ELECTROGENERATED CHEMILUMINESCENCE

PART XXVII. E.C.L. AND ELECTROCHEMICAL STUDIES OF SELECTED LASER DYES

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ABSTRACT

The electrogenerated chemiluminescence (e.c.l.) and electrochemistry of the laser dyes, coumarin-2, coumarin-30, rhodamine-6G (perchlorate), rhodamine-B (perchlorate), oxazine-1 (perchlorate), and Nile Blue (perchlorate) were studied in acetonitrile using 0.1 M tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte. Rather low intensity e.c.l. was obtained for all dyes except Nile Blue. A study of the electrochemical oxidation and reduction of coumarin-30, oxazine-1 and rhodamine-6G using cyclic voltammetry and controlled potential coulometry demonstrated that chemical side reactions of the electrogenerated reactants are responsible for the low e.c.l. efficiency. In several cases the one-electron transfer reaction at the electrode is followed by a dimerization reaction. The neutral free radical formed on reduction of oxazine-1 was investigated by electron spin resonance spectroscopy and coupling constants for it are reported. Some experiments in which the e.c.l. of mixtures of the dyes with rubrene or 9,10-diphenylanthracene were determined are also described.

INTRODUCTION

Although a wide variety of compounds have been employed in electrogenerated chemiluminescence (e.c.l.) experiments [1—7], the highly fluorescent dyes employed in dye lasers have not been investigated, except for a brief study by Han [8]. These dyes are especially interesting in connection with proposed e.c.l. devices, such as displays and lasers [9—15]. The requirements for suitable compounds for intense e.c.l. include not only a high fluorescence quantum efficiency, but also good stability of the oxidized and reduced forms producing the excited states upon electron transfer (frequently radical ions). Moreover the energy of the electron transfer reaction must be sufficient to produce excited states of the products. Thus a brief study of the electrochemical behavior of the compounds to estimate reversible potentials and gauge stability is required.

We report here such studies of some selected laser dyes. Two compounds were chosen from each class of laser dyes. The selection was made on the ba-

TABLE 1

Cyclic voltammetry and e.c.l. results

| Compounds | Solvent | Concn. /mM | Peak potentials [c]/V | | | | | | Reference electrode | $\Delta H^{0\ a}$/ eV | Emission | |
| | | | Oxidation | | | Reduction | | | | | Fluorescence | E.c.l. |
			E_{p_1}	E_{p_2}	E_{p_3}	E_{p_1}	E_{p_2}	E_{p_3}			$h\nu_{fl}$ [b]/nm (eV)	$h\nu_{e.c.l.}$/nm (eV)
Coumarin-2	ACN	1.07	1.004	2.20	—	−2.205	—	—	SCE	3.05	420 (2.95)	~455 (2.72)
	DMF	1.02	1.096	—	—	−2.096	—	—	Ag	3.03	—	434 (2.85) 502 (2.47)
	THF	1.53	1.049	—	—	−2.208	—	—	Ag	3.10	—	Nil
Coumarin-30	ACN	0.96	1.055	1.250 (72)	2.078	−1.780	—	—	SCE	2.68	480 (2.58)	480 (2.58)
	DMF	1.30	1.168	—	—	−1.737	—	—	Ag	2.74	—	Nil
	THF	1.19	1.138	1.279 (79)	—	−1.800	—	—	Ag	2.78	—	Nil
Nile Blue	ACN	0.89	1.164 (60)	1.817	2.1	−0.436 (153)	−1.369 (71)	—	SCE	1.44	700 (1.77)	Nil
	DMF	0.89	1.070	—	—	−0.516 (156)	−1.415 (122)	—	Ag	1.45	—	Nil
	THF	1.20	1.155 (105)	—	—	−0.383 (266)	−1.415 (122)	—	Ag	1.38	—	Nil
Oxazine-1	ACN	1.21	1.226 (68)	1.97	2.36	−0.414 (54)	−1.263 (67)	—	SCE	1.48	699 (1.77)	699 (1.77)
	DMF	0.90	1.205	—	—	−0.440	−1.310	—	Ag	1.48	—	700 (1.77)
	THF	1.25	—	—	—	−0.754 (57)	−1.720 (86)	—	Ag	—	—	—

TABLE 1 (continued)

Compounds	Solvent	Concn. /mM	Peak potentials [c]/V						Reference electrode	ΔH^0 [a]/ eV	Emission	
			Oxidation			Reduction					Fluorescence	E.c.l.
	E	E	E_{p_1}	E_{p_2}	E_{p_3}	E_{p_1}	E_{p_2}	E_{p_3}			$h\nu_{fl}$ [b]/nm (eV)	$h\nu_{e.c.l.}$/nm (eV)
Rhodamine-B	ACN	1.01	1.218 (73)	1.868 (203)	2.2	−0.757	−1.224 (66)	−1.912 (103)	SCE	2.28 [d]	610 (2.03)	610 (2.03)
	DMF	1.35	1.206	—	—	−0.758	−1.086 (116)	−1.763	Ag	2.13	—	Nil
Rhodamine-6G	ACN	0.93	1.258 (79)	1.999 (205)	2.45	−0.916 (82)	−1.694 (118)	−2.3	SCE	2.00	573 (2.16)	573 (2.16)
	DMF	1.09	1.225	—	—	−0.687 (70)	−1.454 (162)	−2.2	Ag	1.75	—	584 (1.81)

[a] ΔH^0 was calculated from eqn. $-\Delta H^0 = E_{p,ox} - E_{p,red} - 0.16$ eV (see ref. 23).

[b] Fluorescence spectra were measured in acetonitrile solutions. Oxazine and rhodamine dyes were in perchlorate forms. E_T's of rhodamine-B and -6G were reported as 2.05 and 1.79 eV, respectively [24]. This triplet energy level of rhodamine-B is higher than the singlet energy level obtained from fluorescence peak in acetonitrile (2.03 eV). This may be due to a solvent effect (water was used in ref. 24).

[c] ΔE_p values were recorded in parentheses below each peak potential where they can be measured.

[d] ΔH^0 for rhodamine-B is for reaction between the first oxidation and second reduction waves.
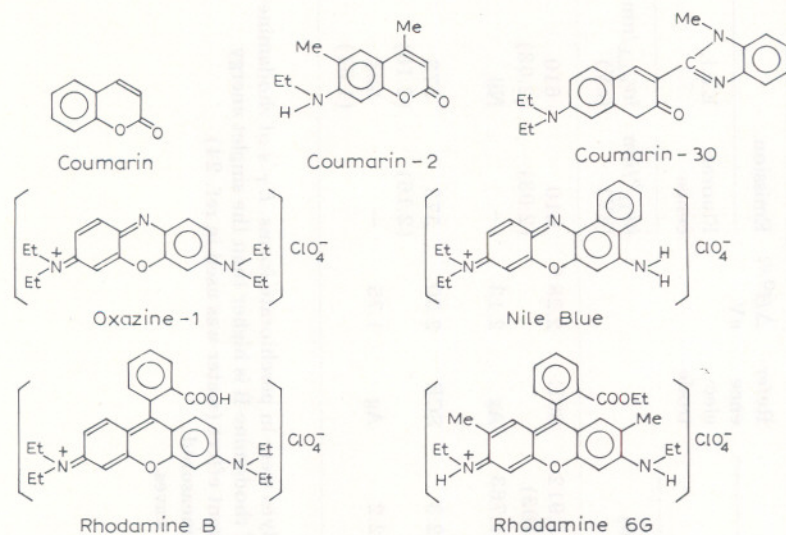
Fig. 1. Molecular structures of compounds used in this study.

sis of the chemical structure of the compounds, choosing those which are expected to show stable electrochemical behavior. The selected compounds, shown in Fig. 1, were coumarin-2 and coumarin-30 from the coumarin dyes, Nile Blue and oxazine-1 perchlorate from the oxazine dyes, and rhodamine-6G and rhodamine-B (both in the perchlorate forms) from the rhodamine dyes.

EXPERIMENTAL

Special laser grade coumarin-2, coumarin-30, and oxazine-1 perchlorate were obtained from Eastman Organic Chemicals and used as received. Nile Blue sulfate (Eastman Organic) was recrystallized from absolute ethanol; the ethanol solution was then passed through Dowex 2-X8 anion exchange resin, which had been converted to the perchlorate form by washing with 5% perchloric acid until no further chloride was detected with silver nitrate. The Nile Blue perchlorate thus prepared was recrystallized twice from absolute ethanol. The chloride forms of rhodamine-6G and rhodamine-B (both Eastman Organic) were also converted to their perchlorate forms by the procedure described above. Rubrene (Aldrich) and p-benzoquinone (Matheson, Coleman and Bell) were used after double vacuum sublimation. Polarographic grade tetra-n-butyl-ammonium perchlorate (TBAP) of Southwestern Analytical Chemicals was used as a supporting electrolyte after being dried in a vacuum oven at 120°C for at least 24 h. This was stored either in the dry box under a helium atmosphere or in a desiccator. Spectroquality acetonitrile (ACN), tetrahydrofuran
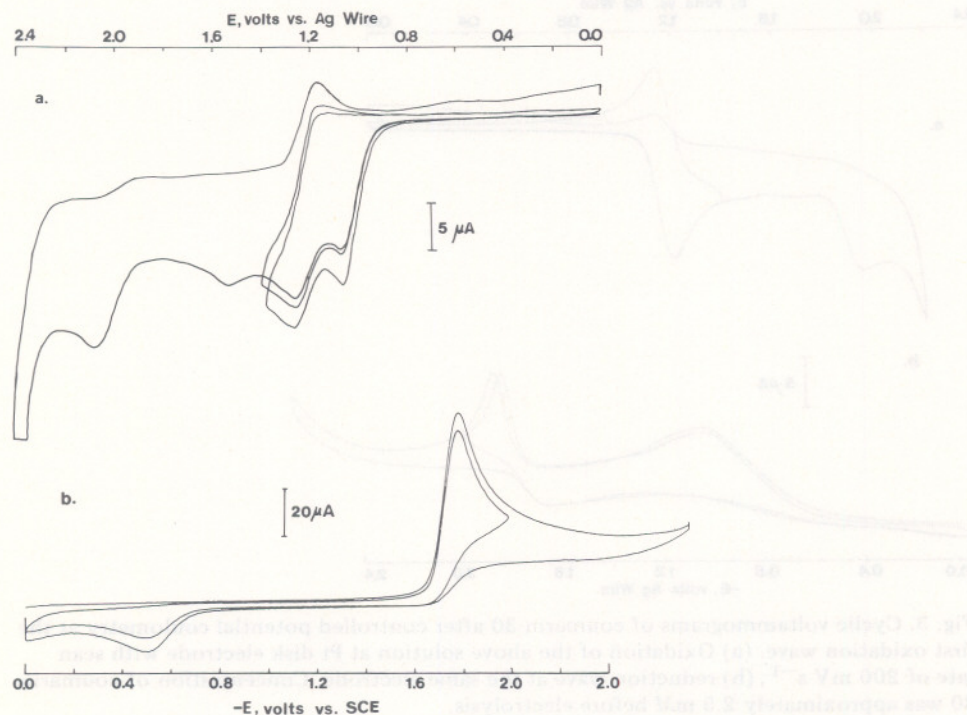
(THF) and benzonitrile (BzCN) (all from Matheson, Coleman and Bell) were used as solvents after drying as previously reported [16]. N,N-dimethylfor-mamide (DMF) was distilled under nitrogen at reduced pressure following a previously described procedure [17] and was stored in an inert atmosphere glove box.

Most of the solutions in this work were prepared in the dry box by adding the solvents directly into a volumetric flask containing weighed amounts of the dyes and the supporting electrolyte (TBAP). THF solutions were prepared by vapor transfer on a vacuum line directly into the cell while the BzCN solution was produced by decanting the solvent into the cell in the open air. Both of these solutions were degassed by repeated freeze-pump-thaw cycles on the vacuum line.

The electrochemical and e.c.l. experiments generally followed procedures and employed instrumentation previously described [16]. All results were obtained with platinum working electrodes.

RESULTS

The electrochemical, fluorescence and e.c.l. measurements are summarized in Table 1. Typical electrochemical and e.c.l. results are shown in Figs. 2—6. Data on the coulometry and cyclic voltammetry of coumarin-30, rhodamine-
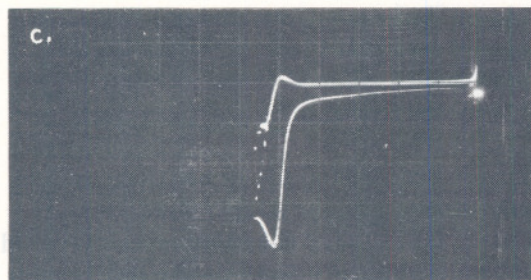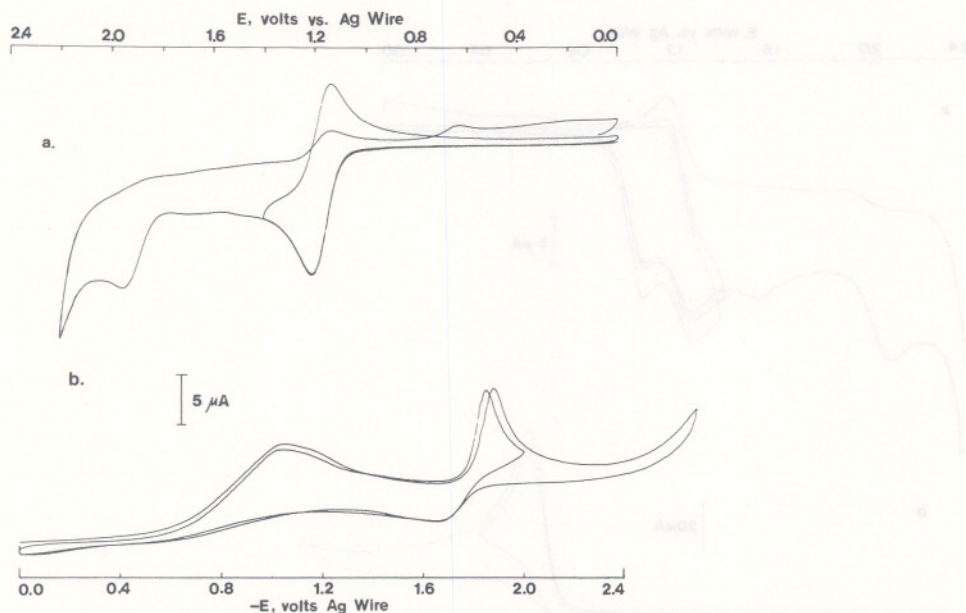

Fig. 3. Cyclic voltammograms of coumarin-30 after controlled potential coulometry. That oxidation wave. (a) Oxidation of the above solution at Pt disk electrode which was at a rate of 500 mV s⁻¹. (b) reduction ... approximately 2.5 mM before electrolysis.

Fig. 2. Cyclic voltammograms of coumarin-30 (1.0 mM) in ACN at Pt wire with scan rate of 200 mV s^{-1}. (a) Oxidation; (b) reduction; (c) oxidation at Pt disk electrode with scan rate of 1 V s^{-1} (1.6 mM).

6G, and oxazine-1 are given in Tables 2 and 3. Only one compound from each class of the laser dyes was chosen for coulometric studies, based on structural and electrochemical considerations. Coumarin-30 was chosen, because it was expected to give a more stable cation radical than coumarin-2. Rhodamine-6G was selected, because rhodamine-B has an easily reducible proton on its carboxylic acid group. Oxazine-1 was chosen because it was probably purer than

Fig. 3. Cyclic voltammograms of coumarin-30 after controlled potential coulometry at the first oxidation wave. (a) Oxidation of the above solution at Pt disk electrode with scan rate of 200 mV s^{-1}; (b) reduction wave at the same electrode. Concentration of coumarin-30 was approximately 2.5 mM before electrolysis.
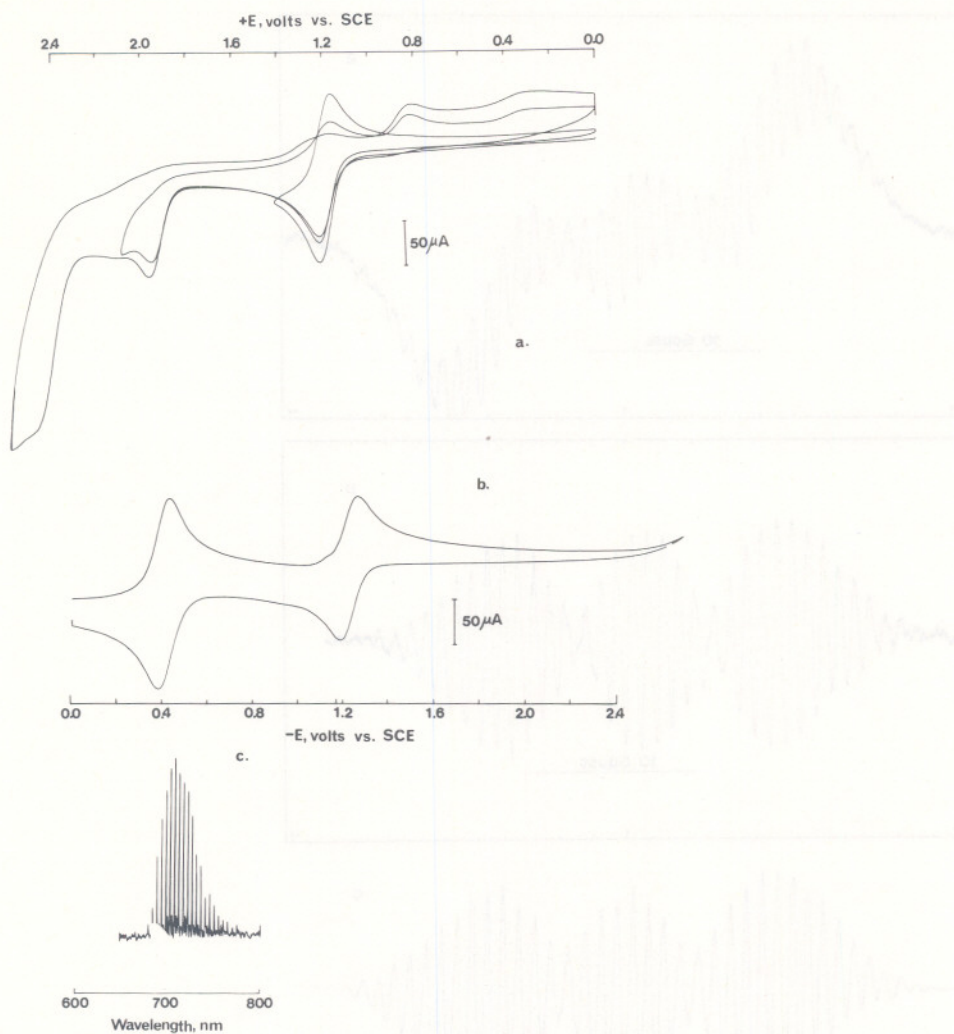
Fig. 4. Cyclic voltammograms of oxazine-1 perchlorate (1.2 mM) in ACN. (a) Oxidation; (b) reduction at Pt wire electrode with scan rate of 200 mV s^{-1}; (c) e.c.l. recorded from above solution with pulse duration of 1 s.

the Nile Blue. Since the electrochemical behavior of these compounds has not been reported previously, the oxidation and reduction peak potentials of all laser dyes in ACN solutions were measured with respect to an aqueous saturated calomel electrode (S.C.E.) in order to document their values vs. a known reference electrode. The values obtained in DMF and THF solutions, mostly for ΔH^0 calculations, were determined against a silver wire pseudo reference electrode.
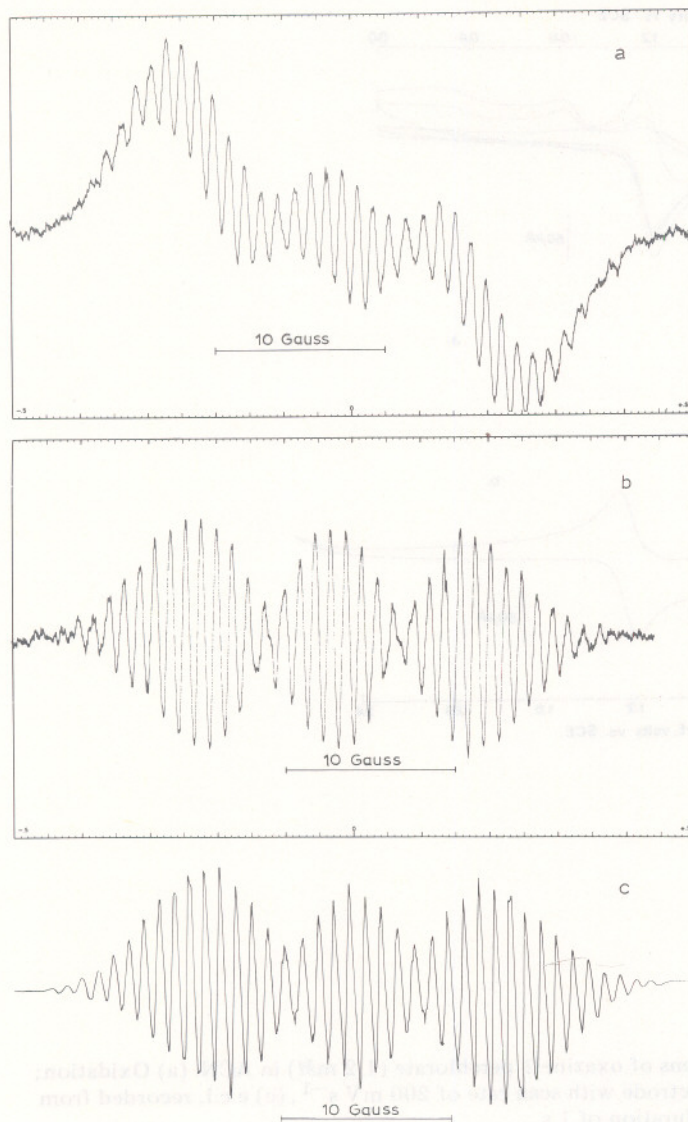
Fig. 5. (a) E.s.r. spectrum recorded for oxazine-1 perchlorate after controlled potential electrolysis at the first reduction wave (c = 2.0 mM before electrolysis); (b) e.s.r. spectrum recorded for the same solution after electrolysis at the second reduction wave; (c) computer simulated spectrum using coupling constants given in Table 4.

These results show qualitatively that oxazine and rhodamine dyes generally form quite stable species upon oxidation or reduction at a platinum electrode. The coumarin dyes generated very unstable radical anions upon reduction, while the stability of the radical cations of the coumarin dyes depended on
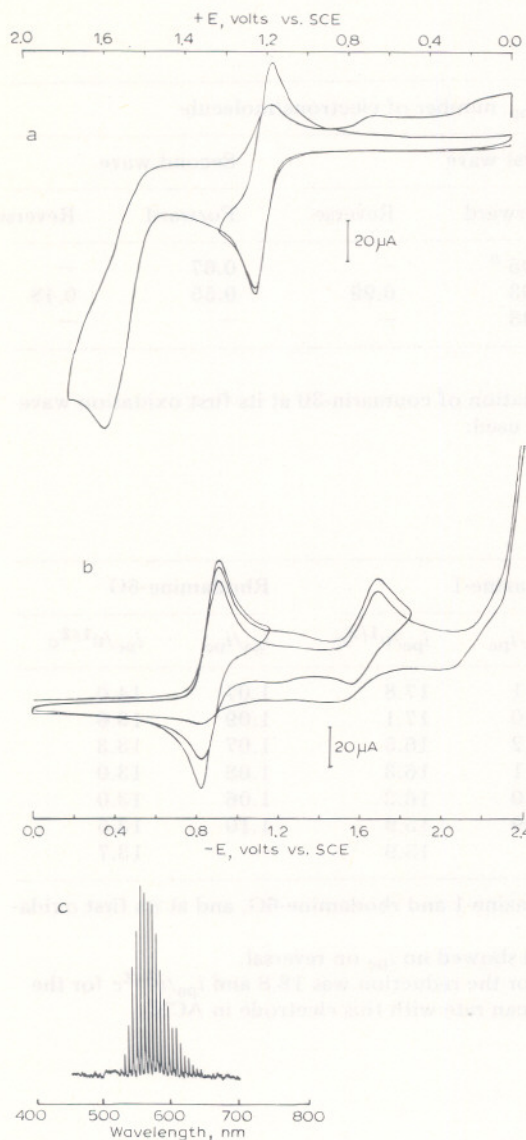
Fig. 6. (a) Oxidation cyclic voltammogram of rhodamine-6G perchlorate (1.1 mM) in ACN at Pt wire electrode, with scan rate of 200 mV s^{-1}; (b) reduction of above solution with scan rate of 200 mV s^{-1}; (c) e.c.l. recorded from above solution with pulse duration of 1 s.

their molecular structures. The electrochemical and e.c.l. results are discussed in more detail for each class of compounds in the next section; no attempt was made in this study to carry out an in depth examination of the mechanisms of the electrode reactions, however.

TABLE 2

Coulometry results

Compounds	Electrolysis direction [a]	n_{app} number of electrons/molecule			
		First wave		Second wave	
		Forward	Reverse	Forward	Reverse
Coumarin-30	Oxidation	1.05 [b]	—	0.67	—
Oxazine-1	Reduction	1.03	0.99	0.55	0.48
Rhodamine-6G	Reduction	1.03	—	—	—

[a] See Table 1 for the peak potentials.
[b] The number of protons released on oxidation of coumarin-30 at its first oxidation wave was 1.00 per molecule of parent molecule used.

TABLE 3

Cyclic voltammetric data for laser dyes [a,c]

Scan rate/ V s^{-1}	Coumarin-30 [b]	Oxazine-1		Rhodamine-6G	
	$i_{pa}/v^{1/2}c$	i_{pa}/i_{pc}	$i_{pc}/v^{1/2}c$	i_{pa}/i_{pc}	$i_{pc}/v^{1/2}c$
0.01	18.6	1.11	17.8	1.07	14.0
0.02	18.5	1.10	17.1	1.09	13.6
0.05	18.2	1.12	16.5	1.07	13.3
0.10	17.9	1.11	16.3	1.08	13.0
0.20	18.0	1.10	16.2	1.06	13.0
0.50	17.8	1.09	15.9	1.10	13.5
1.00	18.5	—	15.9	—	13.7

[a] Measured at first reduction waves for oxazine-1 and rhodamine-6G, and at its first oxidation wave for coumarin-30.
[b] The first oxidation wave of coumarin-30 showed no i_{pc} on reversal.
[c] For 9,10-diphenylanthracene $i_{pc}/v^{1/2}c$ for the reduction was 18.8 and $i_{pa}/v^{1/2}c$ for the oxidation wave was 17.9 at 200 mV s^{-1} scan rate with this electrode in ACN.

DISCUSSION

Coumarin dyes

In ACN the parent molecule coumarin shows irreversible slow scan cyclic voltammetric oxidation and reduction waves at +2.27 and −1.79 V vs. S.C.E., respectively. The introduction of the amine group in coumarin-2 causes an increase in ease of oxidation, with waves at +1.00 and +2.20 V observed. The reduction wave is shifted to −2.21 V. In coumarin-30 a second oxidation wave at +1.25 V following the first (+1.06 V), appears in addition to the wave

at +2.08 V. Thus the wave at about +2.0 V probably represents oxidation of the coumarin nucleus, and the earlier waves at about +1.0 V represent an amine-type oxidation. At scan rates below 0.2 V s^{-1}, the first oxidation wave of coumarin-30 shows no reversal wave, although one is discernable at scans above 1 V s^{-1} (Fig. 2). The $i_p/v^{1/2}c$ value for the first oxidation wave of coumarin-30 is that characteristic of a one-electron process (Table 3). A reversal wave is seen for the small second anodic wave even at slow scan rates in ACN. The general electrochemical behavior is similar in THF solutions but the reversal wave is not observed in DMF.

Controlled potential coulometric oxidation of coumarin-30 at the first wave shows an n_{app} = 1. A cyclic voltammogram taken following this oxidation (Fig. 3) shows the production of a species which shows a reversible oxidation wave at potentials of the parent second anodic wave, a broad new reduction wave at about —1.0 V (which is characteristic of the wave observed for the reduction of protons) and a reduction wave at —1.9 V. The heights of the oxidation and second reduction waves are about one-half those of the parent wave recorded before electrolysis. Controlled potential oxidation at the reversible oxidation wave appears to involve an n_{app} of 0.5 based upon the moles of parent compound; the $Q - t$ curve shows a slow continuous increase after attaining this value so that the measured n_{app} is a little larger than this value, suggesting further reactivity of the species formed at these potentials. Finally reduction at —1.35 V vs. Ag at the proton wave gave results equivalent to the release of 1.00 mole of protons per mole of parent molecule oxidized.

A mechanism consistent with these results is one in which oxidation of the parent coumarin-30 molecule (denoted RH) to the radical cation, is followed by a coupling reaction to produce a dimeric species which is further oxidizable.

$$RH - e \rightarrow RH^{+\cdot} \tag{1}$$

$$2\,RH^{+\cdot} \rightarrow R_2 + 2\,H^+ \tag{2}$$

$$R_2 - e \rightleftharpoons R_2^{+} \tag{3}$$
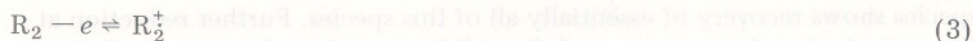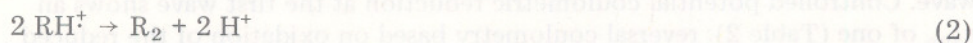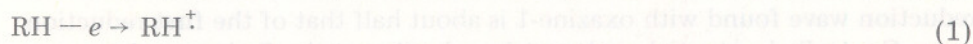
This reaction scheme is frequently found for the oxidations of amines and nitrogen heterocycles (e.g. carbozoles and iminobibenzyls) [18—21]. The details of the reaction path of (2) and the structure of the dimer, R_2, which presumably gives rise to the second reversible wave, were not investigated. Since the position *para* to the diethyl amine group is blocked and coupling *ortho* to this group would be sterically hindered, coupling may occur in this case through the other benzene ring to yield the dimer shown below.
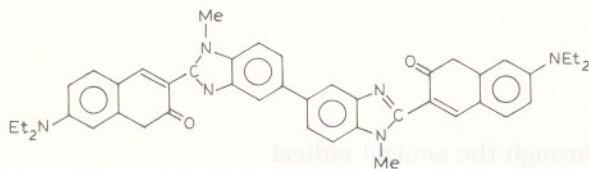
The e.c.l. observed during cyclic pulsing of coumarin-2 or -30 was quite

weak. In coumarin-30 no e.c.l. was observed when the potential was stepped between the first oxidation wave (+1.05 V) and the reduction wave (−1.78 V). Since the parent radical cation is unstable, and the radical anion formed on reduction also decomposes rapidly showing no anodic reversal wave in cyclic voltammetry, this lack of emission can be ascribed to loss of the reactant species and dissipation of the applied electrical energy used to generate these species by following chemical reactions. When the potential was pulsed between the second oxidation wave (+1.3 V) and −1.8 V, weak e.c.l. at wavelengths characteristic of coumarin-30 fluorescence was observed, probably arising from the reaction

$$R_2^+ + RH^{-\cdot} \rightarrow R_2 + RH^* \tag{4}$$
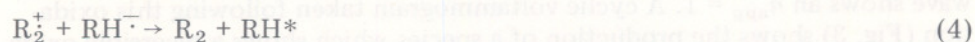
In coumarin-2 the e.c.l. obtained was shifted to longer wavelengths compared to the parent fluorescence. This could be attributable to excimer emission, since excimer emission has been reported for coumarin itself [22]; another possibility is emission from a reaction product, as observed for anthracene and other systems [17]. In general the weak e.c.l. observed in these systems can be attributed to reactant instability.
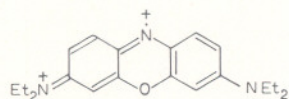
Oxazine dyes

Unlike the coumarin dyes both oxazine-1 and Nile Blue show clean electro-chemistry and reversible cyclic voltammetric waves in all solvents except DMF where the oxidation wave showed no cathodic reversal wave; typical results are shown in Fig. 4. The $i_p/v^{1/2}c$ values of the first oxidation and first reduction waves are characteristic of one-electron reactions. The reversible second reduction wave found with oxazine-1 is about half that of the first reduction wave. Controlled potential coulometric reduction at the first wave shows an n_{app} of one (Table 2); reversal coulometry based on oxidation of the reduced species shows recovery of essentially all of this species. Further reduction at the second wave shows an n_{app} of about 0.5; reversal coulometry similarly shows $n_{app} = 0.5$ for the reoxidation step.

These results can be accounted for by the following reaction scheme for oxazine-1, denoted Oz^+. The reversible oxidation step produces the radical dication
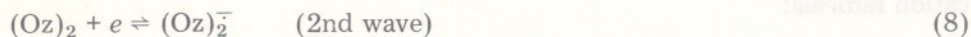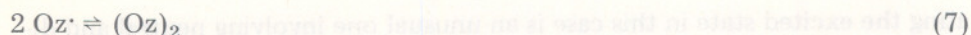
$$Oz^+ \rightleftharpoons Oz^{2+\cdot} + e \tag{5}$$
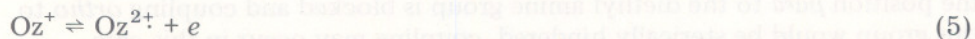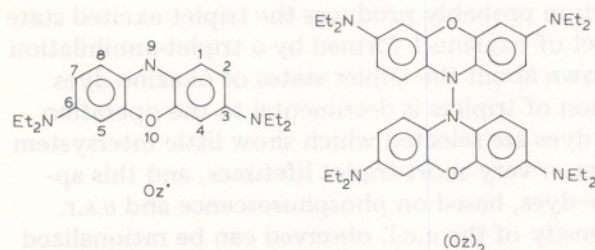
with the possible structure

The reduction would proceed through the neutral radical

$$Oz^+ + e \rightleftharpoons Oz^\cdot \quad \text{(1st wave)} \tag{6}$$

$$2\,Oz^{\cdot} \rightleftharpoons (Oz)_2 \tag{7}$$

$$(Oz)_2 + e \rightleftharpoons (Oz)_2^{-} \qquad (2nd\ wave) \tag{8}$$

$$(Oz)_2^{-} \rightleftharpoons Oz^{-} + Oz^{\cdot} \tag{9}$$

where $Oz^{\cdot}$ and $(Oz)_2$ represent

The nature of the radicals formed on reduction of oxazine-1 was investigated by electron spin resonance (e.s.r.) spectroscopy. The e.s.r. spectra obtained from samples of the oxazine-1 solutions obtained after coulometric reduction at the first and second reduction waves are shown in Fig. 5. The results show that radicals are present in both cases and that the spectrum in Fig. 5a is the same as that in Fig. 5b, with somewhat poorer resolution. The experimental e.s.r. spectrum can be simulated using the coupling constants shown in Table 4 (Fig. 5c). The results are consistent with the neutral radical proposed and show that the largest unpaired electron density is on the central (9-position) nitrogen. The fact that the same species results on exhaustive electrolysis at the second reduction wave leads to the proposed dissociation step, eqn. (9), since we would expect the dimeric radical anion to have a different spectrum from the neutral monomeric free radical.

When the electrode potential was pulsed between the first oxidation wave and the first reduction wave in an ACN solution of oxazine-1 perchlorate, low intensity e.c.l. was observed with a spectral distribution characteristic of oxazine-1 fluorescence (Fig. 5c). Pulsing to potentials of the second reduction wave did not increase this e.c.l. intensity. The electron transfer reaction gener-

TABLE 4

Coupling constants for e.s.r. spectrum of oxazine-1 radical

Nuclei	Position	Number of equivalent nuclei	Coupling constant/gauss
N	9	1	7.63
N	3, 6	2	1.71
H	1, 8	2	0.95
H	2, 4, 5, 7	4	0.19
H	Et [a]	8	1.90

[a] Hydrogens at methylene carbons of an ethyl group.

150

ating the excited state in this case is an unusual one involving neutral and di-cation radicals:

$$Oz^{\cdot} + Oz^{2\ddagger} \rightarrow (Oz^{+})^{*} + Oz^{+} \qquad (10)$$

The reaction can be classified as an energy deficient one, since the ΔH^{0} for the electron transfer is less than the singlet energy of excited Oz^{+} (Table 1). Thus the electron transfer reaction probably produces the triplet excited state with the emitting excited singlet of oxazine-1 formed by a triplet-annihilation reaction. Relatively little is known about the triplet states of oxazine dyes [24,25]. Generally the formation of triplets is detrimental to the operation of dye lasers [26—28], so that dyes are selected which show little intersystem crossing from the excited singlet or very short triplet lifetimes, and this appears to be the case for oxazine dyes, based on phosphorescence and e.s.r. studies [25]. Thus the low intensity of the e.c.l. observed can be rationalized in terms of the energy deficient nature, the short triplet lifetime and the complicating dimerization of the neutral radical. No e.c.l. was observed with Nile Blue perchlorate in any solution with any potential program. The electrochemical behavior of Nile Blue generally paralleled that of oxazine-1, and dimerization of the free radical would be expected to be less important. The lack of e.c.l. in this case might then be caused by a very short triplet lifetime or the nonexistence of a triplet-triplet annihilation reaction to produce excited singlet. Because e.c.l. was not obtained, the details of the electrochemical behavior of this compound and the intermediates formed were not investigated further.

Rhodamine dyes

The electroreduction of rhodamine-6G shows a one-electron reduction wave with an anodic wave on scan reversal (Fig. 6b). Coulometric reduction at this wave shows an $n_{app} = 1$, but the neutral radical product of this reduction is not stable on the coulometric time scale. The first oxidation wave (Fig. 6a) also appears to be a one-electron transfer reaction producing a dication radical which is stable on the cyclic voltammetric time scale. The later reduction and oxidation waves in this system were not investigated. Pulsing the electrode between the first oxidation and reduction waves produced low intensity e.c.l. at wavelengths characteristic of rhodamine-6G fluorescence. As with oxazine-1 the electron transfer reaction involves neutral and dication radical species. Since the energies of the excited singlet and triplet states for rhodamine-6G are about 2.16 and 1.97 eV respectively [24], and the ΔH^{0} for the electron transfer reaction in ACN is 2.00 eV (Table 1), the reaction is energy deficient with respect to the excited singlet with barely enough energy to produce the triplet.

With rhodamine-B the first irreversible reduction wave at about —0.76 V is probably attributable to reduction of the acidic proton on the carboxylic acid group. Pulsing the potential between this wave and the first oxidation wave

did not produce e.c.l. However, weak e.c.l. characteristic of parent fluorescence was generated for pulsing between the second reduction wave (production of a radical anion) and the first oxidation wave (production of radical dication).

Mixed systems

Because the e.c.l. of the laser dye systems alone proved disappointing, we tried some preliminary experiments with systems composed of a dye and a species which would generate a stable radical cation or anion. The following systems showed no e.c.l.: rubrene(+)/oxazine-1 (reduced species), rubrene(+)/Nile Blue (reduced species), and coumarin-30(+)/p-benzoquinone(−). A mixture of rubrene and rhodamine-6G, both of which emit at almost the same wavelengths, showed e.c.l. in ACN that was several times more intense than that found for rhodamine-6G alone when the electrode was pulsed between potentials for the formation of rubrene radical cation and the first reduction wave of the rhodamine-6G. A change in the solvent from ACN to benzonitrile produced an increase in e.c.l. intensity.

We also investigated the rhodamine-6G/9,10-diphenylanthracene (DPA) system. It has been reported [8] that the addition of DPA enhances the e.c.l. of rhodamine up to 100 times. The difficulty encountered with this system, however, is that rhodamine-6G's first and second reduction waves appear before the DPA is reduced. Since the second wave of rhodamine-6G is not reversible (see Fig. 6), the system will become contaminated with the decomposition products during continuous pulsation. An ACN solution containing 1.2 mM rhodamine-6G and 1.0 mM DPA showed e.c.l. consisting of both DPA and rhodamine-6G emissions, when the potential was pulsed such that both DPA radical anion and radical cation were generated alternately. The current normalized rhodamine-6G e.c.l. in this spectrum was about thirty times that of a rhodamine-6G system alone. However, when the potential was pulsed between the oxidation waves of DPA and rhodamine-6G and only the first reduction wave of rhodamine-6G, a very low level of e.c.l. was observed, the shape of the spectrum being exactly the same as that where both DPA⁻ and DPA⁺ were produced. Thus the enhancement of e.c.l. intensity is only accompanied by generating DPA radical anion and radical cation leading to fairly efficient production of the DPA excited singlet, which can then transfer its energy to rhodamine-6G. Since the generation of DPA anion radical is accompanied by the production of the reduced forms of rhodamine-6G, the lifetime of the e.c.l. is greatly reduced (e.g., the intensity of e.c.l. at 580 nm (rhodamine-6G) decreased by one-half within 30 min during continuous pulsing).

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152

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