The Mechanism of Electrochemiluminescence

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SINCE the electrochemiluminescence (ECL) spectra of arylisobenzofurans and similar molecules are identical with that of their fluorescence emission spectra,[1] the electrode processes in some manner must culminate in the generation of the fluorescer in its first excited singlet state. The mechanistic details of the intermediate steps in the analogous electrochemiluminescence process in hydrocarbons has been a matter of considerable conjecture.[2–5]

Direct generation of an excited singlet may occur by cation–anion annihilation in solution or by heterogeneous electron-transfer at the electrode surface. The latter has been held unlikely,[6] since the excess energy would be expected to be transferred preferentially to the low-lying conduction bands of the electrode, producing an excited state of the electrode. Evidence is also available suggesting that luminescent oxidation of anion or reduction of cation occurs in solution by oxidants or reductants, which result from electrolytic decomposition of some component of the system.[3] A further possibility is that the singlet is not formed directly from the ions but rather that triplet species are generated by one of the above processes and that the S_1 state is reached by T–T annihilation.[5] Solid-state luminescence of organic materials at electrodes has recently been reported,[7,8] and a triplet mechanism has been indicated in some instances.[8] In this connection, it has been observed that the voltage required to oxidize rubrene anion or reduce rubrene cation luminescently is considerably less than the energy of the emitted light or of the rubrene 0–0 singlet transition.[9]

In order to gain further information about the processes prior to the culminating excited singlet formation, we have examined the oxidation of the anion and reduction of the cation of arylisobenzofurans and *N*-methylisoindoles under potential limiting conditions. Either a potentiostat square-wave input (0·3 c./sec.) with appropriate selection of positive and negative voltage settings was employed or an excess of an electroactive substance was added which, for example, oxidizes reversibly at a less positive voltage and reduces reversibly at a more positive voltage than the fluorescer. The fluorescer anions and cations were found to undergo electron transfer resulting in electrochemiluminescence under either of these conditions, which are termed pre-annihilative since the reaction of fluorescer cation and anion cannot occur. As shown in the Table, each electrochemiluminescence-emitting substance was found to have its own characteristic pre-annihilation energy input threshold, below which no detectable light was emitted. The threshold overvoltages reported are from the reversible half-wave potentials to the first point where emissive light could be detected. As shown elsewhere,[9] the presence of impurities may effect a shift (decrease) in the overvoltage required for emission.

TABLE

Threshold overvoltages for electrochemiluminescence

Compound	Reduction Potential[a]	Threshold Oxidative Overvoltage	Oxidation Potential[b]	Threshold Reductive Overvoltage
1,3,4,7-Tetraphenylisobenzofuran	−1·86	1·78	+0·89	1·73
1,3-Di-*p*-methoxyphenyl-4,7-diphenylisobenzofuran	−1·92	1·26	+0·84	2·18
N-Methyl-1,3,4,7-tetraphenylisoindole	−2·35	1·59	+0·67	2·12
N-Methyl-1,3-di-*p*-methoxyphenyl-4,7-diphenylisoindole	−2·42	No ECL	+0·59	2·18
Tetracene	−1·58	1·97	+0·77	No ECL

[a] *vs.* Saturated calomel electrode at a dropping Hg electrode in *NN*-dimethylformamide solution.

[b] *vs.* Saturated calomel electrode at a rotating Pt electrode in *NN*-dimethylformamide solution.

Chemical limitation of the potential excursion in the oxidative process was accomplished by adding substances such as 2,6-bis(dimethylamino)naphthalene, 1,2,4,5-tetramethoxybenzene, and *N*-methyl-1,3-di-*p*-methoxyphenyl.4,7-diphenylisoindole (II) in equal molar quantities to an electrochemiluminescence system of 4 or 5 mM-1,3,4,7-tetraphenylisobenzofuran (I) in *NN*-dimethylformamide, with tetra-n-butylammonium perchlorate as the conducting medium. The added substances all oxidize at less positive voltages than (I),* to form stable cations, and are all more difficult to reduce than (I) which forms a relatively stable anion. On passing a 60 c./sec. alternating square-wave current, the mixed systems were all found to electrochemiluminesce dimly with emission characteristic of (I). The fluorescence efficiency of equimolar mixtures of (I) and (II) in *NN*-dimethylformamide (DMF) at the 0·001 and 0·004 molar levels in DMF was found to be additive. The dimness of the emission of the mixed systems is therefore not due to fluorescence quenching from the added substance, but may be due to the potential limitation caused by the added electroactive substance.

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* Oxidation and reduction half-wave potentials are in *NN*-dimethylformamide solution *vs.* a saturated calomel electrode. Oxidation was performed at rotating Pt electrode and reduction at a dropping Hg electrode. Potentials not reported elsewhere are: 2,6-bis(dimethylamino)naphthalene +0·26 v, −2·71 v; cyclohexa-1,3-diene + 1·5 v, −2·9 v; 1,3,5- hexatriene + 2·0 v, − 2·65 v; 1,2,4,5-tetramethoxybenzene + 0·79 v, −2·9 v. We thank W. H. Jura for these half-wave potential measurements.

Electrochemiluminescence of 1,3,4,7-tetraphenylisobenzofuran (I) also occurs in the presence of 0·1 M-hexa-1,3,5-triene (III) which is electroinactive* between the first oxidation and reduction waves of (I). Even the threshold voltages for emission on oxidation of the anion or reduction of the cation of (I) are not significantly affected by the presence of a large excess of (III) or of cyclohexa-1,3-diene.* As (III) has a triplet energy of 47 kcal./mole[10] and cyclohexa-1,3-diene has a triplet energy of 53 kcal./mole,[11] and as (III) in particular is probably not a good triplet energy donor,[12] triplet energy transfer to (III) should compete with *T–T* annihilation of (I). Such competition should diminish the electrochemiluminescence emission if the latter is responsible and if the triplet energy of (I) is equal to or greater than 47 kcal/mole.†

Despite extensive efforts, the triplet energy of (I) could not be determined experimentally. Phosphorescence due to (I) could not be detected when it was irradiated in degassed 3-methylpentane glass at 77°K and no e.s.r. signal attributable to the triplet of (I) could be detected in methyltetrahydrofuran at 77°K on irradiation with a 200 watt mercury arc lamp. Singlet–triplet absorption could not be detected in bromobenzene or iodoethane (poor solubility in the latter) and under high oxygen pressure[10] (2200 p.s.i.g.) in chloroform solution extensive degradation of (I) occurred.

Since the lowest triplet of tetracene (10,250 cm.$^{-1}$), is less than one-half that of its lowest singlet (20,990 cm.$^{-1}$),[13] the report of electrochemiluminescence emission from tetracene being the same as that of its fluorescence[4] may also be regarded as evidence against a ground-state triplet intermediate. As indicated in the Table, we have found that oxidation of tetracene anion at potentials providing less energy than that needed to produce the excited singlet of tetracene, is electrochemiluminescent.

While a bimolecular process is *required* by these results to account for the anti-Stokes behaviour, triplet annihilation seems to be ruled out. Other types of association of the fluorescer or its ions must be considered as possibilities in accounting for this energy doubling effect. Both diamagnetic and paramagnetic ion-radical dimers and other aggregates are known.[14] Co-oxidation of several anions in an anion-radical aggregate of (I), for example, at the threshold voltage may result in cumulative energy transfer to one of the resulting molecules and in this way account for the dim fluorescence emission.

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† Even endothermic energy transfer from the triplet of (I) to the triplet of (III) may compete with *T–T* annihilation.

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