References and Notes

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$$h_{\dot{O}} = -0.96\ \alpha_{\dot{O}} = \alpha_C - 0.96|\beta|;\ k_{C=O} = 1.0$$

$$h_{\ddot{O}} = -2.28\ \alpha_{\ddot{O}} = \alpha_C - 2.28|\beta|;\ k_{C-O-CH_3} = 0.8$$

$$\delta' = 0.1\ \alpha' C_{(C=O)} = \alpha_C - 0.096|\beta_C|$$

$$\delta = 0.05\ \alpha C_{(C-O-CH_3)} = \alpha_C + 0.0435$$

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Electrogenerated Chemiluminescence of Naphthalene Derivatives. Steric Effects on Exciplex Emissions

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Abstract: Electrogenerated chemiluminescence (ecl), electrode potentials, and fluorescence of 14 substituted naphthalenes are reported. Fluorescence maxima of these compounds were rather poorly correlated with electrode potentials. Six of fourteen naphthalenes gave ecl corresponding to their fluorescence emissions. An ecl spectrum having both monomer and excimer bands was observed from 4,5,6,7-tetrahydrodinaphtho[2,1-*g*:1′2′-*i*][1,2]dioxecine, which is a dimeric form of naphthalene. Exciplex emissions were observed from mixed donor–acceptor systems containing naphthalene derivatives and triphenyl amines and the energy of the exciplex was linearly correlated with electrode potentials with smaller slopes than previously reported. This phenomenon was attributed to the entropy effect on the formation of exciplexes between bulky donor and acceptor molecules.

Electrogenerated chemiluminescence (ecl) is a unique technique of exciting ground state molecules to excited ones by an electron transfer reaction from the anion radical to the radical cation (both electrogenerated at the electrode surface),[1-8] i.e.,

$$A^- + D^+ \rightarrow A^* + D \text{ or } A + D^* \qquad (1)$$

The multiplicity of excited states thus produced depends on the energetics of the electron transfer reaction 1. Recently it was reported by several investigators that various excited states, i.e., singlet excited molecules, triplet excited molecules, and/or the excited complex (exciplex) between two molecules A and D,[9-15] can be formed as a result of reaction 1. An exciplex intermediacy in the electron transfer reaction 1 was demonstrated by carrying out a series of experiments using various hydrocarbons as acceptor molecules for the donor molecule, tri-*p*-tolylamine (TPTA).[14] Thus, Park and Bard[14] showed from their experimental observations that, in the homogeneous electron transfer reactions of geometrically smaller molecules, exciplexes are intermediate species before decomposition to the individual excited molecule, A* or D*, while a long-range outer-sphere fast-electron transfer, a model theoretically suggested by Marcus,[16] is more probable in sterically hindered bulky molecules. Absence of exciplex emission in the case of rubrene or 9,10-diphenylanthracene (DPA) is an example of the latter cases. Tachikawa and Faulkner,[15] more recently, observed an exciplex from systems containing 1,4-dicyanobenzene (DCNB) and aromatic hydrocarbons in polar solutions and reported the quantum yield for the exciplex.

Contrary to the theory postulating no intermediacy in the homogeneous electron transfer reaction,[16,17] it now appears to be established that, at least in electron transfer reactions between smaller molecules, an encounter complex, or an exciplex, is formed as an intermediate species as follows:

$$A^{-}\cdot + D^{+}\cdot \rightleftarrows \underset{\text{(exciplex)}}{(A^-D^+)^*} \rightleftarrows A^* + D \text{ or } A + D^* \qquad (2)$$

Depending on the equilibrium situation, reaction 2 may proceed to the right or left hand side. Thus an exciplex can be produced either by quenching of excited molecules or from the recombination reaction of radical ions as shown above. When the potential surface of this exciplex is crossed with those of

Table I. Electrochemical, Spectroscopic, and Ecl Results for Various Substituted Naphthalenes[a]

No.	Compd	Concn, mM[b]	$-E_{p,r}$,[c] V vs. SCE	ΔE_{pc}	$E_{p,o}$,[c] V. vs. SCE	ΔE_{pa}	$-\Delta H°$, eV[d]	Fluorescence max,[e] nm (eV)	Ecl, nm (eV)
1	Naphthalene	2.3	2.64	70	1.69		4.17	322 (3.85), 336 (3.69)[f]	Nil
2	1-Methylnaphthalene	2.9	2.63	60	1.62		4.09	324 (3.82), 339 (3.66)[f]	Nil
3	2-Methylnaphthalene	2.0	2.63	60	1.73		4.20	320 (3.87), 328 (3.79), 335 (370)	~330 (3.76)
4	1,4-Diphenylnaphthalene	1.6	2.39	90	1.57	80	3.80	378 (3.28)	391 (3.18)
5	1,5-Diphenylnaphthalene	1.5	2.41	80	1.58		3.83	372 (3.33)	Nil
6	1,4-Dinaphthylbenzene	1.1	2.22	60	1.57	100	3.63	361 (3.43), 379 (3.27)	Nil
7	2-(2-Fluorenyl)-5-naphthyloxazole[f]	1.3	2.08 2.28	60 100	1.34 1.69		3.26	410 (3.02)	~410 (3.02)
8	1-(6-Phenylindenyl)-naphthalene[f]	1.2	2.32		1.21 1.39	50	3.28	405 (3.06)	408 (3.03)
9	1,1′-Binaphthyl	0.82	2.49		1.55		3.88	365 (3.40)	Nil
10	2,2′-Binaphthyl	9.8	2.32	60	1.50	130	3.66	353 (3.51), 370 (3.35)	Nil
11	6-Phenyl-2,2′-binaphthyl	0.24	2.14	60	1.41 1.65	30	3.39	365 (3.40), 382 (3.25)	Nil
12	Dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin[g]	0.80	2.36	70	1.52		3.72	390 (3.18)	Nil
13	5,6-Dihydro-4*H*-dinaphtho[2,1-*g*:1′,2′-*h*][1,5]-dioxocin[g]	0.78	2.54	100	1.69	120	4.07	370 (3.35)	360 (3.44)
14	4,5,6,7-Tetrahydrodinaphtho[2,1-*g*:1′,2′-*i*]-[1,6]dioxecin[g]	1.6	2.61	60	1.34 1.68	50	3.83	375 (3.31)	380 (2.36) 490 (2.53)

[a] Electrochemical and ecl data were obtained in 1:1 benzene–acetonitrile mixed solvents. [b] Concentrations of fluorescers in ecl experiments. For the fluorescence measurements, see footnote *e*. [c] Electrode potentials were measured against Ag-wire reference electrode and calculated against TPTA as an internal reference ($E_{p,o} = 0.84$ V vs. SCE). [d] $-\Delta H° = E_{p,o} - E_{p,r} - 0.16$ eV; see ref 48. [e] Fluorescence spectra were obtained from the DMF solution except compounds **1**, **2**, and **3** (see below). Concentrations were 5×10^{-5}–1×10^{-4} M in DMF depending on the relative fluorescence intensity. Band-pass of both exciting and emitting monochromators was 5.5 nm with 1 mm slit widths. [f] Estimated from I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed, Academic Press, New York, N.Y., 1971. [g] See Figure 1 for structures of these compounds. See also ref 19 and 20.

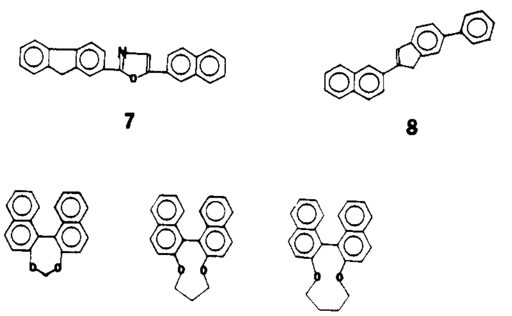

Figure 1. Structures of selected compounds; see Table I for their names.

the individual excited state molecules, a decomposition of the exciplex to the excited state of the component molecules (A* or D*, singlet or triplet states depending on the energy contained in $(A^-D^+)^*$) will result.[18] For bulky molecules the decomposition process should be very fast.

In order to see how substituents affect the exciplex formation in ecl reactions, we carried out ecl experiments on 14 substituted naphthalenes and report the results in this paper. It is also interesting to see how efficient an ecl can be obtained from these various naphthalene derivatives compared with that of naphthalene, since these compounds were actually synthesized as scintillator dyes or potential laser dyes.[19,20]

Experimental Section

Reagents and Chemicals. Spectroquality acetonitrile (ACN; Eastman Organic) was dried by three distillations over P_2O_5 under vacuum. Benzene (spectrograde; Aldrich) was dried either by activated molecular sieves (Linde 4A) or by sodium metal. These solvents were directly distilled into the ecl cell without contacting air for the solution preparation. Spectrograde *N*,*N*-dimethylformamide (DMF) (Eastman Organic) was used as received for the fluorescence and absorption spectrum measurements.

Tetra-*n*-butylammonium perchlorate (TPAP; Eastman Organic's polarographic grade) was dried on the vacuum line by heating at about 95–100 °C for at least 24 h and used as a supporting electrolyte in all electrochemical and ecl experiments.

Naphthalene, 2-methylnaphthalene, and 1,1′-binaphthyl (all Eastman Organic) were purified either by repeated recrystallizations or by sublimations as usual. 1-Methylnaphthalene (Eastman Organic) was used as received.

All other substituted naphthalenes were synthesized by one of us (GHD); the details of procedures for the synthesis and purification were partly reported[19,20] or will be published elsewhere. Structures of selected compounds used in this study are shown in Figure 1.

Substituted triphenylamines, e.g., tri-*p*-tolylamine (TPTA), tri-*p*-anisylamine (TPAA), 4-methyltriphenylamine (MTPA), and 4,4′-dimethoxytriphenylamine (DMTPA), were kindly provided by Professor Ralph N. Adams of the University of Kansas and used as received. Aldrich's triphenylamine (TPA) and Eastman Organic's 10-methylphenothiazine (10-MP) were purified by repeated recrystallizations from appropriate solvents.

Solutions were prepared by distilling solvents directly into the cell containing supporting electrolyte and electroactive compounds under vacuum. This was followed by 3–5 freeze-pump-thaw cycles to remove oxygen from the solution. For the ecl measurements, the conventional three-wire electrode cell, described by Tokel et al.,[21] was used and a platinum disk electrode (area ≃ 0.021 cm^2) sealed with soft glass was used as a working electrode with shielded silver wire reference electrode for the current function measurements listed in Table IV. Electrodes were polished with Gamal Polishing Alumina and Cloth (Fisher) before every ecl and electrochemical measurement.

Equipment. A Princeton Applied Research (PAR) Electrochemistry Model 173 potentiostat-galvanostat along with a PAR Model 175 universal programmer were used for cyclic voltammetric measure-

Table II. Ecl Results for Various Acceptor–TPTA Systems in Benzene–ACN (1:1) Mixed Solvents[a]

Compd	Concn, mM[b]	$-\Delta H°$, eV[c]	Ecl, nm (eV)[d]	I_{exp}/I_m[e]
1	2.2–1.9	3.32	352 (3.52), 469 (2.67)	2.45
2	2.5–1.2	3.31	361 (3.44), 460 (2.64)	1.24
3	2.1–1.5	3.31	369 (3.36), 466 (2.66)	1.41
4	1.5–0.53	3.07	369 (3.39), 485 (2.55)	0.39
5	1.3–0.91	3.09	383 (3.24), 486 (2.55)	1.35
6	1.2–1.1	2.90	368 (3.37), 387 (2.30), 501 (2.48)	0.55
7	1.3–1.0	2.76	390 (3.18), 408 (3.04), 431 (2.88), 508 (2.47)	0.13
8	1.2–0.72	2.91	508 (3.04), 495 (2.51)	0.52
9	1.2–1.1	3.16	Nil	
10	1.5–1.0	3.00	337 (3.67), 364 (3.39), 380 (3.26), 517 (2.40)	0.74
11	1.1–1.4	2.82	388 (3.20), 517 (2.40)	0.62
12	1.0–1.2	3.04	377 (3.28), 397 (3.11), 497 (2.49)	1.32
13	1.1–1.2	3.22	521 (2.38)	
14	1.3–1.0	3.29	379 (3.26), 472 (2.63)	0.89

[a] For other data, see Table I. [b] Concentrations of donor molecules are followed by those of TPTA in ecl experiments. [c] $-\Delta H° = E_{p,o,TPTA} - E_{p,r} - 0.16$ (eV). [d] The longer wavelength maxima were taken from the corrected spectra using a standard quinine sulfate solution (1 μg/mL of solution). [e] I_{exp}/I_m is the intensity ratio of exciplex and monomer emissions at room temperature.

Table III. Electrochemical, Spectroscopic, and Ecl Data for Various Donor–2,2′-Dinaphthyl Systems in Benzene–ACN (1:1) Mixture

No.	Donor molecules	Concn, mM[b]	$E_{p,o}$, V vs. SCE	$-\Delta H°$, eV	E_s, eV	Ecl, nm (eV)[e]	I_{exp}/i_m
1	TPAA	1.2–1.3	0.66	2.76	3.26[a]	341 (3.65), 362 (3.41), 380 (3.26), 408 (3.04), 553 (2.24)	0.39
2	TPTA	1.0–1.5	0.84	3.00	3.51[a]	337 (3.67), 364 (3.69), 380 (3.26), 517 (2.40)	0.74
3	10-MP	1.4–1.4	0.88	2.94	3.41[c]	352 (3.52), 367 (3.34), 536 (2.31)	0.78
4	MTPA	1.3–1.4	1.01	3.19		351 (3.53), 499 (2.49)	0.53
5	TPA	1.0–1.2	1.03	3.21	3.5[d]	360 (3.44), 382 (3.24), 405 (3.06), 497 (2.50)	0.70

[a] Taken from ref 10. [b] Concentrations of donor molecules are followed by those of 2,2′-dinaphthyl. [c] Taken from ref 47. [d] Estimated from I. B. Berlman, "Handbook for Fluorescence Spectra of Aromatic Molecules", 2nd ed, Academic Press, New York, N.Y., 1971. [e] See footnote *c*, Table II.

Table IV. Cyclic Voltammetric Current Functions of Dimeric Naphthalenes[a]

	Reduction				Oxidation			
Compd	E_{p_1}	n_1[e]	$E_{p_2}(n_1 + n_2)$[c]	n_2[e]	E_{p_1}	n_1[e]	$E_{p_2}(n_1 + n_2)$[c]	n_2[e]
9	~34.7[b]	~1	87.3	2	85.6	3		
10	26.9	1			81.2	3		
11	25.5	1			26.2	1	73.7	2
12	28.3	1			57.3	2		
13	~35.4[b]	~1			~30.4[b]	~1		
14	~33.3[b]	~1			28.7	1		
DPA[d]	24.0	1			24.3	1		

[a] Current function = $(i_p/v^{1/2}C)(\mu A/[(V/s)^{1/2}\ mol/L])$. This was measured in mixed solvent (ACN–benzene) with a platinum disk electrode (area = 0.021 cm^2) at a voltage scan rate of 100 mV/s. [b] The first waves were closely followed by the next ones and the waves (peaks) were not very well defined. [c] Calculated from i_p's for $E_{p_1} + E_{p_2}$. [d] DPA = 9,10-diphenylanthracene; this was used as a reference compound. [e] Apparent number of electrons transferred.

ments and ecl experiments. Ecl spectra were detected by an Aminco-Bowman spectrophotofluorometer with an RCA IP28 photomultiplier tube and recorded on a Mosely x-y recorder. The same spectrophotofluorometer and a Cary-14 absorption spectrophotometer were used for fluorescence and absorption spectroscopic measurements, respectively.

Results and Discussion

The electrochemical, fluorescence, and ecl measurements are summarized in Tables I–IV. Results from naphthalene derivatives alone are listed in Table I; in Tables II and III, results from the mixed systems are listed. Typical cyclic voltammetry and ecl spectra from 4,5,6,7-tetrahydrodinaphtho[2,1:1′,2′-*i*][1,6]dioxecine and its mixed system with TPTA are shown in Figure 2. Data on cyclic voltammetric current functions are given in Table IV for several selected dimer naphthalene molecules in order to determine the number of electrons transferred (*n*) in their electrochemical reactions by comparing with a well-established compound, 910-diphenylanthracene (DPA). A more detailed discussion of results follows.

Fluorescence and Electrochemical Results. Since some of the compounds used in this study are new, fluorescence spectra were measured in DMF and reported in Table I. DMF was used for fluorescence measurements because many of the compounds studied here were not soluble in the other solvents. While smaller molecules have well-resolved vibrational structure in their fluorescence spectra, most large molecules or dimer naphthalenes had single round peaks having no vibrational structure. Most of them did not show the mirror image relation with the absorption spectrum. The lowest singlet excited state energy levels therefore were difficult to obtain.

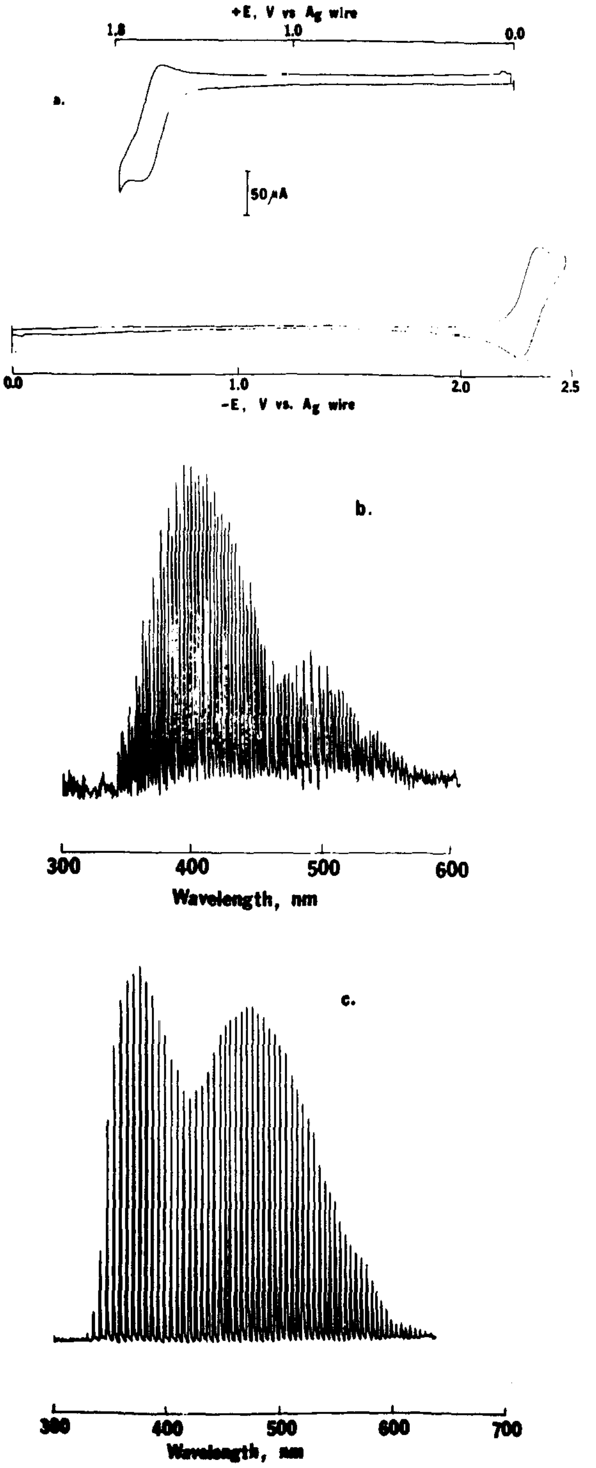

Figure 2. (a) Cyclic voltammograms of 1.6 mM 4,5,6,7-tetrahydrodinaphtho[2,1-*g*:1′,2′-*i*][1,6]dioxecine (**14**) at the platinum-wire electrode with a scan rate of 100 mV/s: (1) oxidation and (2) reduction. The solvent was a (1:1) benzene-acetonitrile mixture. (b) Ecl spectrum of the above solution; pulse duration was 1 s. (c) Ecl spectrum of the **14**-TPTA mixed system with **14** = 1.3 mM and TPTA = 1.0 mM; pulse duration was 1 s.

There have been many efforts to correlate the spectral data with electrochemical potentials in the literature.[22-30] We therefore plotted fluorescence maximum energy against reduction potentials in Figure 3a. In Figure 3b, the same energy is plotted against $\Delta E_p(E_{p,o} - E_{p,r})$, since several investigators have suggested from theoretical calculations that ΔE_p or $\Delta E_{1/2}$ correlates better with molecular orbital parameters.[30-32] In both Figures 3a and 3b, the data points are fairly scattered. There, however, certainly exists a correlation or at least a trend.

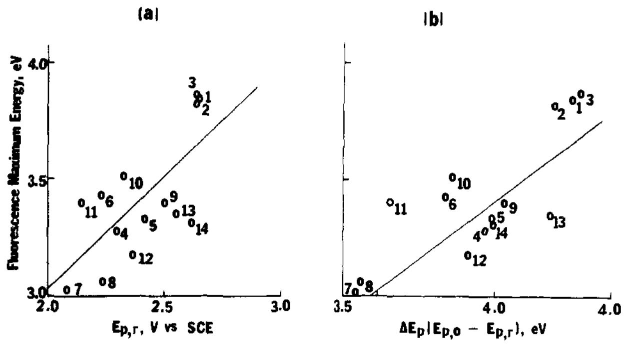

Figure 3. Fluorescence maxima vs. reduction potentials of substituted naphthalenes; 0–0 band energy was taken where possible.

This linear correlation is not better than those reported previously, for example, for a series of the lowest triplet energy of carbonyl compounds plotted against their reduction potentials.[25]

This reflects a difficulty of measuring the energy level of the lowest singlet excited state of these molecules (0–0 bands), a nonprogressive nature of the change in electronic transition energy for the change in structures, and difficulty of measuring accurate redox potentials due to the irreversible electrode processes, particularly for the oxidation potentials in several instances. This may explain why the fluorescence maximum vs. ΔE_p plot is not improved.

Substitution of various groups on the naphthalene ring stabilizes the radical cation. The cyclic voltammogram (see, for example, Figure 2a) indicates that the oxidation of compound **14** is fairly reversible. This is quite contrary to that of 1,1′-binaphthyl, in which both oxidation and reduction waves are ill-defined. 1,1′-Binaphthyl is different only in that it lacks the ethereal linkage in the β position of the naphthalene rings. However, the oxidation of 1,1′-binaphthyl is an apparent 3-electron transfer process as can be seen in Table IV. This suggests that the radical cation produced by oxidation of 1,1′-binaphthyl is rapidly followed by the fast chemical reaction to give an overall 2–3-electron process.

Most compounds showed reversal currents as indicated in Table I in both ΔE_{pc} and ΔE_{pa}. Those that do not have ΔE_p values in the table did not show any reversal currents. Potentials reported here were measured against a silver wire reference electrode in the presence of an internal reference TPTA and were calibrated against the oxidation potential of TPTA, assuming that there is no substantial donor-acceptor complex formation in the ground state between these hydrocarbons and TPTA.[33] They are all measured in a 1:1 mixture of acetonitrile and benzene with TBAP as a supporting electrolyte. The reason that we did not use DMF for electrochemical measurements is that DMF has a low anodic background potential (ca. 1.30 V vs. SCE) compared with the oxidation potentials of most compounds studied.

Ecl of Single Systems. As already pointed out, most of these compounds were synthesized as potential laser dyes, and the ecl behavior was examined in the hope of finding efficient and stable ecl systems. Possible applicability of good ecl systems to practical devices has been suggested in the literature.[34-41] Ecl behavior shown by these compounds in general is not very satisfying in terms of efficiency and stability. The efficiency was lower than that of DPA by several orders of magnitude. As the substituents become larger, the radical cations are more stable, and thus they exhibited ecl corresponding to their fluorescence emissions without having another source of the radical cations, but more than half the systems examined did not give any ecl, as listed in Table I.

In all cases, the enthalpy changes ($-\Delta H°$) of the homogeneous electron-transfer reactions from the anion radical to the radical cation were greater than the energy of the fluorescence maximum, except in compounds **10** and **11**, for which they may be about the same. From the consideration of energetics, therefore, excited molecules may be formed directly from the reaction,

$$R^{-}\cdot + R^{+}\cdot \rightarrow {}^{1}R^{*} + R \qquad (3)$$

and the fluorescence light is observed as a result of a transition to the ground state. Even with this energy sufficiency, most systems did not give a satisfactory result. Compound **7** can hardly be considered a naphthalene derivative; rather it is a naphthalene-substituted oxazole. We notice also that binaphthyls (compounds **9–12**) did not produce an ecl. This is because a radical cation is not available as a result of oxidation at the anode. Low intrinsic fluorescence yield due to the flexibility around the single bonds could also be a reason for this.

Ecl of 4,5,6,7-Tetrahydrodinaphtho[2,1-*g*:1′,2′-*i*]dioxecine. This compound produces a stable anion radical upon reduction as well as a fairly stable radical cation upon oxidation, as shown in Figure 2a. The system is energy sufficient, since $-\Delta H° = 3.82$ eV and $E_s = 3.31$ eV. The excited state should therefore be produced through an S route. Potential pulsing between +1.34 and −2.61 V leads to light emission as shown in Figure 2b. Short-wavelength emission at 380 nm and broad longer wavelength emission at 490 nm are apparent in the figure shown. This is the only system emitting at two different wavelengths. An emission peak at 380 nm is unambiguously assigned to be its own fluorescence from comparison with fluorescence maximum in DMF. Longer wavelength emission at 490 nm is designated here as an excimer emission. There have been some disputes over this type of longer wavelength emission.[42,43] The longer wavelength emission in the anthracene ecl system, assumed to be an excimer by Chandross et al.,[42] was later found to be originated from a reaction product between the anthracene radical cation and a trace of water in DMF by Faulkner and Bard from their detailed experiments.[43] Maloy and Bard[44] observed excimer emission from the pyrene system in DMF solution, which was later supported by Honda et al.[45] with a kinetic analysis in ACN solution.

In our system, the radical cation is reasonably stable, and one may not expect to have a reaction product from an ecl type reaction, as is shown in Figure 2a. We may at least expect the radical cation not to decay fast enough to produce a substantial amount of product which can accept the excited energy from the parent molecule. Emission from a product is thus not likely. An experimental observation that the ecl spectrum is essentially not dependent on the pulse frequency (1–100 Hz) supports this fact.

The same emission is not observed from the other dimer molecules, and to seek an explanation for this current functions of cyclic voltammetry at the platinum electrode (area = 0.021 cm^2) were measured in acetonitrile solution and the results are listed in Table IV. From the current functions ($i_p/v^{1/2}C$) shown, we recognize by comparison with a reference compound, DPA, known to have a 1-electron transfer, that reduction of binaphthyls is characterized by 1-electron processes, although it is not as well defined in compounds **9, 13,** and **14.** This is because the first electron transfer was followed very closely by the second electron transfer, and hence the two different waves overlap. The oxidation of compounds is characterized by an apparent 1–3-electron transfer as is evident from the table. This shows the evidence that radical cations generated are not stable. Therefore, we can expect to have ecl only from compounds **11, 13,** and **14.** Actually ecl was only observed from compounds **13** and **14,** because of the instability of the radical cation of **11.** Of two compounds for which ecl was observed, an excimer was observed only from **14.** One can therefore conclude that only the reaction between stable $R^{-}\cdot$ and $R^{+}\cdot$ lead to the production of the excited state and thus an excimer.

One additional piece of evidence supporting our argument is the so-called 6000-cm^{-1} rule, calculated by Azumi.[46] The energy difference between the monomer and the excimer of aromatic hydrocarbons is calculated to be approximately 6000 cm^{-1}: it was 5900–6200 cm^{-1} in our case.

The same band, however, was not observed in our photoexcitation experiment, probably because of lower concentration. We measured the fluorescence spectrum up to approximately 2 mM solution in benzene; there was however not a new band observed, although concentration quenching was observed. The fact that one does not observe an excimer from photoexcitation indicates that direct formation from the ionic recombination reaction seems more important. This compound was not dissolved in solvents such as cyclohexane. More quantitative studies were not performed, because the ecl intensity was not great enough.

Ecl of Mixed Systems. To investigate how substituents will affect exciplex emission in donor–acceptor mixed ecl systems, several tertiary amines were added to the substituted naphthalene systems and ecl experiments were performed. A typical ecl spectrum thus obtained from the TPTA(+)-4,5,6,7-tetrahydrodinaphtho[2,1-*g*:1′,2′-*i*][1,6]dioxecine system is shown in Figure 2b, and the results for the TPTA(+)-substituted naphthalene(−) systems and various tertiary amines-(+)-2,2′-binaphthyl(−) systems are listed in Tables II and III. As shown in the tables, exciplex emissions were observed from all systems examined, except **9** (1,1′-binaphthyl). The reduction of 1,1′-binaphthyl was irreversible, suggesting instability of the anion radical with subsequent failure to react with TPTA$^{+}\cdot$, which is why the ecl was not observed. Due to the lower oxidation potential of TPTA (0.84 V vs. SCE), the reaction enthalpy of most of these systems was not sufficient to produce the singlet excited states of both the donor molecule (TPTA) and acceptor molecule, except in two systems, **12** and **14,** in which $-\Delta H°$ is comparable with E_s. In all systems except **13,** however, shorter wavelength emissions were observed. Emissions at shorter wavelengths correspond to fluorescence from either acceptor molecules or TPTA, or both. In a system such as **10,** it is obvious that the lowest singlet excited state of compound **10** is the source of the emission at 337 nm, and hence the emission at 380 nm must be from TPTA. Either an emission peak is due to an acceptor or a donor molecule or, in many cases, fluorescence from both acceptor and donor is overlapped forming a single peak. In practically all cases, the enthalpy is not sufficient and both donor and/or acceptor emissions are produced by an energy doubling scheme, triplet-triplet annihilation (TTA), i.e.,

$${}^{3}R^{*} + {}^{3}R^{*} \rightarrow {}^{1}R^{*} + R \qquad (4)$$

The TTA mechanism of generating emission from singlet excited state is very well established in solution ecl and well documented in the literature.[1-8,47,48] We do not have data on triplet energy levels of compounds **4–14** because they are all new compounds, but it seems obvious that the lowest triplet energy levels are lower than the $-\Delta H°$ values listed in Tables II and III, considering that the lowest triplet excited energy levels are substantially lower than the lowest singlet excited energy levels in most aromatic hydrocarbons containing π–π^* transitions.

The exciplex energies of mixed systems containing TPTA and substituted naphthalenes were linearly correlated with redox potentials of acceptor or donor molecules as shown in Figures 4 and 5. In Figure 4, in which the exciplex emission energy is plotted vs. the reduction potentials of acceptor molecules, compound **13** exhibits a marked deviation. Reasons for this deviation are not clear. It could be an experimental error due to the instability of the ecl system rather than a true de-

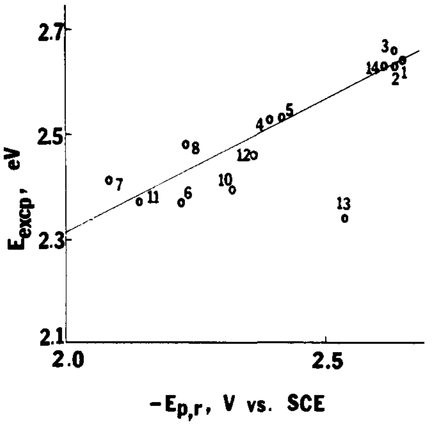

Figure 4. Exciplex energies vs. reduction potentials of the acceptor molecules; the numbers indicate acceptor molecules (substituted naphthalenes) listed in Table I and II.

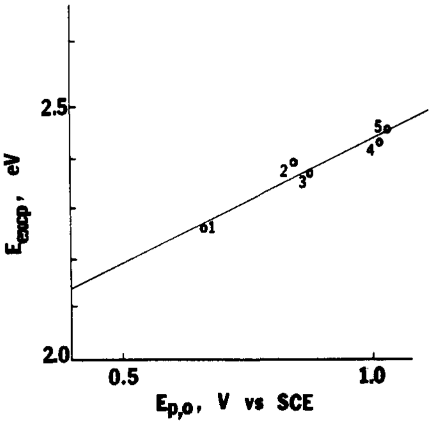

Figure 5. Exciplex energies vs. oxidation potentials of the donor molecules; the numbers indicate donor molecules (substituted triphenylamines) in Table III.

viation. This system was very unstable, and a good ecl spectrum could not be recorded. Excluding compound **13**, the correlation is good but the slope of the line (0.48 from a least-squares fit) was less than the ones reported (0.65–0.68.).[14,49] This indicates that the free energy change ($\Delta G°$) for the formation of exciplexes in reaction 2 becomes larger as the substituents on the naphthalene ring become greater. That is, from the equation

$$\Delta G° = \Delta H° - T\Delta S° \qquad (5)$$

the effect of the $T\Delta S°$ term becomes more important in deciding $\Delta G°$ for the formation of an exciplex, since larger acceptor and donor molecules require larger entropy decreases for the association process. On the contrary, however, redox potentials are expected to become lower by introducing substituents due to the stabilization of resulting radical species through more extensive resonance, etc. Thus, energy of exciplex emission will be larger than that predicted from the redox potential mainly due to the entropy effect. One also can recognize in Figure 4 that compound **7**, which has bulkier substituents than the other acceptors, shows slight deviations, indicating that emission energy of exciplexes formed between this acceptor and TPTA is higher. The negative deviation of compound **10** can also be explained on the same grounds. Since the bulky substituents affect the change in redox potentials and exciplex energies oppositely, the slope of the curve should be less. Steric effects on the formation of the exciplex can also be seen in Table II, in which the ratio of exciplex emission to that of monomer, I_{exp}/I_m, is listed. The intensity ratio of the exciplex to the monomer is lower for compound **7** than for the others. The I_{exp}/I_m values listed in Tables II and III are generally on trend, although this parameter is dependent on the concentrations of donor and acceptor and on the temperature,[14] etc., and it is very difficult to correlate this parameter with bulkiness of substituents.

For a system containing 2,2′-binaphthyl and various donor molecules, the exciplex energy is again linearly correlated with the oxidation potentials of donor molecules as pointed out. The slope (0.70) is lower than expected and the reason for this is not clear.

From the observations we have discussed thus far, one may conclude that the exciplex is formed between the radical cation of donor molecules and the anion radical of the naphthalene ring. Therefore, substitution on the naphthalene lowers the redox potentials of the parent ring and raises the free energy for the formation of an exciplex, resulting in lower slopes in the exciplex energy–electrode potential plot. As long as the anion radical produced from a planar naphthalene ring is available, the exciplex seems to be formed with higher energy and thus with lower rate. If, however, the approach to the ring of an anion radical is severely hindered, the formation of an exciplex may not be possible. Systems containing compounds such as 2,3,6,7-tetramethyl- or tetraphenylnaphthalene, if available, could support such a conclusion.

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Electrogenerated Chemiluminescence. 30. Electrochemical Oxidation of Oxalate Ion in the Presence of Luminescers in Acetonitrile Solutions

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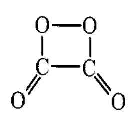
Abstract: The electrochemical oxidation of oxalate at a platinum electrode in acetonitrile solutions as studied by cyclic and rotating-ring disk voltammetry and controlled potential coulometry shows an irreversible two-electron oxidation at ca. 0.3 V vs. SCE to CO_2 with no intermediates detectable by these techniques. The oxidation of oxalate in the presence of several fluorescers (such as rubrene, 9,10-diphenylanthracene, and the bipyridyl chelates of ruthenium(II) and osmium(II)) does not produce light, but emission characteristic of the fluorescer occurs during the simultaneous oxidation of the additive and oxalate. Studies of the conditions for emission in the presence of thianthrene and naphthalene lead to a mechanism for the oxidation of oxalate and the excitation process based on oxidation of oxalate to $C_2O_4^{-}\cdot$, which undergoes rapid decomposition to CO_2 and $CO_2^{-}\cdot$. The $CO_2^{-}\cdot$ can transfer an electron to the additive molecule to produce a radical anion, which can then undergo an ecl annihilation reaction with the electrogenerated radical cation.

There has been much interest in the intense chemiluminescence which results from the reaction of oxalyl chloride or oxalate esters and hydrogen peroxide in the presence of fluorescent compounds in nonaqueous solvents.[1-3] In the proposed mechanism for these processes, the reaction between the oxalate ester and H_2O_2 produces the dioxetanedione (**1**) as an intermediate. This forms a complex with the fluorescer which decomposes to two molecules of CO_2 and the fluorescer in the excited state. Attempts at isolating and observing this intermediate have generally not been successful. Thus, Heller et al.[4] identified the dioxetanedione in the mass spectrum of the products of the reaction of an oxalate ester and H_2O_2. However, the studies of DeCorpo et al.[5] on the relative concentrations of the positive ions of C_2O_4 and CO_2 as a function of ion residence time suggest that the $C_2O_4^+$ was not formed in the chemiluminescent reaction. Indeed in a recent review Hastings and Wilson[6] state: "In the reaction of oxalic esters, the mythical intermediate dioxetanedione remains as seductive and elusive as ever. The chemiluminescence community should offer a reward for its capture." In an attempt to find this intermediate we studied the electrochemical oxidation of oxalate ion, $C_2O_4^{2-}$, in acetonitrile (ACN).



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The electrochemical oxidation of oxalate in aqueous solutions leads to CO_2; the mechanism of this reaction has not been established. The only previous study of the oxidation of oxalate in an aprotic solvent was that of Jacobsen and Sawyer.[7] These authors studied the oxidation at a gold electrode in dimethyl sulfoxide solutions. They found an overall oxidation to CO_2 and proposed that an unstable intermediate was formed during the oxidation. However, the low solubility of the oxalate salts (Na^+, Li^+, NH_4^+, tetraethylammonium) and the difficulty of excluding water from the solutions led to experimental problems and prevented the establishment of the reaction mechanism. We report here a study of the oxidation of oxalate in ACN in the presence of several fluorescers. While no evidence of the dioxetanedione as an intermediate was found in these studies, a new chemiluminescent reaction was discovered when oxalate and a fluorescent compound were oxidized at the same time at a platinum electrode. The nature of this reaction was investigated. The results provide some insight into the mechanism of oxalate oxidation at an electrode and demonstrate the interesting phenomenon of the production of a strong reductant upon oxidation.

Experimental Section

The apparatus and general techniques in the ecl and electrochemical measurements have been reported previously.[8] The simple three-electrode ecl cell incorporating a silver pseudo-reference electrode was employed for ecl measurements[9] and a three-compartment coulometry cell for electrochemical measurements.[10] The rotating ring-disk electrode (RRDE) and associated apparatus have also been described.[11,12] Tetra-*n*-butylammonium oxalate (TBAOX) was prepared by mixing oxalic acid (Baker Analyzed) and tetra-*n*-butylammonium hydroxide (Southwestern Analytical Chemicals, Inc.) in a mole ratio of 1:2 followed by evaporation and drying in a rotary evaporator. The CO_2 gas (Big Three Industries, Inc.) was used as