

# Chapter 1: Fundamentals of Electrogenerated Chemiluminescence (ECL)

## 1.1 Introduction

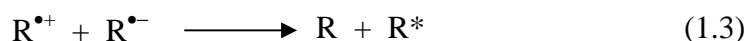
The electrogenerated chemiluminescence (ECL) is a phenomenon that a light emission arises from the high energy electron transfer reaction between electrogenerated species, which is usually accompanied with the regeneration of emitting species. Although a luminescence during electrolysis was already observed<sup>1-3</sup> in 1920's, the first detailed ECL<sup>4</sup> was reported by Hercules back in 1964. Then ECL has been extensively investigated to elucidate the mechanism and origin of ECL, and many reviews<sup>5-10</sup> are available in literatures.

ECL is a sort of chemiluminescence (CL), in that a light emission is produced by the energetic electron transfer reaction. However, the difference between CL and ECL is how to control a light emission. In CL, luminescence is governed by merely mixing or flowing an emitter with necessary reagents in a reaction vessel. In contrast, a light emission is controlled by turning on/off the electrode potential in ECL. As an analytical technique, ECL has some advantages over CL: (1) ECL has more spatial freedom than CL in that the emission spot can be controlled and manipulated by moving an electrode or varying the size/number of electrodes because ECL reaction occurs only in the diffusion layer of an electrode, (2) ECL can be more selective than CL in that the generation of excited states can be selectively controlled by varying the electrode potentials, (3) ECL is a non-destructive technique because ECL emitters are regenerated after the ECL emission. In this chapter, the fundamental principles of ECL will be reviewed before the main topics are discussed.

## 1.2 Ion Annihilation

ECL by ion annihilation is possible when the emitter (R) can electrochemically produce both a sufficiently stable radical cation ( $R^{\bullet+}$ ) and anion ( $R^{\bullet-}$ ). The produced radical ion is annihilated by the oppositely charged radical ion to generate the excited state ( $R^*$ ), as shown in Scheme 1.1.

**Scheme 1.1**

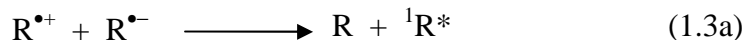


Depending on the energy available in an ion annihilation, eq. (1.3), the produced  $R^*$  could be either the lowest excited singlet state species ( $^1R^*$ ) or the triplet state species ( $^3R^*$ ). The energy available in eq. (1.3) can be calculated from the electrode potentials for eq. (1.1) and eq. (1.2) as defined in eq. (1.5)<sup>5</sup>.

$$-DH_{\text{ann}} = E_p(R/R^{\bullet+}) - E_p(R/R^{\bullet-}) - 0.1 \text{ eV} \quad (1.5)$$

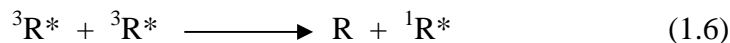
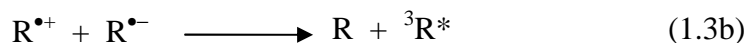
where  $-DH_{\text{ann}}$  (eV) is the enthalpy for ion annihilation,  $E_p$  is the peak potential for the electrochemical oxidation or reduction, and 0.1 eV is the entropy approximation term ( $TDS$ ) at 25 °C. If the energy ( $-DH_{\text{ann}}$ ) estimated from eq. (1.5) is larger than the energy ( $E_s$ ) required to produce the lowest excited singlet state from the ground state, it is possible to directly generate  $^1R^*$  from eq. (1.3), and this system is called *the energy-sufficient system* or *the S-route*. The typical example of the energy-sufficient system is the  $DPA^{\bullet+}/DPA^{\bullet-}$  ( $DPA = 9,10$ -diphenylanthracene) system.<sup>11,12</sup>

### S-route



In contrast, if  $-DH_{\text{ann}}$  is smaller than  $E_s$  but larger than the triplet state energy ( $E_t$ ),  $^3R^*$  is initially formed, and then  $^1R^*$  can be formed by the triplet-triplet annihilation (TTA) as shown in eq. (1.6). This is called *the energy-deficient system* or *the T-route*. The typical examples of the energy deficient system are  $TMPD^{\bullet+}/DPA^{\bullet-}$  and  $TMPD^{\bullet+}/AN^{\bullet-}$  ( $TMPD = N,N,N',N'$ -tetramethyl-*p*-phenylenediamine and  $AN =$  anthracene).<sup>11,13</sup> The efficiency of direct emission from  $^3R^*$  is usually low in a solution phase because of the long radiative lifetime of  $^3R^*$  and its quenching by radical ions or other species, such as molecular oxygen.

### T-route



If  $-DH_{\text{ann}}$  is nearly marginal to  $E_s$ , the T-route can contribute to the formation of  $^1R^*$  in addition to the S-route and it is called *the ST-route*. Although the T-route is inefficient in the presence of considerable S-route,<sup>12,14–16</sup> it is still possible for the ST-route to exist. The typical example is the rubrene anion-cation annihilation<sup>17–19</sup>.

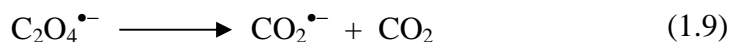
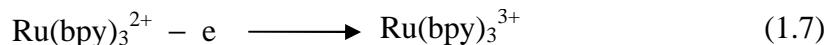
## 1.3 Coreactants

A coreactant is a compound that can produce a reactive intermediate (a strong reducing or

oxidizing agent) by a reaction following the electrochemical or chemical electron transfer reaction. Use of a coreactant is useful especially when one of  $R^{\bullet+}$  or  $R^{\bullet-}$  is not stable enough for ECL reaction, or when the ECL solvent has a narrow potential window so that  $R^{\bullet+}$  or  $R^{\bullet-}$  cannot be formed. In an aqueous solvent, the use of a coreactant is very important because water has the narrow potential window, the low solubility of many organic compounds, and many radical ions of organic emitters are unstable in an aqueous solvent.

The first coreactant used for ECL was oxalate ion ( $C_2O_4^{2-}$ ).<sup>20,21</sup> When  $C_2O_4^{2-}$  is oxidized, it produces the strong reducing agent,  $CO_2^{\bullet-}$  ( $E^\circ = -1.9$  V vs NHE<sup>22</sup>), and  $CO_2$ . For example, the aqueous solution of  $Ru(bpy)_3^{2+}$  can produce ECL in the presence of  $C_2O_4^{2-}$  via Scheme 1.2. In addition, aliphatic amines<sup>23–26</sup> and peroxydisulfate ( $S_2O_8^{2-}$ )<sup>27–29</sup> have been used as coreactants.

### Scheme 1.2

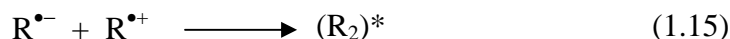
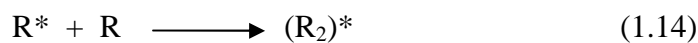


To be a good coreactant, the following conditions should be met: (1) the coreactant should be reasonably soluble in a solvent because the ECL intensity is generally proportional to the concentration of it, (2) the reactive intermediate species generated electrochemically and chemically should be stable enough for the duration of the ECL experiment, (3) the coreactant should be easily oxidized or reduced with the ECL emitter at or near the electrode and undergo a rapid following chemical reaction to form a reactive intermediate, (4) the rate of a reaction between the intermediate and the radical ion of an ECL emitter must be rapid, (5) the coreactant and its intermediate should have inert or weak quenching effect on ECL, and (6) the coreactant itself should not produce any light emission.

## 1.4 Formation of Excimers or Exciplexes

In fluorescence, excimers (excited dimers) are formed by a reaction of ground state (R) and excited state ( $R^*$ ) species [eq. (1.14)]. Unlike fluorescence, the direct generation of excimers ( $(R_2)^*$ ) can occur in addition to eq. (1.14) during the ion annihilation for ECL [eq. (1.15)].

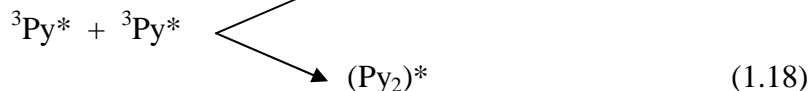
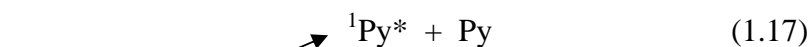
Depending on the molecular structure of R and the lifetime of R\*, eq. (1.14) may be negligible in ECL.



Chandross<sup>30</sup>, *et. al.*, first reported the excimer formation of 9,10-dimethylantracene, phenanthrene, perylene, and 3,4-benzpyrene during electrolysis and they suggested that excimer might be mainly formed by eq. (1.15).

The excimer can also be formed during the triplet-triplet annihilation (TTA). Bard<sup>31</sup>, *et. al.* demonstrated the excimer formation of pyrene when the radical anion of pyrene (Py) was annihilated by the radical cation of TMPD (T-route) at the rotating ring-disk electrode as shown in Scheme 1.3.

**Scheme 1.3**

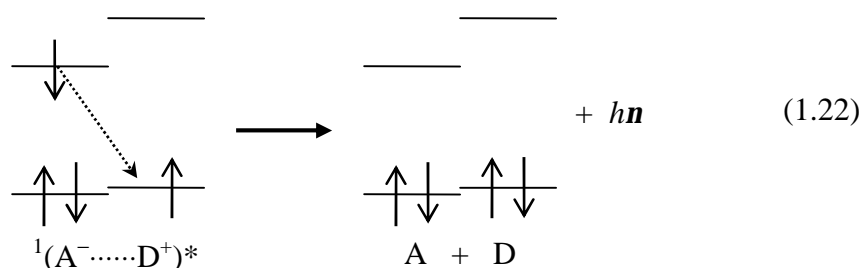


Similar to the formation of excimers, the exciplex (excited complex) can be formed by eqs. (1.19), (1.20), and (1.21). In ECL, the exciplex emission arises mainly through eq. (1.19)<sup>32</sup>, although the mode of exciplex formation depends primarily on the energy available in ion annihilation. The singlet quenching path, eq. (1.20), is inefficient in ECL unless the excited singlet state is produced in proximity of D.



The emission of formed exciplexes may be rationalized by the following scheme 1.4.

**Scheme 1.4**



A typical example is the ECL of  $\text{PTP}^{\bullet-}/\text{TPTA}^{\bullet+}$  (PTP = *p*-terphenyl and TPTA = tri-*p*-tolylamine) system in acetonitrile.<sup>33</sup>

### 1.5 Preannihilation ECL

It was reported that ECL was produced when only  $\text{R}^{\bullet+}$  or  $\text{R}^{\bullet-}$  was generated in a solvent without any coreactants.<sup>34–37</sup> Such luminescence is called as the preannihilation ECL and it is usually thought that a light emission may be generated by a reacting species produced from solvents, electrolytes, or impurities. For example, when rubrene was electrochemically reduced at – 1.6 V in DMF and then the electrode potential was scanned back to – 0.2 V, a light emission was observed.<sup>35</sup>

### 1.6 Concluding Remark

Recently, ECL is of great interest for analytical applications as a result of its high sensitivity and selectivity. ECL produced by a coreactant has been employed in a variety of areas: fiber optic ECL sensor<sup>38–40</sup>, detection method for HPLC<sup>41–43</sup>, ECL biosensing<sup>44–46</sup>, immunoassay and DNA-probe assay analyses<sup>47–49</sup>, and etc. Therefore, it is important to understand ECL reaction mechanisms and reactivities of coreactants. In this dissertation, the reaction mechanisms and reactivities of amine (Chapters 2 and 3) and benzoyl peroxide (Chapters 4 and 5) coreactants are described for the ECL of  $\text{Ru}(\text{bpy})_3^{2+}$ , neutral red, and ter(9,9-diarylfluorene)s.

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