

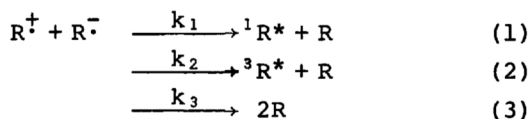
A METHOD FOR A MEASUREMENT OF THE ELECTRON TRANSFER  
RATE CONSTANT IN ECL

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A simple method for measuring reaction rate constants of anion-cation annihilation reactions is proposed. The method is principally capable of obtaining an accurate value of the total reaction rate constant  $K$  in Eq.(4). A preliminary result is given for the diphenylanthracene - benzonitrile system.

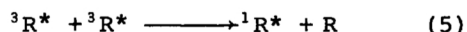
Homogeneous reactions in the electrochemiluminescence (ecl) contain an electron transfer process yielding an electronically excited molecule and a ground state molecule. Such a process is the back reaction of the electron transfer quenching of an electronically excited molecule. Kinetic analysis of the anion-cation annihilation reaction accompanied by a generation of excited molecules and that of the electron transfer quenching are complementary to each other for the analysis of electron transfer reactions. However, there has been reported much less kinetic studies of ecl compared with the electron transfer quenching<sup>1)</sup> or ground state electron exchange reactions.<sup>2)</sup> For instance, discrepancy from Marcus' theory has been reported for the rate constant of the electron transfer fluorescence quenching,<sup>3)</sup> but no kinetic data on the reverse process have been available yet.

The fundamental scheme of the anion-cation annihilation reaction in the ecl is as follows.



$$K = k_1 + k_2 + k_3 \quad (4)$$

Reaction (2) is, in some cases, followed by the triplet-triplet annihilation.



It has been believed that reaction (1) occurs in the so called "normal region" in the potential energy diagram while reaction (2) and (3) in the "abnormal region".<sup>4)</sup> If we can measure the rate of each reaction, such information should be very useful for the study of electron transfer reactions.

The rate constant of reaction (1) can be measured from the total reaction rate constant  $K$ , and the ecl efficiency, that of reaction (2) might be measured by a triplet quencher method, and that of reaction (3) will be obtained from Eq.(4).

There have been reported a few attempts to measure the total reaction rate constant,  $K$ . All of those investigations were carried out by the method to observe the number of photons emitted from singlet molecules yielded from reaction (1) since the singlet formation by reaction (5) is of no significance in the systems investigated.

Bard et al. obtained a lower limit of  $K$  as  $K > 10^7 \text{M}^{-1} \text{sec}^{-1}$  for the diphenylanthracene (DPA)-dimethylformamide system, by the use of the RRDE and a simulation technique.<sup>5)</sup> Van Duyne estimated as  $K < 10^{10} \text{M}^{-1} \text{sec}^{-1}$  for the DPA-acetonitrile system<sup>6)</sup> applying the double potential step method of Feldberg<sup>7)</sup> and the single photon counting method. The limitation of the measurement of Bard et al. is caused by a mechanical difficulty in rotating electrodes. In Van Duyne's case since the differential equation contains non-linear terms, fitting of an experimental curve to a theoretical one was difficult. In general, the difficulty of the analysis of an anion-cation annihilation reaction in ecl arises from non-linear reaction terms in the differential equations, because sources of anions and cations are not homogeneously distributed in the system under a real experimental condition.

Under the condition of homogeneous concentration of ion radicals in an ecl system, the rate equations for the radical species are given as follows.

$$\frac{d}{dt}[\text{R}^-] = -K[\text{R}^-][\text{R}^+] - k^-[\text{R}^-] + \frac{i}{VF} \left\{ 1 - a^- - \frac{(1-a^-)[\text{R}^+]}{[\text{R}] + [\text{R}^+]} - \frac{(1-a^+)[\text{R}^-]}{[\text{R}] + [\text{R}^+]} \right\} \quad (6)$$

$$\frac{d}{dt}[\text{R}^+] = -K[\text{R}^-][\text{R}^+] - k^+[\text{R}^+] + \frac{i}{VF} \left\{ 1 - a^+ - \frac{(1-a^-)[\text{R}^+]}{[\text{R}] + [\text{R}^+]} - \frac{(1-a^+)[\text{R}^-]}{[\text{R}] + [\text{R}^+]} \right\} \quad (7)$$

Here,  $i$  is the current of the electrode reactions,  $V$  is the solution volume,  $F$  is the Faraday constant,  $a^-$ ,  $a^+$  are portions of subreactions at the cathode and anode respectively, such as reduction and oxidation of the solvent,  $k^-$ ,  $k^+$  are respectively the pseudo uni-molecular reaction rate constants of anion and cation radicals: We assumed in the last terms of Eqs.(6) and (7) that the electrode reactions are diffusion limited, and took the discharge of radicals into consideration.

When the condition that the concentration of one radical species,  $\text{R}^+$  or  $\text{R}^-$ , is much greater than the other is fulfilled, we are able to reduce the rate equations to linear ones. For example, in the case that the efficiency of the production of  $\text{R}^-$  is sufficiently large compared with that of  $\text{R}^+$  and the lifetime of  $\text{R}^-$  is long enough, we can see from Eqs.(6) and (7) that the concentration of  $\text{R}^-$  becomes extremely larger than that of  $\text{R}^+$  in the stationary state. We are also able to see from Eqs.(6) and (7) that the time constant of  $\text{R}^-$  to reach such a stationary state is much larger than that of  $\text{R}^+$ : roughly speaking, the time constant is  $\left\{ \frac{i}{VF} + K[\text{R}^+] \right\}^{-1}$  for  $\text{R}^-$  and  $\{K[\text{R}^-]\}^{-1}$  for  $\text{R}^+$ . Since  $[\text{R}^-]$  is more than  $10^2 \times [\text{R}^+]$  and the two terms in the time constant of  $\text{R}^-$  is of the same order under our experimental condition; the time constant for  $\text{R}^-$  can be regarded as sufficiently larger than that of  $\text{R}^+$ . In such a case, at a time when only the concentration of  $\text{R}^+$  is in the stationary state we can replace  $[\text{R}^+]$  by  $[\text{R}^+]_\infty$  in Eq.(6), and the time dependence of  $[\text{R}^-]$  becomes as follows;

$$[\text{R}^-] = [\text{R}^-]_\infty \left[ 1 - \exp\left\{-\left(K[\text{R}^+] + \frac{i}{VFA}(1-a^+)\right)t\right\} \right] \quad (8)$$

$$[\text{R}^-]_\infty = \frac{i}{VF} / \left\{ K[\text{R}^+] + \frac{i}{VF}(1-a^-) \right\} = \frac{i\tau_1}{VFA} \quad (9)$$

Here,  $A = [R] + [R^{\dagger}] + [R^{\bar{\cdot}}]$  and  $\tau_1 = \{K[R^{\dagger}]_{\infty} + \frac{i}{\sqrt{F}}(1-a^{-})\}^{-1}$ , the latter being the value to be obtained experimentally. The variation of  $A$  within the time of measurement can be neglected. Emission intensity,  $I$ , from  ${}^1R^*$  is proportional to  $K_1[R^{\dagger}][R^{\bar{\cdot}}]$ , or to  $[R^{\bar{\cdot}}]$  in the above case, so we can obtain  $\tau_1$  from the time dependence of  $I$ . The value of  $\tau_1$  is used in the estimation of  $K$ .

Now we consider the other extreme condition. When we cut off the current in a stationary state, we can put  $i = 0$  and  $[R^{\bar{\cdot}}] = [R^{\bar{\cdot}}]_{\infty}$ . Then the time dependence of  $I$  is given as follows;

$$I \propto [R^{\dagger}] = [R^{\dagger}]_{\infty} \exp(-\tau_2 t) \quad (10)$$

$$\tau_2 = \{K[R^{\bar{\cdot}}]_{\infty} + k^{\dagger}\}^{-1} \quad (11)$$

We can estimate  $K$  from Eqs. (9) and (11) if we know the value of  $k^{\dagger}$ .

As an example of applying the above method, we made an experiment as follows. Direct current electrolysis was carried out under the condition of continuous stirring for DPA-benzonitrile system in which the lifetimes of the radical species,  $DPA^{\dagger}$  and  $DPA^{\bar{\cdot}}$ , are long enough and the condition,  $[R^{\bar{\cdot}}] \gg [R^{\dagger}]$ , is satisfied in the stationary state by the fact,  $a^+ > a^-$ , which was ascertained by the method of cyclic voltammetry. Moreover  $k^{\dagger}$  in Eq. (11) can be neglected since  $(k^{\dagger})^{-1}$  is of the order of 10 sec while  $\tau_2$  is  $10^{-3}$  sec.<sup>(8)</sup> The input voltage was 3.6V at which both the electrode reactions can be regarded as diffusion limited. The current was constant for more than two hours. Intensity of the emitted light was measured with a photomultiplier attached at a hole of an integrating box. The result are shown in Fig.1 and Fig.2.

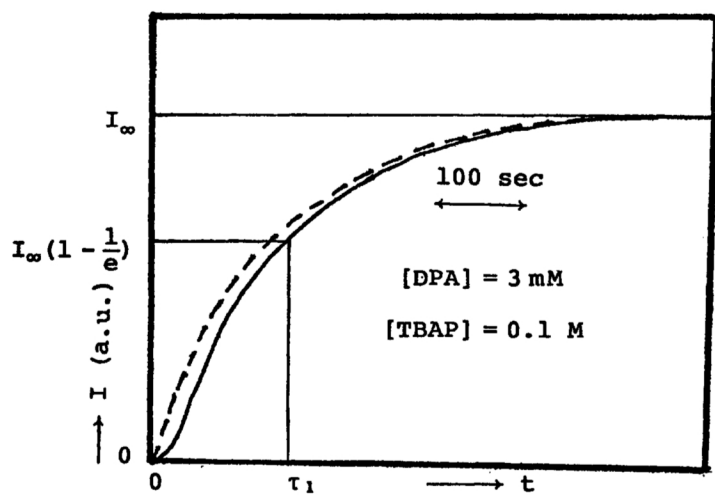


Fig.1 Time dependence of  $I$  after switching on the current

----- calculated curve  
 ————— experimental curve

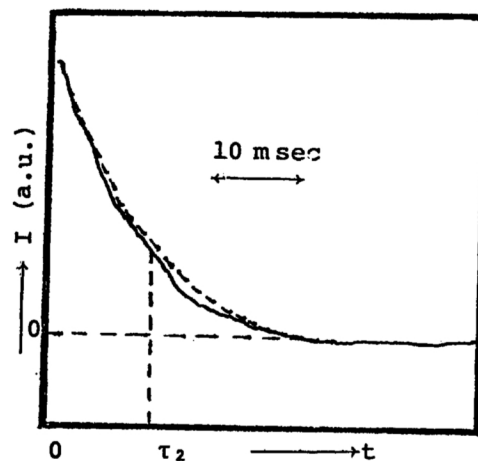


Fig.2 Time dependence of  $I$  after switching off the current

----- calculated curve  
 ————— experimental curve

The discrepancy of the experimental curve from the calculated one near  $t=0$  in Fig.1 is brought about from the fact that the time constant of  $[R^{\ddagger}]$  to reach the stationary state is not zero, though small enough.  $\tau_1$  was obtained from Fig.1 to be 185 sec. In Fig.2 the experimental curve does not show a simple exponential decay. This occurs from the fact that the concentration of the radical species is not ideally homogeneous in the solution, because the stirring was not sufficiently fast. For the sake of improving the homogeneity, current was reduced in the stationary state to make  $[R^{\ddagger}]$  small. In fact, we observed that the decay form of I became nearly exponential with diminishing current. We obtained the value of  $\tau_1$  to be  $1.5 \times 10^{-3}$  sec by extrapolating the current to zero. With this procedure K was estimated as  $2.5 \times 10^6 \text{M}^{-1} \text{sec}^{-1}$ .

Unfortunately, the time constant of the electric circuit in the present experiment was of the order of  $10^{-3}$  sec, so  $\tau_2$  might be controlled by this time constant. Therefore, it should be considered that  $\tau_2 < 1.5 \times 10^{-3}$  sec and  $K > 2.5 \times 10^6 \text{M}^{-1} \text{sec}^{-1}$ .

Although the present method is very simple and easily carried out, it is necessary to make the time constant of the circuit smaller than  $\tau_2$  to obtain an accurate value of K. The time constant of the circuit is nearly proportional to the electrode size; it becomes  $10^{-6}$  sec when the electrode size is 0.1 mm  $\phi$ . At a low concentration of  $[R^{\cdot-}]$ , e.g.  $[R^{\cdot-}] = 10^{-6} \text{M}$ ,  $\tau_2$  becomes  $10^{-4}$  sec assuming that  $K = 10^{10} \text{M}^{-1} \text{sec}^{-1}$ . Smaller value of  $[R^{\cdot-}]$  results in larger  $\tau_2$ , so it would be useful to apply the single photon counting method for obtaining accurate values of the rate parameters.

#### References

- 1) H.Shomberg, H.Staerk, and A.Weller, Chem. Phys. Lett., 22 1 (1973)
- 2) B.A.Kowert, L.Marcoux, and A.J.Bard, J. Amer. Chem. Soc., 94 5538 (1972)
- 3) H.Shomberg, H.Staerk, and A.Weller, Chem. Phys. Lett., 21 433 (1973);  
S.Efrima and M.Bixon, Chem. Phys. Lett., 25 34 (1974)
- 4) R.A.Marcus, J. Phys. Chem., 52 2803 (1970)
- 5) J.T.Malloy, K.B.Prater, and A.J.Bard, J. Amer. Chem. Soc., 93 5959 (1971)
- 6) P.Van Duyne, and S.F.Fischer, Chem. Phys., 5 183 (1974)
- 7) S.W.Feldberg, J. Phys. Chem., 70 3928 (1966)
- 8)  $k^+$  was roughly estimated as follows: First, potentiostatic electrolysis of the system under consideration was carried out without stirring for a certain period, then the system was kept at rest for a while. If the stirring was started after a certain period, cation and anion radicals which did not react with impurity or so reacted with each other and light emission was observed. We can estimate the lifetime of the radical species whose lifetime is shorter from the variation of emission intensity with the period of keeping the system at rest. By the above procedure we got the value of  $(k^+)^{-1}$  of the order of 10 sec.

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