400</u> , <u>402</u> , 425, 565.	+1.21	-2.22 -2.61
Triptycene.	-1.3 to -3.5	490, <u>520.</u>	-	-
Anthanthrene.	+0.8 to -3.3	510, <u>530.</u>	+0.93	-1.61 -2.23
Periflanthene.	+1.4 to -3.6	475, <u>550.</u>	-	-
Rubrene.	+1.3 to -1.3	<u>578.</u>	+1.02 +1.32	-1.25 -1.92
Rubicene.	+1.7 to -1.1	<u>565.</u>	+1.29	-1.05 -1.38

of ecl except for picene.

Because of the low solubility of pentacene in DMF, a 10^{-4} M solution of this compound was used, instead of the 10^{-3} M solutions usually used for the measurement of spectral characteristics. The ecl emission from this compound was very weak indeed, although stable with respect to time. The emission from picene was also rather weak, and it was necessary to use a potential sweep more positive than that required to oxidise the hydrocarbon, in order to observe ecl emission. The spectral peak at 565 nm increased slowly in intensity with respect to time by comparison with the peaks at shorter wavelengths.

Only very weak emission was obtained from triptycene, after electrolysis of several minutes. The emission peaks were very broad, and probably contained unresolved components. Examination of the solution after electrolysis showed that fluorescence emission similar to the ecl emission had appeared.

No emission was obtained when potentials sufficient to produce the anion and cation were applied to a 10^{-3} M solution of anthanthrene. However, at the potential limits in Table 3.9, intense emission rapidly appeared, and increased with time until maximum intensity had been reached after ten minutes. The emission remained at this intensity for a further ten minutes, before finally decaying.

Like pentacene, the solubility of periflanthene in DMF was very low, and measurements could only be made on solutions less concentrated

than 10^{-4} M. At this concentration, the emission was very weak, and short-lived.

Rubrene has been the object of very many investigations of the ecl process (see Chapter I). The emission that was obtained was very intense and stable, surpassing any other compound in these respects except for, perhaps, DPA. The emission was almost equally intense in either stirred or unstirred solutions, and did not change appreciably with time. Very dilute solutions decomposed if deoxygenation had not been carried out, giving an additional ecl peak at 425 nm. (The compound is reported to readily undergo photooxidation, to give a bridged peroxide species⁶⁸). In methylene chloride, the ecl emission from rubrene was equally intense as in DMF, but the spectral maximum was shifted to 587 nm. Because of its low oxidation and reduction potentials, rubrene emission was obtained from any mixture containing this compound (Chapter IV) that was examined. The emission from traces of rubrene could be increased by the addition of an excess of another hydrocarbon such as DPA.

Rubicene exhibited very similar ecl characteristics to rubrene, but the emission was slightly less intense, and decayed more rapidly. Ecl emission from unstirred solutions of rubicene was much less intense than that from stirred solutions, and had reduced to less than one tenth of its initial brightness within three minutes.

The ecl emission from phenanthrene was stable and moderately intense.

Table 3.10

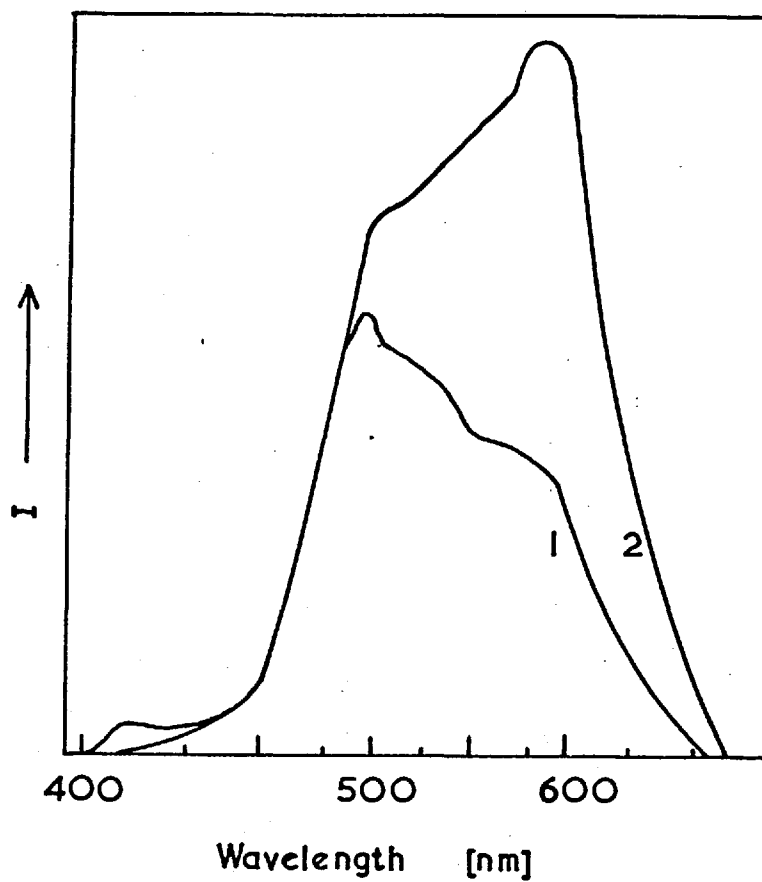
<u>Compound.</u>	<u>Applied Potential.</u> (V vs. Ag.)	<u>Ecl Maxima.</u> (nm)	<u>Oxidn. Peaks</u>	<u>Redn. Peaks.</u> (V vs. S.C.E.)
Phenanthrene.	+0.3 to -2.7	<u>520.</u>		
	+2.4 to -2.8	< <u>400</u> , 520, 530.		
" ,4,5-methylene	+2.0 to -2.7	414, <u>500</u> , 570.	+1.57	-2.43
	-1.2 to -3.6	500, <u>570.</u>		
" ,9,10-benzo	+1.6 to -3.2	510, <u>530.</u> (st.) <u>460.</u> (unst.)	-	-2.48
Chrysene.	+1.9 to -2.6	< <u>400</u> , <u>403</u> , 433.	+1.54	-2.33
Perylene.	+1.0 to -1.8	<u>475</u> , 520.	+1.08	-1.83
	+1.4 to -2.0	475, <u>525.</u>		-2.24
" ,(ghi)benzo	+1.4 to -2.0	418, <u>455</u> , <u>475.</u>	+1.05	-1.83
				-2.31
Coronene.	+1.6 to -2.4	<u>452</u> , 545.	+1.24	-2.14

If large potential limits were used (Table 3.10), the principal emission maximum was found to lie below 400 nm, and a structured peak with maxima at 520 and 530 nm slowly increased in intensity with time. Using the alternative potential limits listed, a structured peak at 520 nm appeared rapidly, and its intensity soon reached a stable maximum. Controversy exists (see Chapter I) as to whether this long-wavelength emission arises from the triplet state of phenanthrene, or from a decomposition product.

At potentials sufficient to generate both the anion and cation, the ecl emission from 4,5-methylenephenanthrene contained a weak component at 414 nm, and structured components between 500 and 570 nm. The use of greater potential limits produced a marked change in the shape of the spectrum, and an increase in intensity (Fig. 3.14). At neither potential limits was the emission intense enough to permit sensitive calibration data to be obtained for this compound.

The emission from 9,10-benzophenanthrene was also rather weak, and only appeared at potentials in excess of those required for anion and cation formation. The emission obtained from unstirred solutions was of higher intensity than that from stirred solutions, and at a shorter wavelength. Neither corresponded to the fluorescence emission maxima reported by Van Duuren⁶¹ (345, 360, 400 nm).

When stirred, chrysene solutions gave intense ecl at wavelengths corresponding to the fluorescence emission maxima reported by Van Duuren⁶¹



4,5-methylenepheneanthrene.

1. +2.0 to -2.7 V vs Ag
2. +1.2 to -3.6 V vs Ag

(same I scales.)

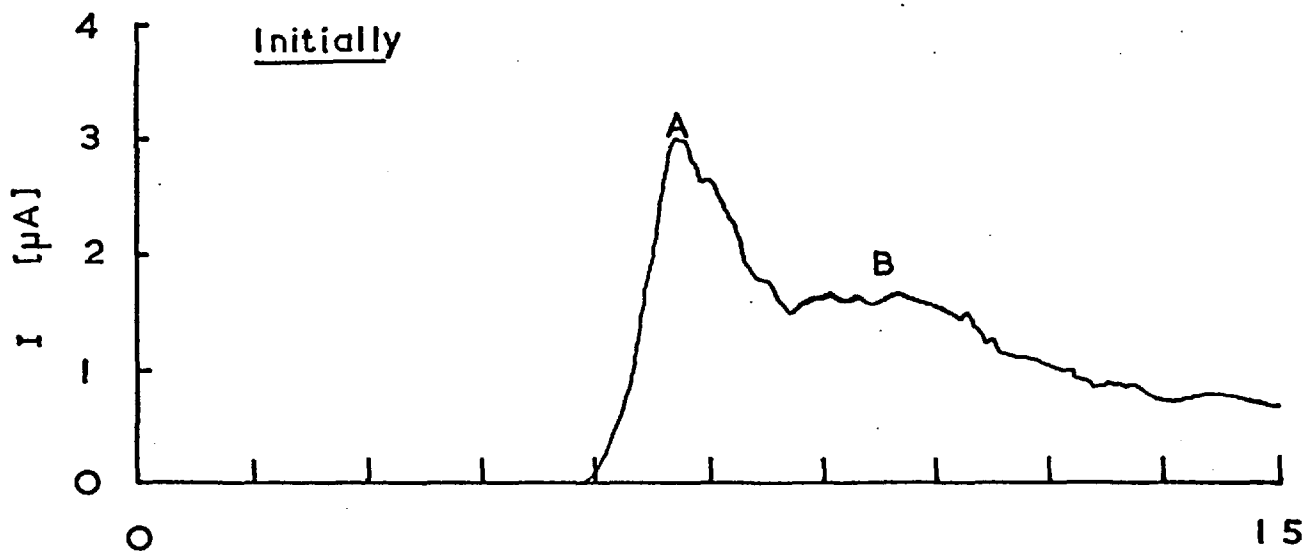
Fig. 3.14

(362, 385, 405, 430 nm). If the stirring was discontinued, the ecl emission slowly decreased in intensity, and a new peak grew at 480 nm. The shape of the emission pulse following the + ve to - ve potential switch was examined oscilloscopically, and revealed that two emission components existed. Fig. 3.15 shows the light pulse initially, and after ten seconds. The light emission appearing most rapidly after the potential switch (Peak A) was found to have an emission spectrum corresponding to the chrysene fluorescence emission. The broad peak B, which grew slowly with time, had an emission maximum at 480 nm.

A possible explanation for this is that, due to the short lifetime of the cation, anions diffusing away from the working electrode initially meet and react with the cation itself, giving the normal singlet emission.

However, anions produced subsequent to this do not interact with cations, which will either have reacted already, or decomposed spontaneously, but rather with cation decomposition products around the electrode. Emission from these could then occur as a result of the mixed annihilation process suggested by Werner⁵⁰ for the anthracenes.

The ecl emission from perylene was intense, but very transient. If the radical anion and cation were generated (Table 3.10), the emission obtained was initially at 475 nm, but very rapidly weakened, and an intense peak at 525 nm appeared. If lower potential limits were used, the emission was less intense, but the peak at 475 nm



Chrysene: 33 Hz +1.9 to -2.6 V

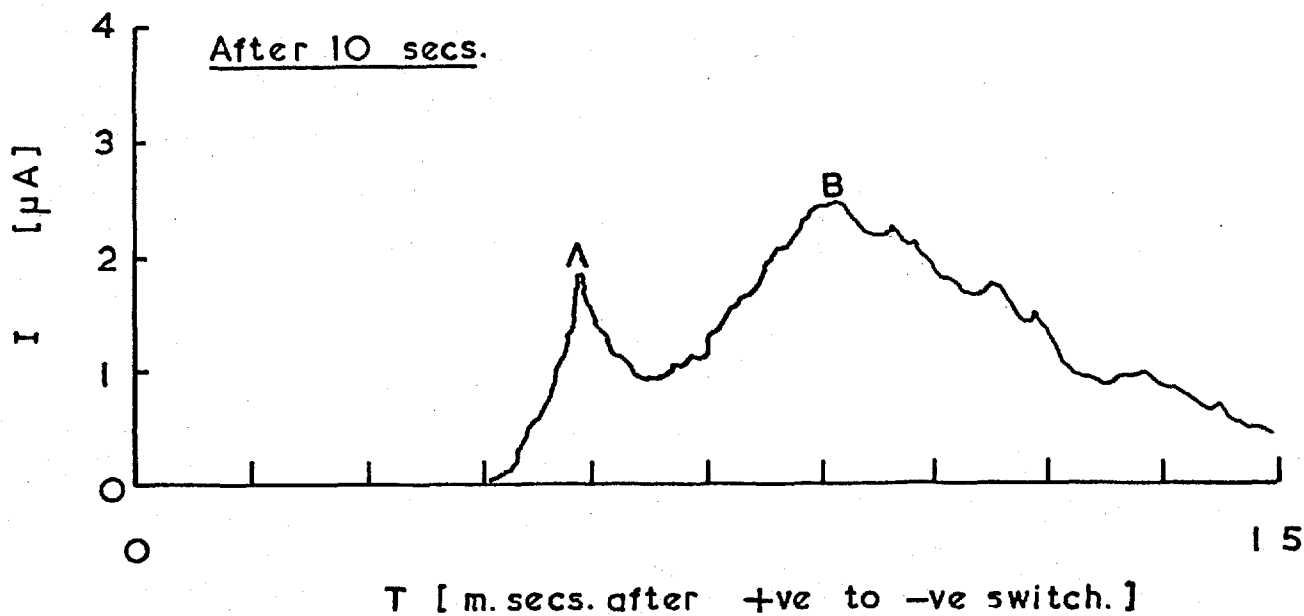


Fig. 3.15

remained stable for several minutes.

(ghi)benzoperylene emitted far more intense ecl, and the spectral distribution did not change with time. The light emission was most intense when the anion and cation were generated, and was much more stable with respect to time than perylene itself.

The ecl from coronene contained two components at 452 and 545 nm. In stirred solution, the peak at 452 nm predominated, and was stable and moderately intense. In the absence of stirring, the peak at 452 nm gradually decreased in height, and the peak at 545 nm began to predominate. Self-absorption of short wavelength components was variable, and was most noticeable immediately after stirring was terminated, and before the peak at 545 nm had begun to increase. This gave rise to the apparent change in the shape of the spectrum noticed in the preliminary experiments (Chapter II).

3.8 Heterocycles and Related Compounds

A number of oxygen, nitrogen and sulphur heterocyclic compounds were available from commercial sources: repeated purification of these was often necessary, in order to obtain literature melting point values for samples that were used. The ecl emission, although bright, was not very reproducible with respect to intensity, and with several of the compounds such as diphenylene oxide, carbazole and indole, very frequent cleaning of the electrodes was needed. Visible tarnishing of the

Table 3.11

<u>Compound.</u>	<u>Ecl Maxima.</u> (nm)	<u>Applied Potential.</u> (V vs. Ag.)
Acridine.	<u>485.</u>	-0.7 to -3.6, 74 Hz, Sq. wave stirred.
Carbazole.	<u>550,</u> 570.	+1.2 to -3.0, 74 Hz, Sq. wave stirred.
Diphenylene oxide.	<u>462.</u>	+1.0 to -2.9, 74 Hz, Sq. wave stirred.
Dibenzothiophene.	<u>538.</u>	-0.5 to -3.5, 74 Hz, Sq. wave stirred.
Phenothiazine.	<u>530.</u>	-2.0 to -3.0, 10 Hz, Triang. wave, unstirred.
Indole.	510, <u>540,</u> 580.	+1.2 to -3.6, 74 Hz, Sq. wave stirred.
N-phenylpyrrole.	<u>525.</u>	+1.5 to -3.0, 74 Hz, Sq. wave unstirred.
1,10-phenanth- roline.	<u>530.</u>	-1.7 V D.C. (MeCl) 2

working electrode occurred in these cases, with concurrent attenuation of the emission intensity. Very few of the compounds showed well-defined oxidation or reduction peaks under the conditions used, and hence the applied potentials in Table 3.11 for the optimum excitation conditions are not particularly critical (c.f. aromatic hydrocarbons), due to the drawn-out nature of oxidation and reduction peaks. Emission only occurred in all cases after several voltage cycles: in the case of phenothiazine, maximum intensity was obtained after several minutes, or less if reduction at ca. -3.0 V (vs. Ag) had been carried out previously.

1,10-phenanthroline gave no light emission in DMF, but intense ecl resulted when reduction at -1.70 V was carried out in methylene chloride solution. This was totally quenched by the addition of small amounts (< 1 mg) of ferrous bromide to the cell, to form a ferrous-phenanthroline complex.

It has been reported¹⁹ that the ecl emission from carbazole under different conditions results from a protonated carbazole anion, or an excited dimeric species. The displacement of most of the ecl spectra of the range of heterocyclic molecules studied from their normal fluorescence singlet emission maxima (usually in the region 300 - 400 nm)⁶³ leads to the conclusion that similar species (or other products) are implicated in the ecl emission of these compounds.

3.9 Alkaloids

The preliminary experiments had shown that several of the alkaloids which were available did show weak ecl after several seconds of electrolysis had elapsed. The optimum conditions found to generate the light emission using 10^{-3} M solutions of the compounds in DMF containing 10^{-1} M TBAP are shown in Table 3.12. In all cases, the ecl intensity rose gradually to a steady value, achieved after about five minutes, and remained at this intensity for at least thirty minutes. Examination of the solutions during the progress of the electrolysis showed that fluorescence at the same wavelength as the ecl emission gradually appeared, accompanied by solution discolouration. The ecl emission was greatest in unstirred solutions, and appeared at voltages corresponding to the reduction of the solvent-electrolyte system itself.

Morphine and thebaine contain a hydro-phenanthrene ring system, which, under some reduction conditions⁶⁸, can be degraded to phenanthrene or phenanthrene derivatives. It seems likely, therefore, that the ecl emission arises from similar compounds formed under the severe conditions of electrolysis used. The brucine molecule contains the indole nucleus, and like strychnine⁶⁸, gives degradation products that are allied to indole, such as carbazole and tryptamine.

Table 3.12

<u>Compound.</u>	<u>Ecl Maximum.</u> (nm)	<u>Applied Potential.</u> (V vs. Ag.)
Brucine.	<u>490.</u>	-0.5 to -3.8 10 Hz, Sq. wave unstirred.
Thebaine.	<u>485.</u>	"
Morphine.	<u>485.</u>	"

3.10 Some Azo Dyes

A large number of azo dyes were examined for ecl using the two-electrode assembly. Compounds which gave moderate to strong ecl emission were examined further using the potentiostat-interference filter assembly.

Table 3.13 lists the ecl characteristics of the more strongly emitting compounds. The signal applied to the working electrode was in all cases a 10 Hz square wave (unstirred solution), except for 2-(2-hydroxy-1-naphthylazo)chrysene, where a 74 Hz square wave (stirred solution) was used.

With the exception of this latter compound, and also 1-phenyl-azo-2-methoxynaphthalene, the intensity of the emission observed was not very great. However, these two compounds gave intense emission, that was stable for at least ten minutes. Shifts in the emission maxima with concentration were observed for both compounds (Fig. 3.16).

Table 3.13

<u>Compound.</u>	<u>Ecl Maxima.</u> (nm)	<u>Applied Potential.</u> (V vs. Ag.)
p-methoxyazobenzene.	<u>550.</u>	+0.2 to -3.0
p-dimethylaminoazobenzene.	<u>550.</u>	"
1-phenylazonaphthalene.	<u>592.</u>	"
1-phenylazo-2- methoxynaphthalene.	<u>595.</u>	"
1-phenylazo-2- hydroxynaphthalene.	<u>595.</u>	"
1-phenylazo-4- methoxynaphthalene.	<u>602.</u>	"
1-(4-methoxyphenylazo) naphthalene.	<u>575.</u>	"
1-hydroxy-8-(1-naphthylazo) naphthalene.	<u>620.</u>	"
2-(2-hydroxy-1-naphthylazo) chrysene.	465, <u>610.</u>	+0.6 to -3.6

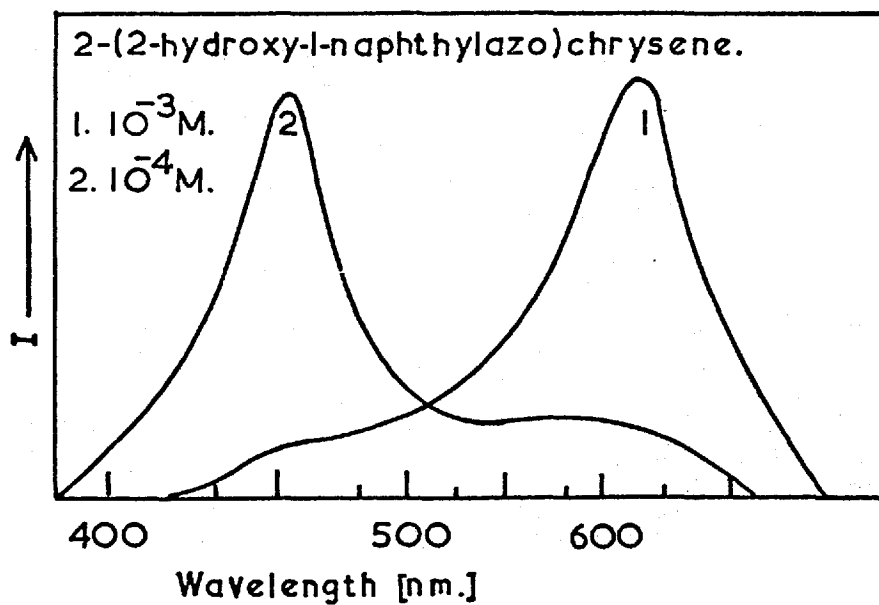
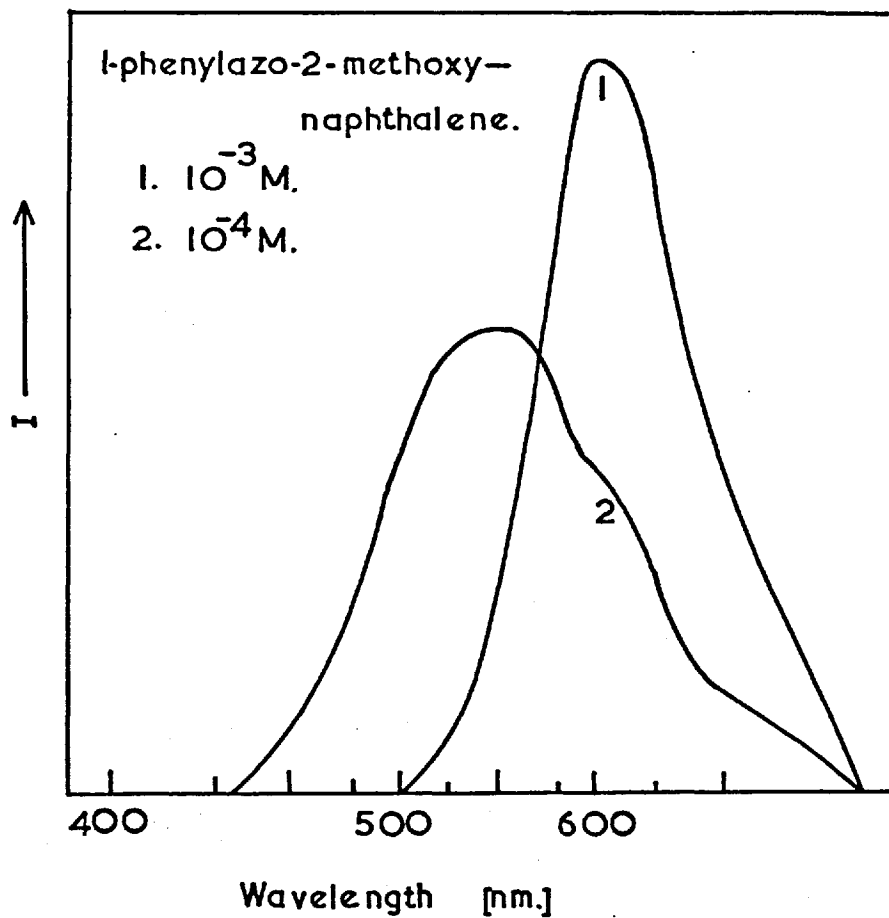


Fig.3.16

CHAPTER IV

Quantitative Measurements of ecl

4.1 Concentration-Intensity relationships

using simple two-electrode systems

In initial experiments to establish the relationship between the ecl emission intensity and concentration over a wide range, the simple two electrode assembly in Fig. 2.1b was used. Solutions were prepared in the cell using a micro syringe. Nitrogen was then passed through the solution, and the total emission intensity measured using the sensitive microammeter.

Fig. 4.1 shows the concentration-intensity relationships obtained for coronene and anthracene over the range 10^{-7} to 10^{-4} M, and 10^{-9} to 10^{-2} M respectively using logarithmic axes. At the relatively large a.c. voltage applied to the electrodes (± 3.5 V), an appreciable emission background of 0.02 μ A photocurrent was obtained for the solvent and supporting electrolyte alone.

Further measurements were made using the spiral electrode pair (Fig. 2.1a) placed in the cell compartment of the Aminco-Bowman spectrofluorimeter. Emission intensities were measured at the experimentally established emission maxima (Fig. 2.2) and plotted on both linear and logarithmic co-ordinates (Fig. 4.2). Each value is the average of four measurements, and was reproducible to within $\pm 5\%$ when care was taken to de-gas the solution for a fixed period of time

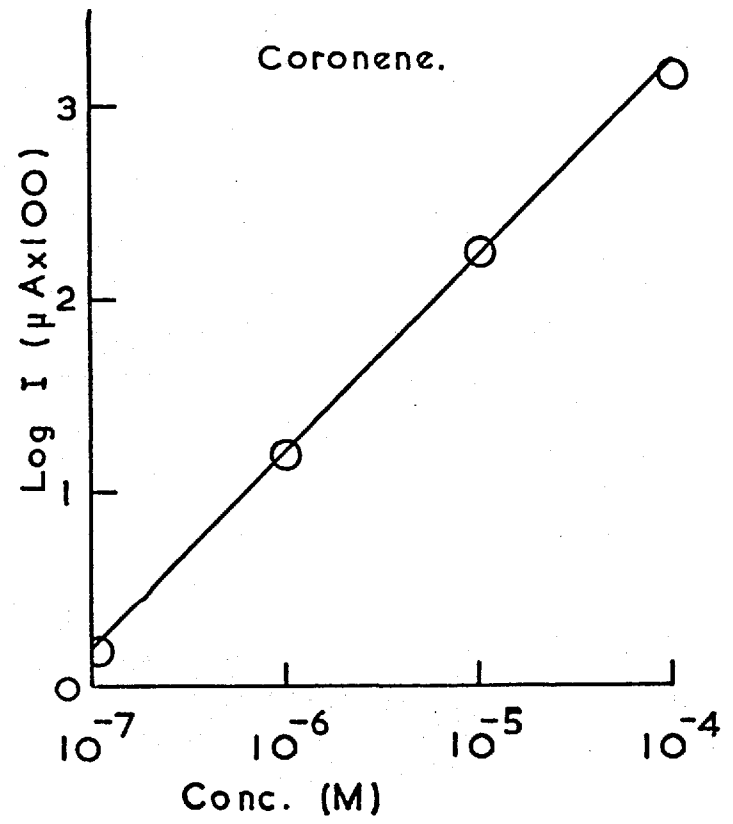
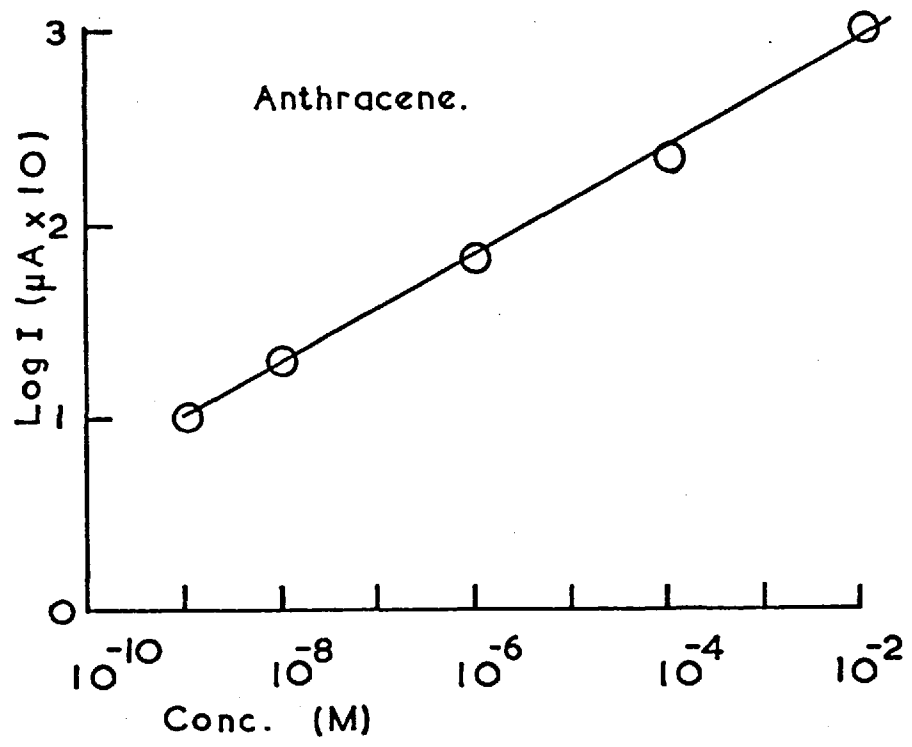
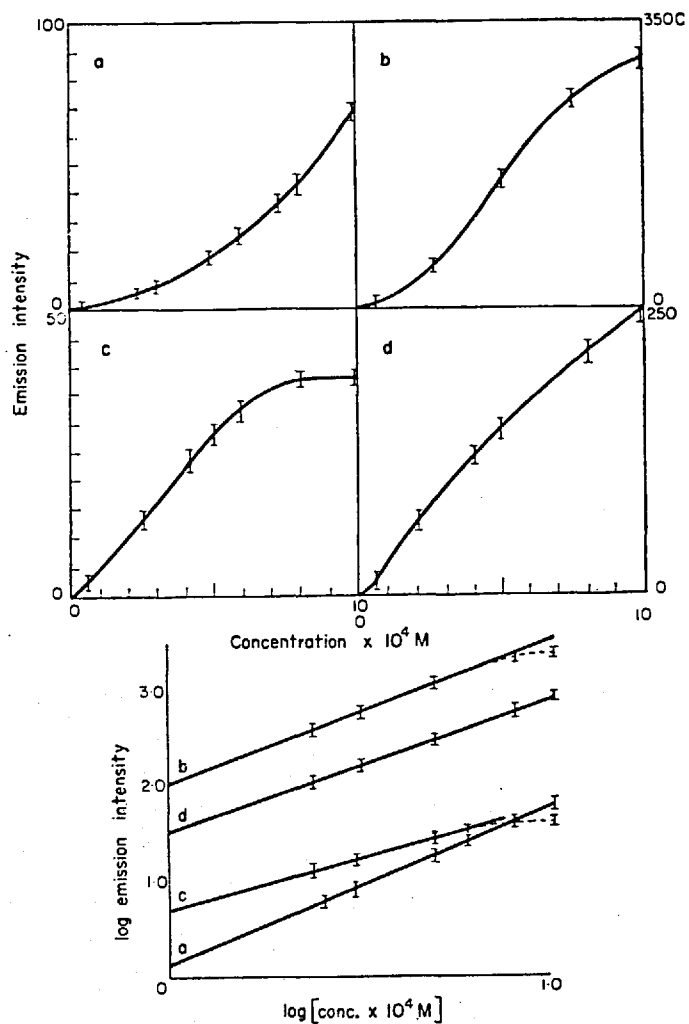


Fig. 4.1



- a. Anthracene.
- b. 9-phenylanthracene.
- c. Pyrene.
- d. Coronene.

in DMF, $\pm 3V$ Applied.

Fig. 4.2

before each measurement was taken. The intensity given is that immediately after the voltage was applied to the electrodes, as rapid decay occurred in all cases.

The lowest concentration detectable was decided principally by the sensitivity of the instrument, as no background emission could be seen, and the baseline noise was very low. As can be seen from the log I vs log C curves, both 9-phenylanthracene and pyrene exhibit concentration quenching effects above about 5×10^{-4} M.

4.2 Quantitative measurements using the potentiostat system

The relationship between the emission intensity and concentration was measured for a representative number of compounds using the potentiostat-interference filter system. The potential and waveform applied to the electrode was that which had been found (Chapter 3) to give optimum emission intensity and stability for 10^{-3} M solutions. The photomultiplier output (measured at the wavelength of maximum emission) was displayed on the potentiometric chart recorder.

The lowest concentration limit in all cases represents the detection limit, which was the concentration sufficient to give a signal to noise ratio of unity. With the exception of phenothiazine, the emission intensity recorded on the chart recorder for concentrations less than ca. 10^{-5} M rapidly reached a peak, and then decayed. Concentrations greater than this produced quite stable readings for most compounds.

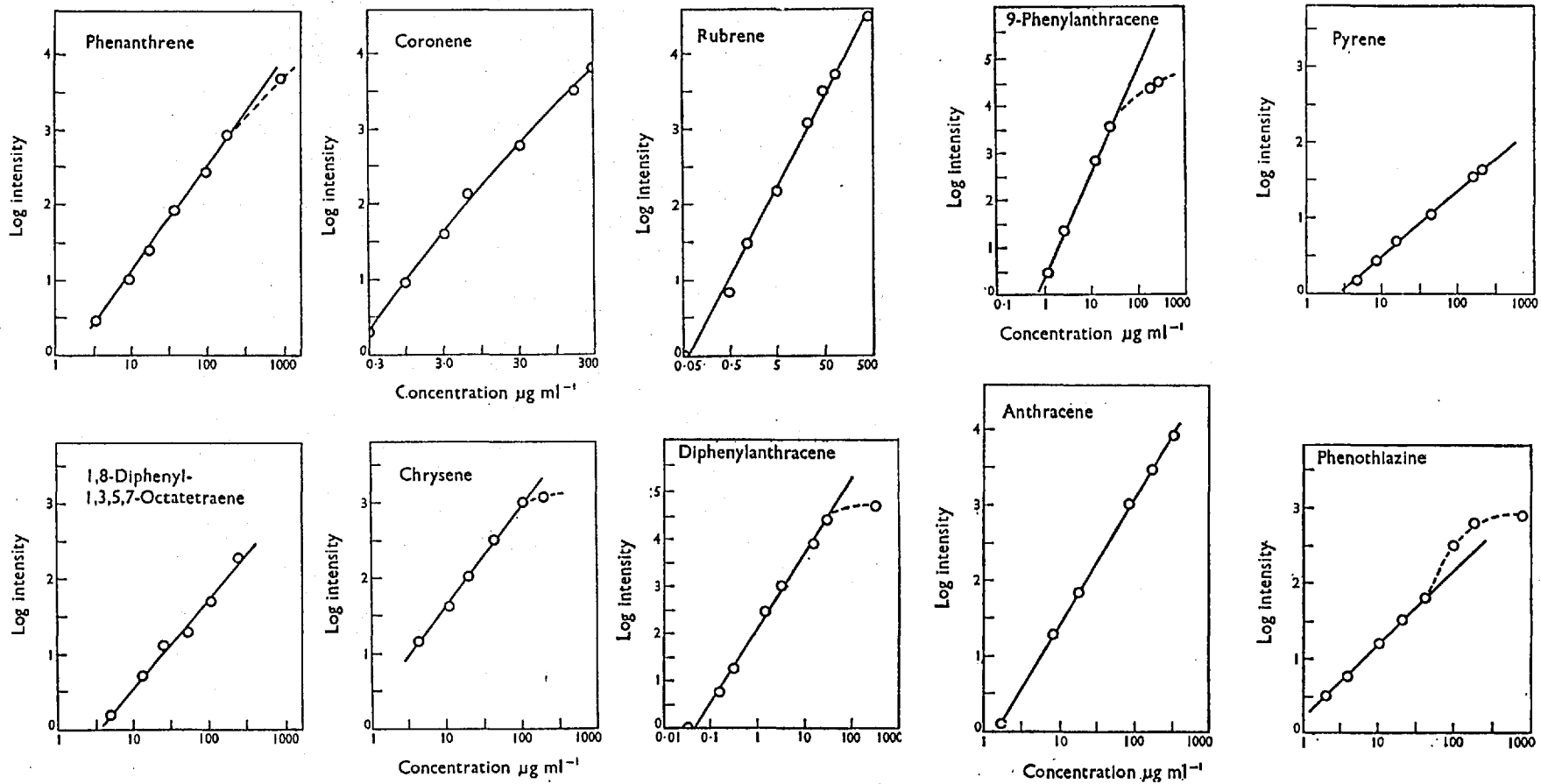


Fig. 4.3

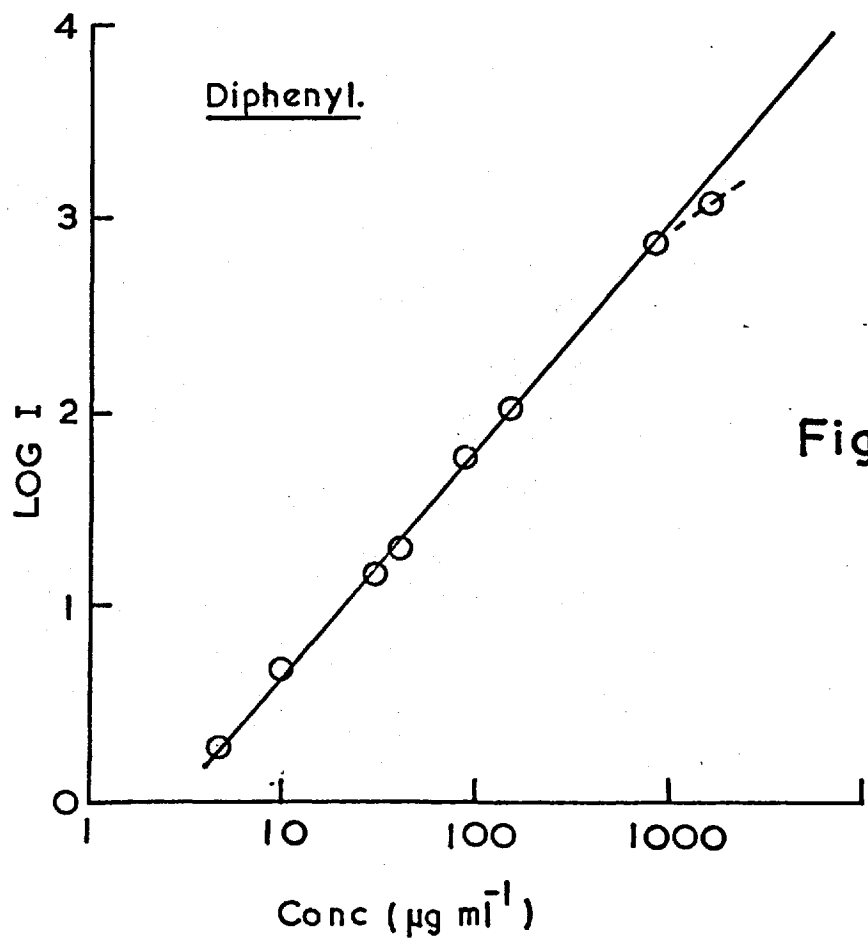
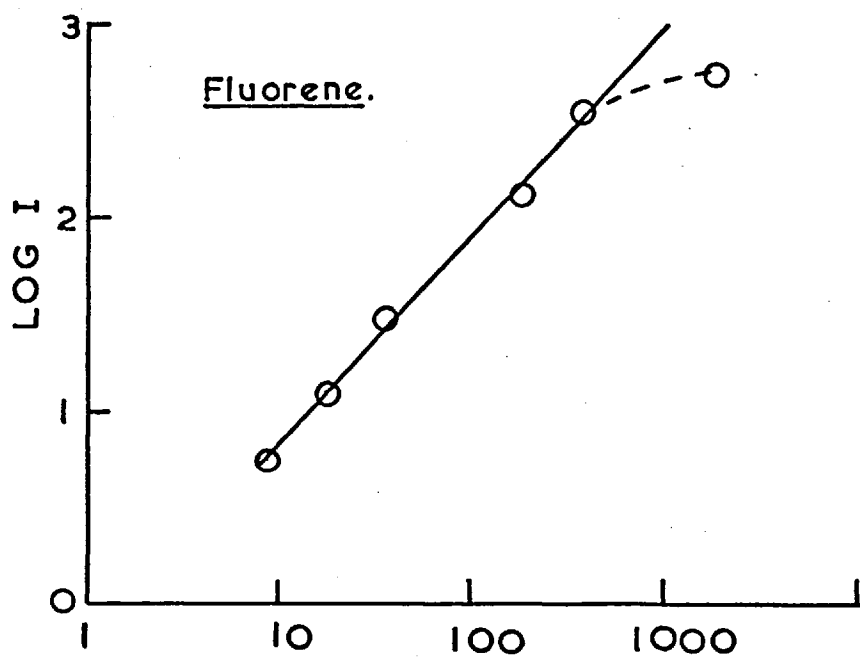
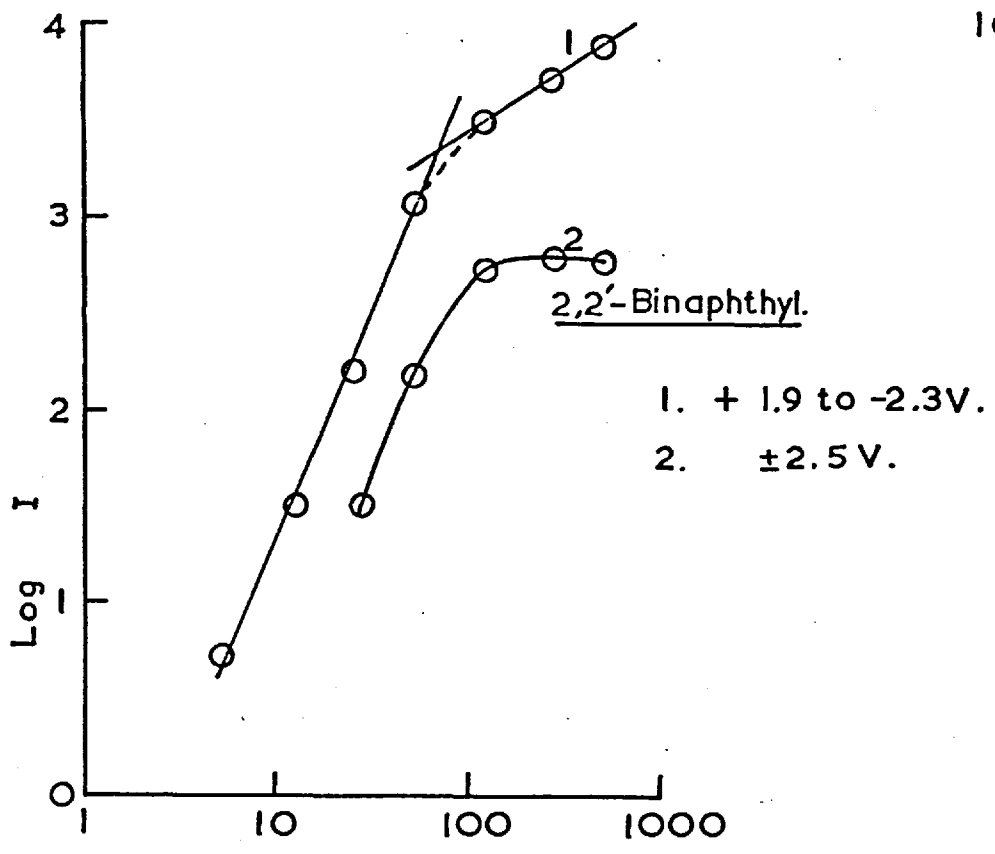


Fig.4.4

At all concentrations, phenothiazine showed a gradual increase in emission intensity with time, reaching a stable maximum within two minutes, and then remaining constant for a considerable period of time (more than 1 hour). The intensity taken for the calibration data was the maximum recorded intensity. In all cases, no background emission was seen for the solvent and supporting electrolyte, provided the voltage limits used did not reach those necessary to both oxidise and reduce the solvent-electrolyte system.

The base-line noise was found to depend only on the dark current variations within the photomultiplier, and on the electronic noise associated with the power supply and the chart recorder. Reductions in the noise level with a corresponding increase in the detection limit, would be obtained by cooling the photomultiplier.

Figs 4.3 and 4.4 show the calibration curves obtained for a number of compounds, with both axes expressed in logarithmic units. Most show a linear portion, curving off towards the concentration axis at high concentrations for some compounds, e.g. phenothiazine. Curvature is much more pronounced if different voltage limits are used than those which correspond to the formation of R^+ and R^- . Fig. 4.5 shows the logarithmic calibration data obtained for the compounds dinaphthyl and fluoranthene using the indicated voltage limits. The use of non-optimum voltage limits results in a loss of sensitivity in both cases, and more pronounced curvature of the calibration graph.



Fluoranthene.

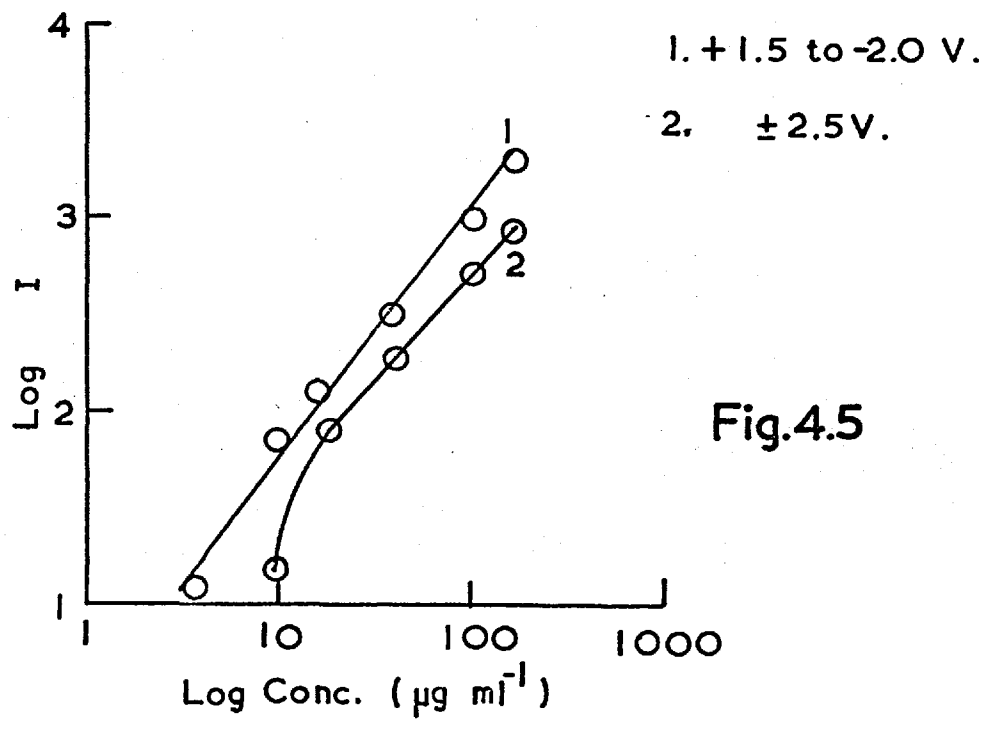


Fig.4.5

All of the intensity figures given are the average of four readings, and the precision is represented in the figures by the size of the circle used at each concentration. The main causes of poor reproducibility in the initial measurements were found to be (i) prolonged or too rapid passage of nitrogen through the sample, with subsequent evaporation and temperature changes of the solution, and (ii) irreproducibility of the surface of the working electrode. This latter effect was best overcome by frequently cleaning the electrodes by vigorous a.c. electrolysis in 0.1 M perchloric acid, and then conditioning by electrolysis of a solution of 10^{-1} M tetrabutylammonium perchlorate solution with a high current density for several minutes. This raised the reproducibility of measurements with compounds such as diphenylanthracene to ca. $\pm 5\%$, although heterocyclic compounds such as carbazole and biphenylene oxide at no time gave results which were reproducible to better than $\pm 25\%$.

Other Solvent Systems

Although solutions of aromatic hydrocarbons in acetonitrile more concentrated than 10^{-4} M gave a weak emission compared to DMF which rapidly decayed as the solution discoloured, very dilute solutions gave a much more stable emission. Fig. 4.6 shows the variation of $\log I$ vs $\log C$ for DPA in acetonitrile. As can be seen, the intensity levels off abruptly above ca. 10^{-6} M, and finally begins to decrease at a high enough concentration. At concentrations less than

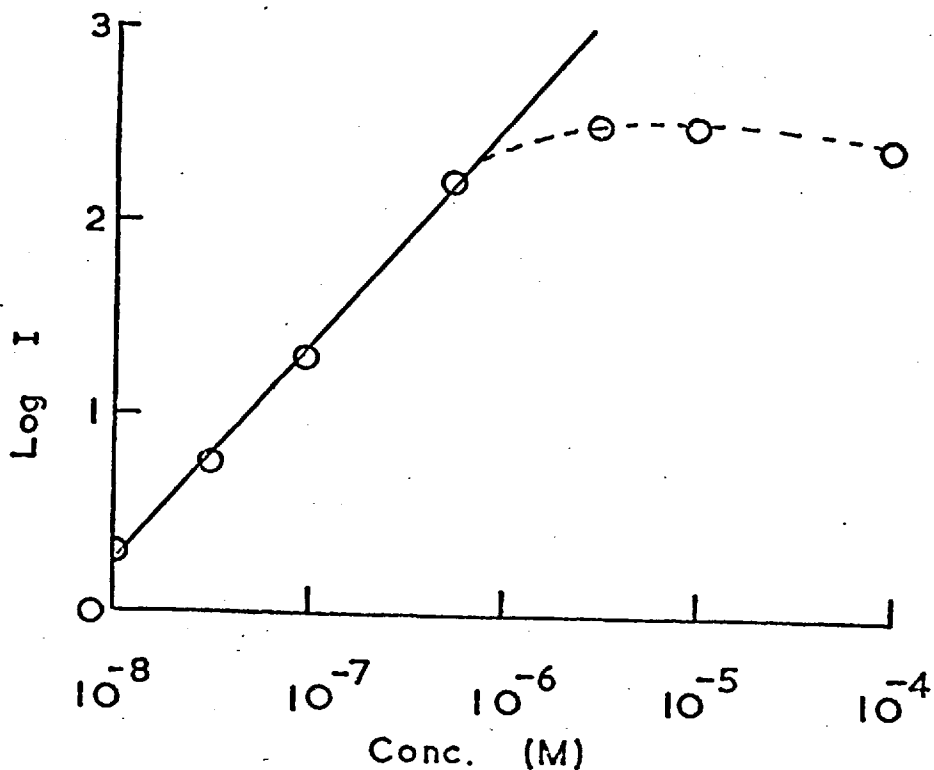


Fig. 4.6

10^{-6} M, the intensity rapidly reached a constant value when the potential was applied to the working electrode, and remained stable for several minutes.

When the solution was allowed to cool down by evaporation, as a result of too rapid gas passage, it was observed that the emission intensity then increased considerably. A 5×10^{-9} M solution of DPA gave a signal which was about eight times above the baseline noise level.

Experiments conducted by freezing the cell contents in an acetone/solid carbon dioxide cooling bath, and allowing them to warm up slowly to room temperature, showed that the emission reached a maximum, and then fell again as room temperature was reached. However, reproducible emission intensity measurements could not be made to take advantage of this increase, without the use of a thermostatted and refrigerated cell compartment as slight temperature changes gave rise to large variations of the emission intensity. DPA solutions in methylene chloride also displayed this increased emission intensity at low temperatures, although the effect was less marked than with acetonitrile.

4.3 The ecl of Solution Mixtures

In order to establish the feasibility of the determination of one hydrocarbon in the presence of others, a series of measurements was made using rubrene and diphenylanthracene as a model system. These were chosen because they had well-separated, intense emission peaks, which did not decay rapidly or give rise to emission from decomposition products. Also, both hydrocarbons gave well defined oxidation and reduction peaks, with a reasonable voltage separation between those of each compound.

To determine the extent of the interference of rubrene upon the ecl of DPA, successive quantities of rubrene, corresponding to concentrations of 0 to 10^{-4} M were added to solutions containing 10^{-3} M DPA and 10^{-1} M

TBAP in DMF. The ecl spectrum of each of these solutions was then obtained, plotted at the optimum potential limits for DPA (Chapter 3), in both stirred and unstirred solutions. Fig. 4.7 shows the resultant variation in intensity of the DPA emission.

The reverse procedure was also carried out, using 10^{-3} M rubrene and successive additions of DPA up to concentrations of 10^{-4} M, electrolysing at the rubrene potential limits. However, this produced no change in the rubrene emission intensity whatsoever, and no DPA emission was seen.

Fig. 4.8 shows the effect on the rubrene and DPA emission intensities of a solution containing 5×10^{-4} M DPA, 5×10^{-4} M rubrene and 10^{-1} M TBAP in DMF when it was electrolysed with a variable amplitude 74 Hz square wave signal.

It can be seen that the emission of light from rubrene is favoured in most cases, compared to emission from DPA, with the result that severe interference is encountered in all measurements of DPA emission intensity; even when the concentration of rubrene is only 10^{-6} M (unstirred), the DPA signal is attenuated by more than 50%. It is evident from the fact that the rubrene signal obtained in this instance is more than thirty times more intense than that obtained for 10^{-6} M rubrene alone, that some form of energy transfer occurs. This could arise from a trivial absorption-re-emission effect, from the overlap of the DPA emission and the rubrene absorption peaks (both at ca. 430 nm), as has been suggested to explain the long-wavelength

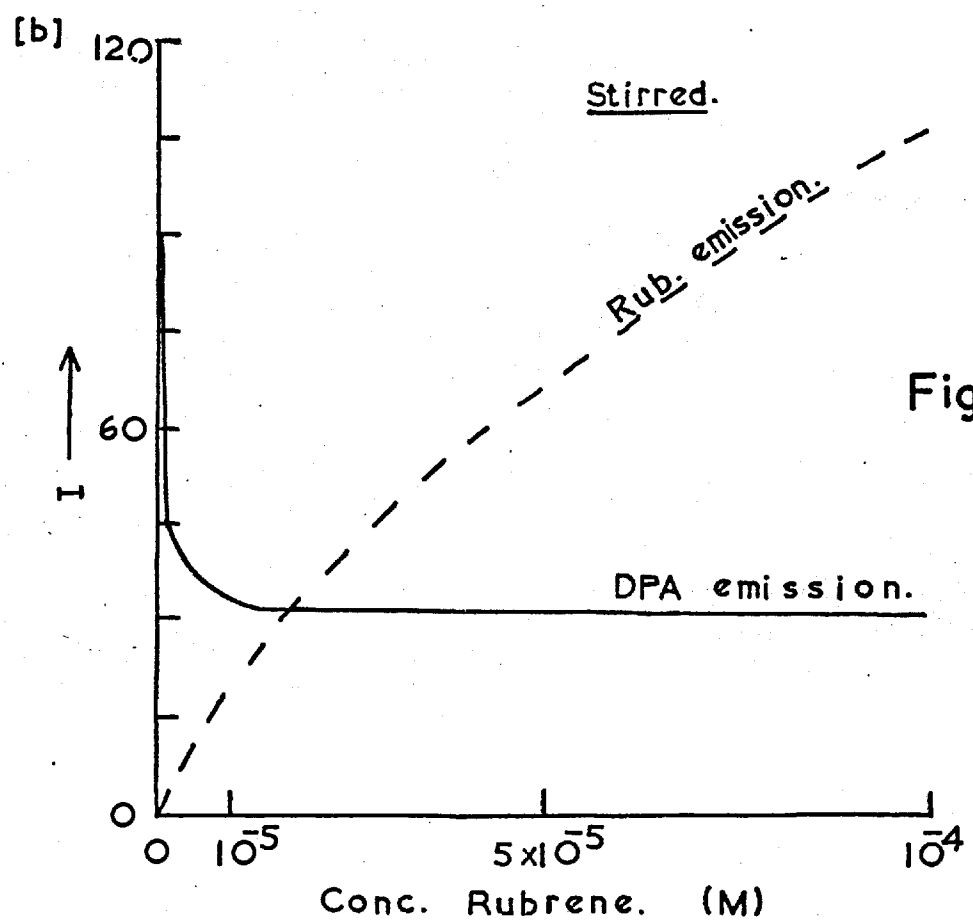
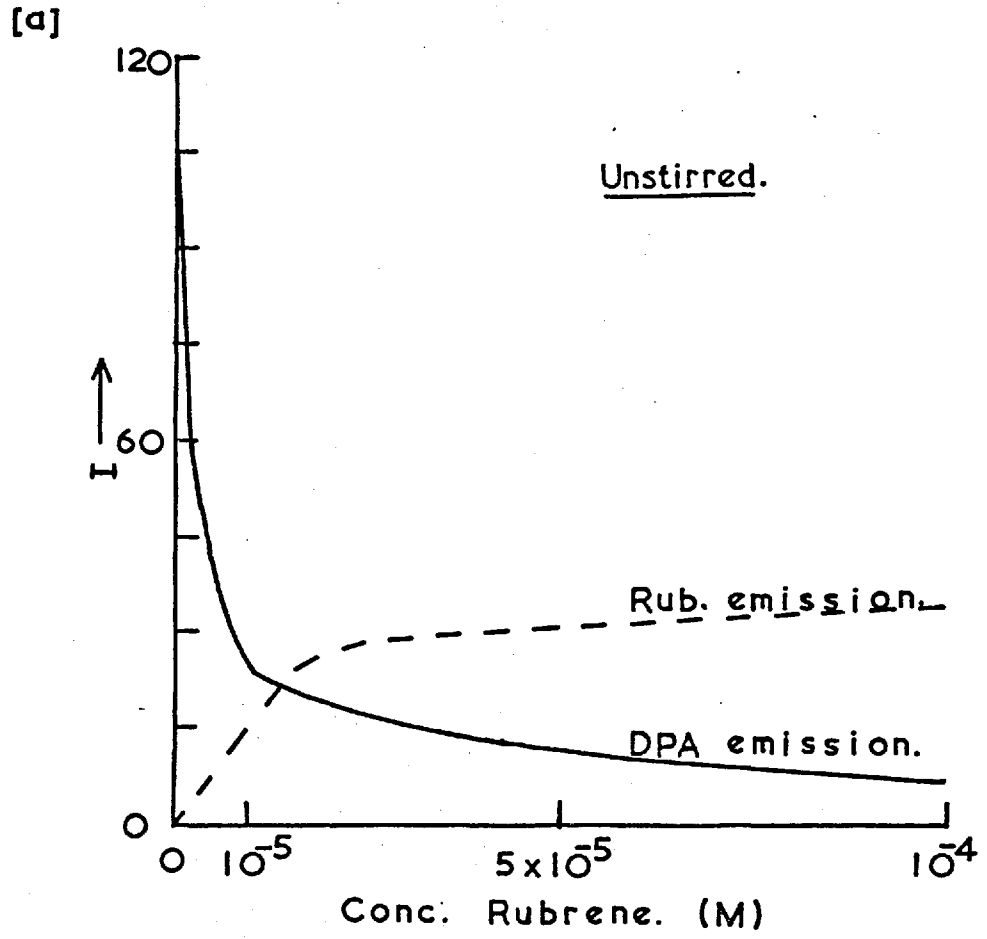


Fig.4.7

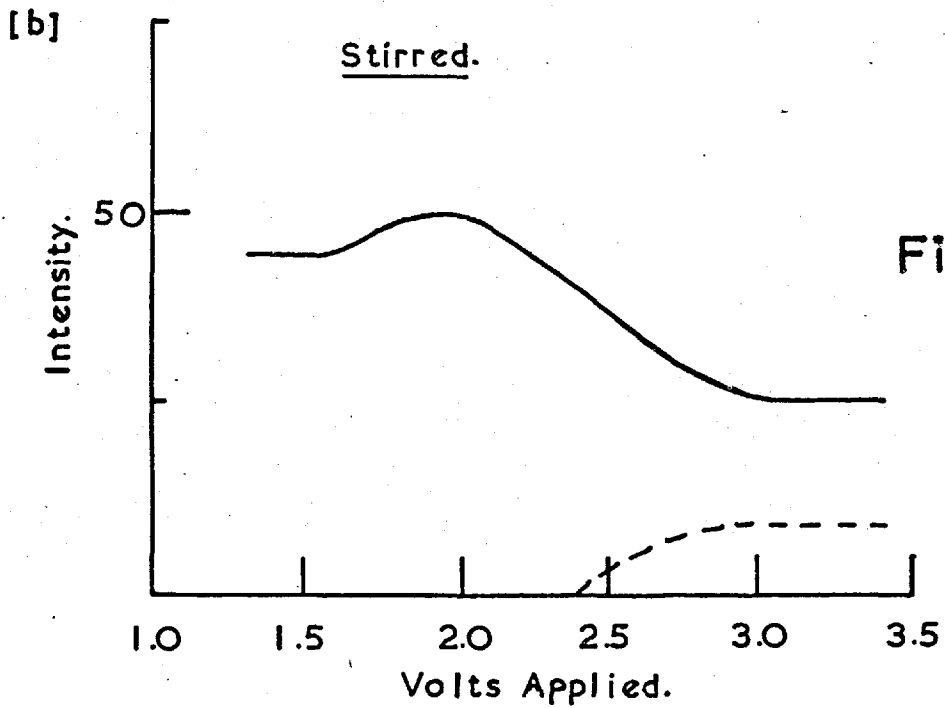
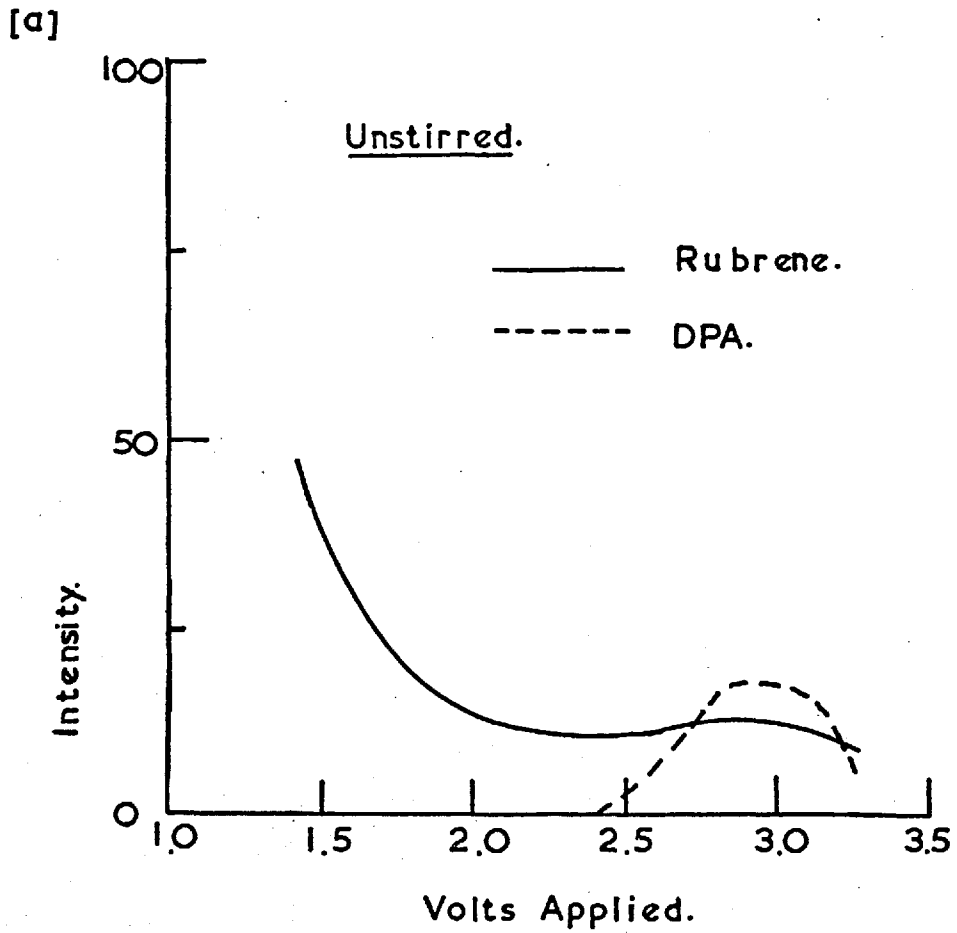


Fig.4.8

emission of anthracene⁴⁹ due to the formation of impurities. Other possibilities that have been suggested for energy transfer in ecl are:-



direct energy transfer from the excited state⁵⁰



mixed cation-anion annihilation reactions⁵⁰.

All of these mechanisms could be operative to some extent, although the first is less likely to be a major contributor, because the interference is severe even when the concentration of rubrene is so small that the absorption of the emitted radiation would not be very strong.

Examination of a series of mixtures of 9-phenylanthracene and anthracene with rubrene showed that a similar effect occurs; emission from rubrene predominated, even when present at very low levels. If a triangular or sine waveform was used to generate the emission, the attenuation of the anthracene or 9-phenylanthracene emission was even greater than with a square waveform, unless very large applied potentials were used. When the potential limits were greater than those required to oxidise and reduce the solvent/supporting-electrolyte system, intense emission was observed from both constituents of the mixture. However, the use of such large potentials precludes the possibility of the selective excitation of individual compounds present.

The addition of many other substances to the DPA system caused a marked reduction in the light emission. Compounds such as quinones etc, whose oxidation or reduction peaks lie between those for DPA, severely attenuated the emission intensity. The addition of water to the system produced a slight enhancement up to levels of ca. 1%, but greater concentrations than this reduced the light emission. All concentrations of water above ca. 100 p.p.m. caused a more rapid decay of the emission and caused the solution to discolour more rapidly.

CHAPTER V

The use of ecl as an additional aid in the identification of aromatic hydrocarbons separated from cigarette tar residues by gas chromatography

5.1 Introduction

Numerous reports linking smoking and health⁶⁹ have led to the analysis of tobacco tar residues for aromatic hydrocarbons of a carcinogenic nature. Very many of these compounds have been identified⁶⁷ by chemical or physical means, following some prior separation step. Because the actual concentration of these compounds in tobacco smoke is very low, the techniques of thin-layer and gas chromatography have been used extensively to separate the components, prior to identification using fluorescence spectroscopy.

Because of its similarity to the technique of solution fluorimetry, it was decided to investigate the application of ecl as an additional technique for the identification of some aromatic polycyclic hydrocarbons, separated from tobacco smoke tar by chemical procedures, followed by preparative gas chromatography.

5.2 Experimental

The instrument used was a Perkin-Elmer F21 Preparative Gas Chromatograph, fitted with a 5 ft x $\frac{1}{4}$ " (10% S.E. 52 on celite) column for preparative work, or a 50 ft x $\frac{1}{8}$ " column containing the same material for analytical measurements. In the preparative mode, 3% of the column eluent was passed to the flame ionization detector, and the remaining 97% was passed into one of eight spiral glass traps, and condensed. The carrier gas used was nitrogen (White-Spot, British Oxygen Co.). The injection head, the collection head and the connecting tube of the instrument were all maintained at 400°C, in order to prevent condensation of the hydrocarbons before reaching the collector.

The column conditions found to give the best separations of synthetic or tobacco smoke mixtures were, for the preparative column: 120 ml per minute carrier gas flow rate, and an exponential temperature increase (Rate 4.5) between 150° and 250°C. With the analytical column, a flow rate of 30 ml per minute was used, and an exponential temperature rate between 150° and 245°C (Rate 3.7), with an initial period of two minutes at 150°C.

The tar mixture was obtained already separated by the method of Ayres and Thornton⁷⁰ from the smoke of 1,500 cigarettes, and was dissolved in cyclohexane (1 ml). Injection of the sample was achieved using a 10 or 50 μ l syringe (Hamilton, Bonaduz, Switzerland). The size

of the sample injected was 3.0 μ l with the analytical column, or 20 μ l with the preparative column.

Peaks which were chosen for collection were trapped out, and the solid material dissolved in 2.0 ml of pure DMF. The u.v. absorption spectrum of this solution was then measured using an S.P. 800 (Unicam Instruments, Cambridge) and the solution fluorescence excitation and emission wavelengths measured using a spectrofluorimeter (Aminco-Bowman, American Instruments Co., Maryland, U.S.A.).

10^{-1} M TBAP was then added, and the ecl properties of the solution established. In addition to this data, GLC retention time measurements were made for each peak, and the number of carbon atoms established by preliminary experiments using the log retention time method⁷¹. Comparison between the analytical and the preparative gas chromatograms obtained assisted in the estimation of the number of components collected as one preparative peak. Identification of the components collected was then attempted using the u.v. absorption maxima listed by Karr⁶⁶, reported values of the fluorescence maxima^{61,63,65} and the list of readily identifiable aromatic hydrocarbons isolated from cigarette tar, compiled by Stedman⁶⁷.

5.3 Results

Fig. 5.1 shows the preparative gas chromatogram that was obtained. Peaks marked as "a, b, c and d" were collected as these were well

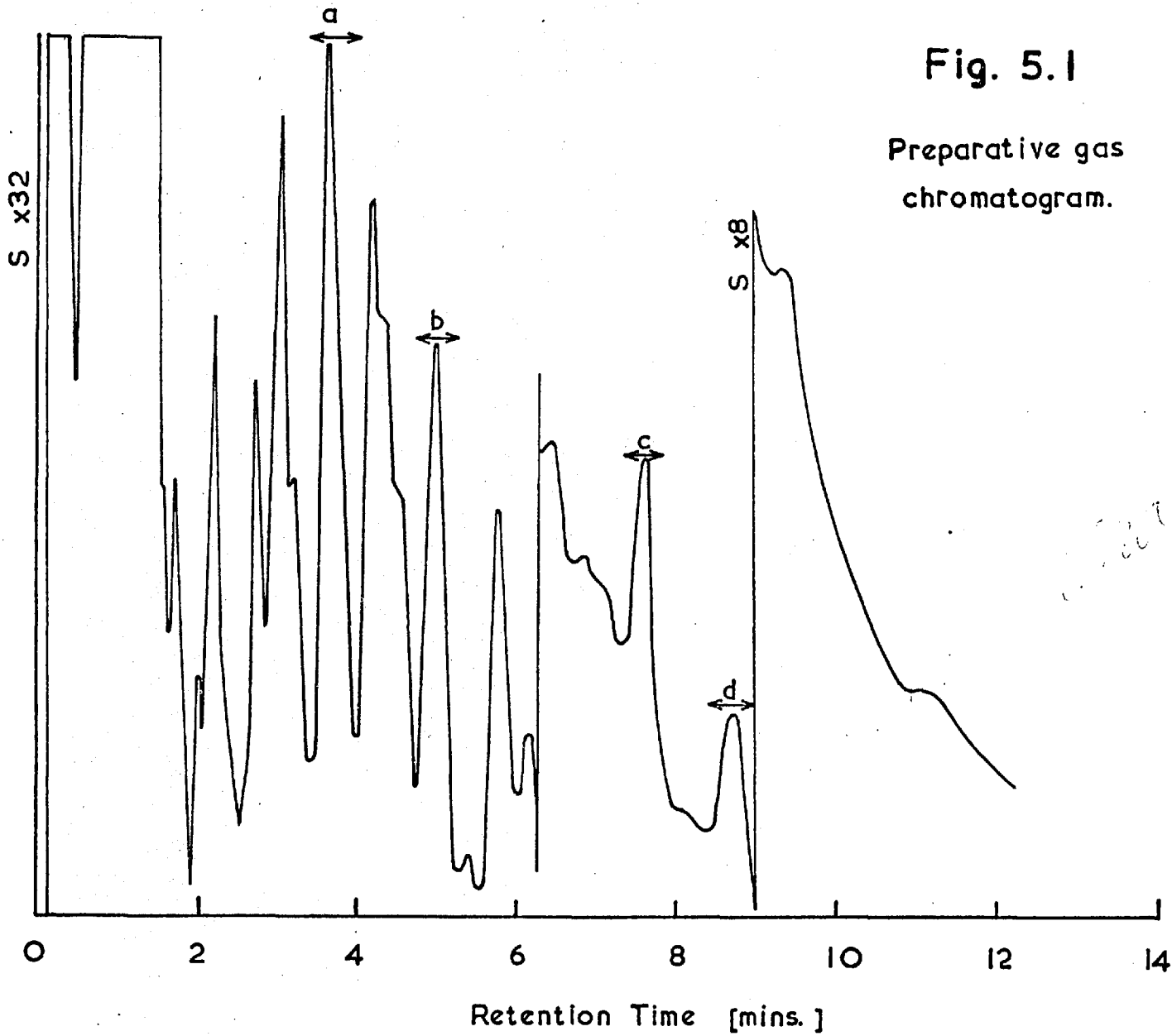


Fig. 5.1

Preparative gas chromatogram.

defined, and corresponded to major components of the mixture. Collection was carried out between the points indicated on each peak. Fig. 5.2 shows the analytical gas chromatogram that was obtained, with the peaks corresponding to a, b, c and d indicated.

Peak (a) (Fourteen Carbon atoms)

Ecl emission maxima:

455, 568 nm

(+ 0.7 → -3.3 V)

U.V. absorption maxima:

287, 308, 325, 340 nm

Fluorescence emission maximum:

335 nm

(Excitation maximum at
300 nm)

These figures correspond very closely to those for 2-methylfluorene, which is a known constituent of cigarette tars. The principal ecl maximum is very similar to that established experimentally for the pure material (570 nm, Chapter III). The fluorescence excitation and emission maxima are also very similar to those of the pure compound (295 and 335 nm respectively). Addition of a very small amount of pure 2-methylfluorene to the aromatic polycyclic fraction before injection into the gas chromatograph caused an increase in the peak height relative to those peaks which occurred at shorter and longer retention times.

It is most probable that peak "a" largely consists of 2-methylfluorene, although it is almost certainly contaminated by other methyl-substituted fluorenes.

Peak (b) (Fifteen Carbon atoms)

Ecl emission maxima:

415, 455 nm (+ 0.9 → -2.6 V)

550 nm (0 → -3.6 V)

U.V. absorption maxima:

267, 271, 285, 293, 310, 322,

362, 381 nm

Fluorescence emission maxima:

345, 352, 370, 387, 412 nm (Excitation maximum at 315 nm)

368, 395, 415, 438 nm (Excitation maxima at 325,

345, 362, 382 nm)

Comparison of the preparative and analytical gas chromatograms showed that this peak is a complex mixture of components. The most intensely fluorescent component (maxima at 368, 395, 415, 438 nm) gave an emission spectrum which greatly resembled anthracene. As this peak is composed of compounds with fifteen carbon atoms, this probably originated from a methyl-substituted anthracene. Other compounds present in this peak probably include methyl-substituted phenanthrene

derivatives. However, the mixture is too complex to allow resolution by this method.

Peak (c) (Seventeen Carbon atoms)

Ecl emission maxima:

406, 428, 440, 535 nm (+ 1.1 → -2.1 V)

560 nm (0 → -3.6 V)

Fluorescence emission maxima:

368, 380 nm (Excitation maxima at 287,
317 nm)

383, 396, 420 nm (Excitation maxima at 330,
342, 380 nm)

U.V. absorption maxima:

315, 328, 345 nm

(Also, weak absorption at 267,

277, 283, 295, 360, 380 nm)

The principal cigarette tar constituents having seventeen carbon atoms include methyl-substituted pyrenes, methyl-substituted fluoranthenes and benz-substituted fluorenes.

The fluorescent component with emission maxima at 383, 396 and 420 nm, and principal excitation maxima at 342 and 380 nm is probably 1-methylpyrene which exhibits emission maxima at 420, 395, 390, 385, 380, 374 nm⁶⁰, and strong absorption bands at 376.5 and 343.5 nm⁶⁶.

Identification from the ecl data was not possible in this case, because no sample of pure 1-methylpyrene was available.

The remaining intense u.v. absorbance peak at 315 nm probably arises from the presence of benzfluorenes. These all have absorption maxima between 336 to 345 nm, and 311 to 317 nm⁶⁶. Neither the ecl nor fluorescence emission spectra was sufficiently resolved or intense to allow more precise identification.

Peak (d) (Eighteen Carbon atoms)

Ecl emission maxima:

540, 578, 620 nm (0 → -3.6 V)

Fluorescence emission maxima:

394, 405, 428, 455 nm (Excitation maxima at 340,
360, 377 nm)

375 nm (Excitation maximum at 325 nm)

U.V. absorption maxima:

267, 275, 277, 283, 295, 310,

325, 338, 343, 347, 360, 378 nm

No identification of this component was achieved. The fluorescence emission at 394, 405, 428 and 455 nm was very well defined, and similar to that of anthracene and alkyl-substituted anthracenes.

5.4 Conclusions

Because of the gas chromatographic system available, it was not possible to obtain reasonably pure components from the cigarette tar. The resolution of the preparative column was not good, as can be seen by a comparison of the analytical and preparative gas chromatograms. Because the analytical column was not of top quality, the resolution obtained with this could be improved considerably. Attempts to obtain purer components by collection of the fractions eluted from the analytical column were not successful, because the response time of the collection system used in the Perkin-Elmer F21 was such that small volumes of carrier gas and material could not be collected without mixing occurring.

With the exception of the first peak, which could be positively identified as 2-methylfluorene, the purity of the other components was not high enough to permit identification by this method. Identification of complex mixtures by ecl was not possible because of the lack of resolution of many ecl spectra observed, and the low resolution of the instrument itself. The latter is a direct consequence of the low intensity of ecl emission compared to solution fluorescence emission. Identification using ecl would only be possible if the GLC peaks collected corresponded to nearly pure compounds.

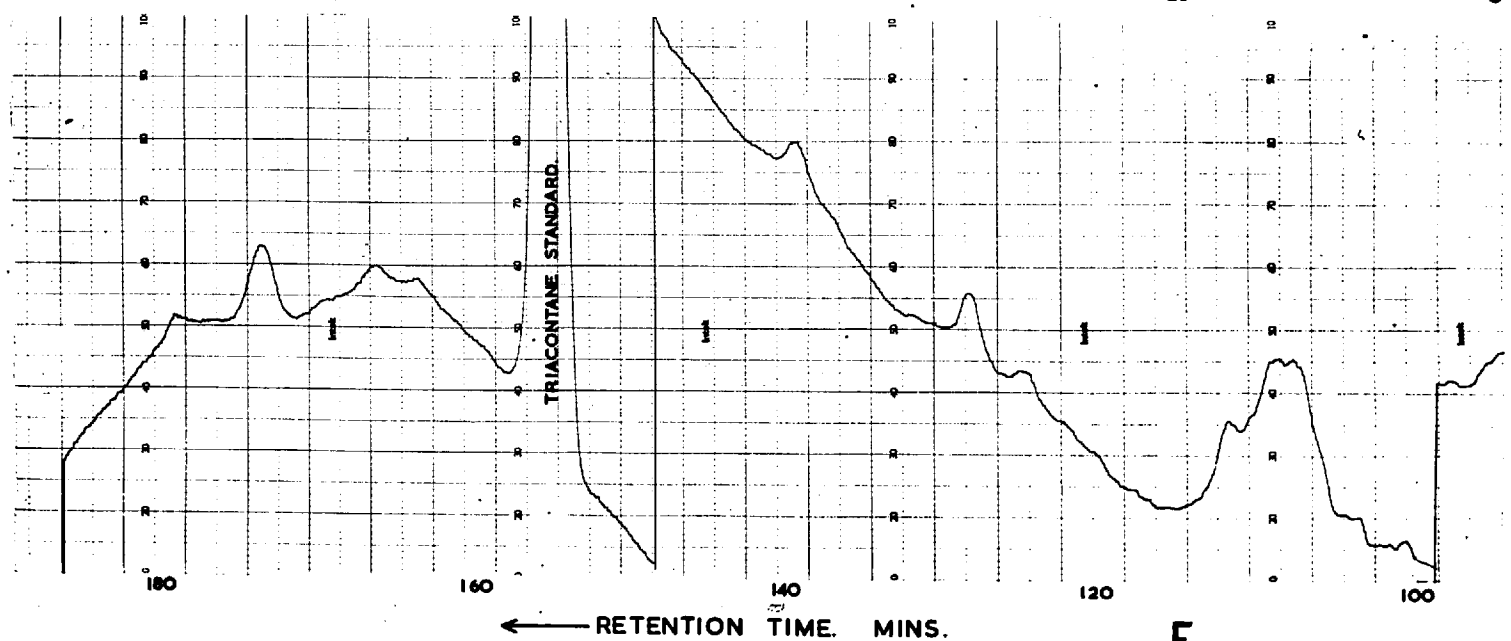
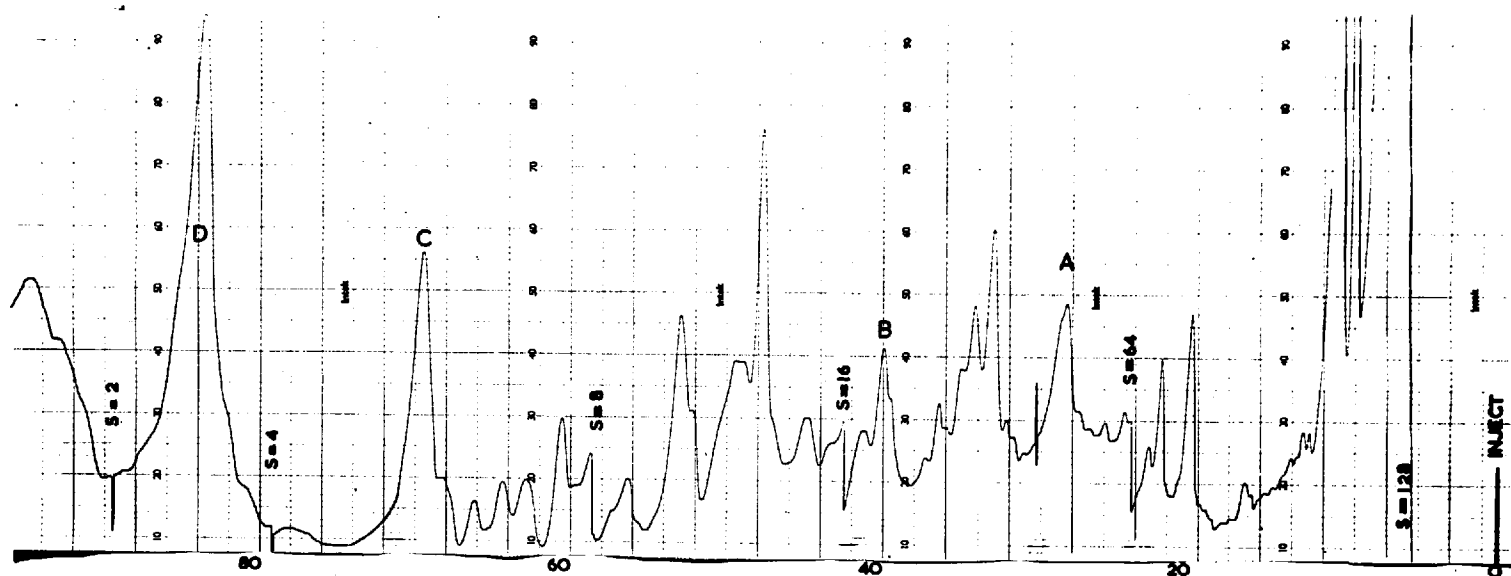


FIG 5.2

CHAPTER VIConclusions and Suggestions for Further Work

Any critical assessment of ecl as a potential analytical technique must inevitably compare it to the technique of solution spectrofluorimetry. In most cases where the hydrocarbon is stable and intensely fluorescent, the emitted fluorescence or ecl radiation arises from the same excited singlet state. This can be seen by a comparison of the wavelengths of ecl and fluorescence emission maxima of many compounds, which are often very similar. In addition, a number of compounds which form excimer species under solution fluorimetry conditions also do so during the ecl process. The principal difference between the two techniques lies in the method of populating the excited state initially.

The excitation of R to R^* by the absorption of radiation is a very rapid process compared to the reaction of R^+ and R^- to give R^* . This must mean that ecl is much more prone to quenching during the initial excitation step than is fluorescence. Other intermediate processes may greatly alter the overall amount and nature of the emission. For example, the condition of the electrode surface has a great influence upon the efficiency of the emission. In addition, the radical ions may react with other species, and give rise to long wavelength emission peaks.

In cases where triplet-triplet annihilation must be invoked to account for the formation of the excited singlet state, then additional intermediate reactions must also be considered. These might be expected to further lower the overall efficiency and reproducibility of the ecl process compared to fluorescence. An examination of, for example, the pyrene series of compounds (Chapter III) shows that triplet involvement must necessarily be a common process. 3,4-benzpyrene, (ah)-dibenzpyrene and (ai)-dibenzpyrene have insufficient energy available from cation-anion annihilation to equal or exceed the singlet energy (calculated from the longest wavelength u.v. absorption band). In addition, some triplet state involvement might be expected in systems where there is only just sufficient energy available.

These factors together help to account for the low intensity of ecl emission compared to fluorescence, and for the difficulty experienced in obtaining reproducible calibration data in some cases.

The initial excitation step is less selective in ecl, because when anions and cations of one component in a mixture are generated, those of other components formed less positively or negatively are also produced. Hence reactions of mixed hydrocarbon anions and cations may occur. However, the excitation step in fluorescence may often be selective, due to the non-overlap of the excitation spectra of individual components in a mixture.

The actual nature of the emitted radiation during ecl tends to be more variable than in solution fluorescence. The lifetime of the emission is often very short and the shape of the emission spectrum may vary considerably during this time. Because of the inherent low-intensity of ecl emission, it is difficult to adequately resolve spectral peaks. In addition, unlike solution fluorescence, the excitation intensity cannot be increased in order to increase the emission intensity. However, no scatter or background exists in ecl, so that very low level ecl signals could be measured if the detection system was sensitive enough, eg. using photon counting, or by cooling the photomultiplier tube. This represents an advantage compared to solution fluorescence, where the detection limit may often be controlled by the scatter from the source.

However, the sensitivity of the potentiostat-interference filter assembly that has been constructed is considerably greater than that of other systems used for the quantitative measurement of ecl reported previously (see Chapter I).

The precision of ecl measurements tends to be rather low, due to the difficulty of obtaining a reproducible electrode surface, and, in some cases, of controlling the temperature. Also, because stirring of the solution is often necessary, a noise component is present on the emission signal, although this can largely be removed by increasing the time constant of the recorder.

However, the biggest limitation on the use of ecl as an analytical technique is the tendency of many compounds to give variable emission maxima depending on the applied potential etc. While this means that compounds such as fluorene and diphenyl can readily be determined (in pure solution), it also means that the technique required for the analysis of mixtures of compounds other than certain stable hydrocarbons (such as rubrene and DPA) would be very complex indeed. This is borne out by the difficulty in interpreting the ecl emission spectra of the separated cigarette tars, (Chapter V).

A possible solution to this problem would be to use a solvent-electrolyte combination which would control the formation of decomposition products to give, for example, only phenolic species, or to use a solvent in which both cationic and anionic radical ions are stable. However, this does not appear to be feasible at the present time.

Ecl is an attractive proposition as a method of studying the nature of certain electrode processes; used in conjunction with optical absorption techniques at the electrode surface, much useful information might be obtained about oxidation and reduction processes of aromatic hydrocarbons in aprotic solvents.

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