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On the Excimer Formation of Pyrene in Electrochemiluminescenece

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Temperature effect in electrochemiluminescenece (ECL) of pyrene was investigated in order to clarify the formation of excimers. The ratio of intensity of excimer to monomer emission was measured on solutions of pyrene in *N*,*N*-dimethylformamide (DMF) at various temperatures from the decay curves of excimer emission due to pulse excitation with a nitrogen laser. The temperature change of concentration dependence of the ratio was derived from the rate equations for the respective direct and indirect formation of excimers. The mechanism of direct excimer formation was confirmed in ECL of pyrene more clearly by analysis of the temperature effect than by that of the concentration effect at a certain temperature.

Electrochemiluminescence (ECL) from pyrene has been studied by several workers since Hercules[1)] first recognized the blue emission in *N*,*N*-dimethylformamide (DMF). Fleet *et al.*[2)] reported on ECL spectra containing an excimer emission. Kihara *et al.*[3)] proposed the formation of the excited state of pyrene *via* anion-cation annihilation in acetonitrile, but carried out measurements only at room temperature. Very few measurements have been made on the temperature effect on ECL. Recently, we reported on the temperature dependence of the red emission in ECL of pyrene.[4)] The temperature effect in ECL of pyrene from monomer and excimers does not seem to have been measured.

This paper deals with the excimer formation process by the temperature effect in emission intensity and relevant rate constants. The rate constants can be analyzed from the decay curves of the excited state of pyrene in DMF under pulse excitation with a nitrogen laser.

Experimental

Pyrene was recrystallized carefully from benzen solution. Tetrabutylammonium bromide (TBAB) used as a supporting electrolyte was recrystallized from ethyl acetate solution. The ECL was observed in a pyrex glass cell equipped with two Pt wire electrodes. The cell was cooled by cold N_2 gas through a copper tube around the cell. ECL spectrum was measured with a fluorescence spectrophotometer (Hitachi MPF-2A) at room temperature and a Hamamatsu T.V. R375 photomultiplier and a photon counting system through interference filter (center wavelength: 386 nm, half width: 13 nm) at low temperatures. The decay curve of excimer emission by nitrogen laser excitation was measured with an oscilloscope, the result being analyzed following the method of Birks.[5)] The measurement was performed under the same conditions as those for ECL measurements, a solution degassed by N_2 gas and containing 1×10^{-2} mol dm^{-3} supporting electrolyte being used. Transmittance of the interference filter was compensated by the spectrum measured with MPF-2A at room temperature.

Results and Discussion

The relationship between ECL emission and the formation of anion-cation was investigated by means of a double potential step and/or triangular potential sweep. Emission with steady intensity was obtained with applied voltage DC 4 V, the solution being stirred. Figure 1 shows the ECL spectrum and the fluorescence spectra. The concentration dependence of the emission

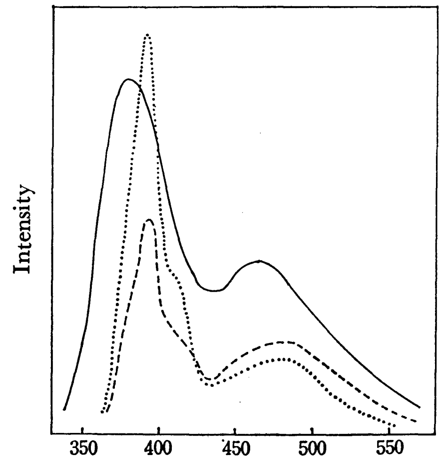

Fig. 1. Emission spectra of pyrene.
——: ECL spectrum at room temperature, pyrene 0.8×10^{-3} mol dm^{-3}, ----: fluorescence spectrum at room temperature, pyrene 6×10^{-3} mol dm^{-3}, ...: fluorescence spectrum at −38 °C, pyrene 6×10^{-3} mol dm^{-3}.

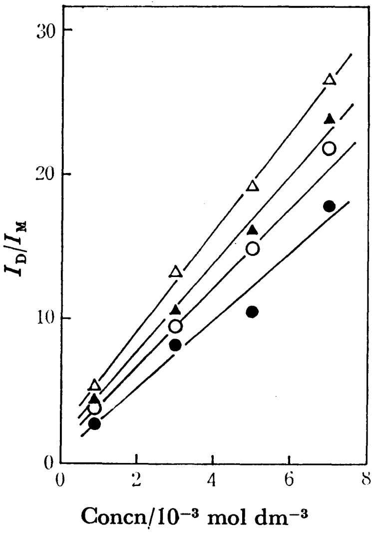

Fig. 2. Concentration dependence of the ratio excimer to monomer emission in ECL at various temperatures.
●: 20 °C, ○: 0 °C, ▲: −10 °C, △: −30 °C.

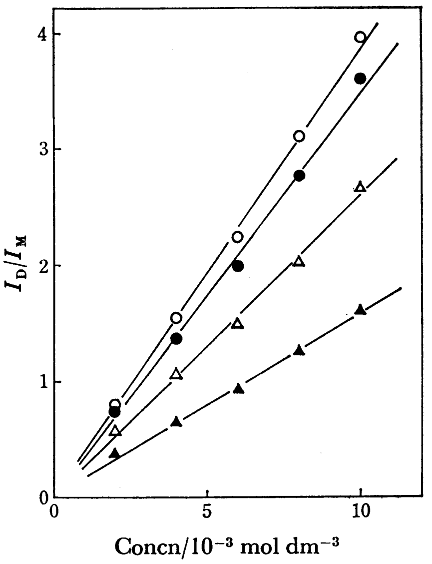

Fig. 3. Concentration dependence of the ratio of excimer to monomer emission in case of photoexcitation at various temperatures.
○: 20 °C, ●: 0 °C, △: −20 °C, ▲: −40 °C.

intensity ratio of excimer to monomer (I_D/I_M) on temperature is shown for ECL and emission by photoexcitation in Figs. 2 and 3, respectively. The results show linearity as regards concentration. The results were analyzed assuming the following reaction scheme:[3)]

$$M^+ + M^- \xrightarrow{k_A} M^* + M, \tag{1}$$

$$M^+ + M^- \xrightarrow{k_B} D^*, \tag{2}$$

$$M^* \xrightarrow{k_{FM}} M + h\nu \qquad M^* \xrightarrow{k_{GM}} M, \tag{3}$$

$$D^* \xrightarrow{k_{FD}} 2M + h\nu' \qquad D^* \xrightarrow{k_{GD}} 2M, \tag{4}$$

$$M^* + M \underset{k_{MD}}{\overset{k_{DM}}{\rightleftarrows}} D^*, \tag{5}$$

where M, M^+, M^-, and D^+ denote the pyrene molecule, its cation, anion, and excimer, respectively, and k denotes the rate constants of each reaction.

In the steady state we have

$$\frac{d[M^*]}{dt} = 0, \quad \frac{d[D^*]}{dt} = 0. \tag{6}$$

Thus

$$\frac{I_D}{I_M} = \frac{k_{FD}}{k_{FM}} \frac{ak_M + (1+a)k_{DM}[M]}{k_D + (1+a)k_{MD}} \equiv K + K'[M], \tag{7}$$

where

$$\frac{I_D}{I_M} = \frac{k_{FD}[D^*]}{k_{FM}[M^*]},$$

and

$$k_M = k_{FM} + k_{GM}, \; k_D = k_{FD} + k_{GD}, \; k_B/k_A = a. \tag{8}$$

On the other hand, k_B is zero in the case of photoexcitation, since excited states are given by the following process instead of processes (1) and (2):

$$M + h\nu \longrightarrow M^*.$$

Thus

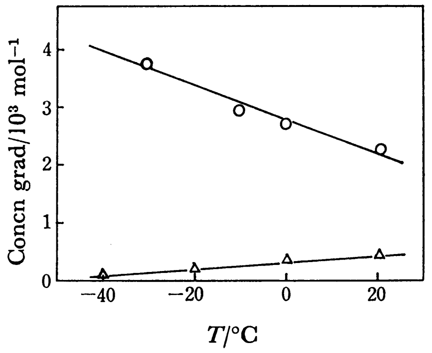

Fig. 4. Temperature dependence of concentration gradient obtained from Figs. 2 and 3.
○: ECL, △: photoexcitation.

$$\frac{I_D}{I_M} = \frac{k_{FD}}{k_{FM}} \frac{k_{DM}[M]}{k_D + k_{MD}} \equiv K''[M]. \tag{9}$$

From Eqs. 7 and 9 and experimental results (Figs. 2 and 3), the formation of the excited state *via* anion-cation annihilation is suggested. Plots of the gradient of I_D/I_M *vs.* temperature from data in Figs. 2 and 3 are shown in Fig. 4. The gradient increases in the case of ECL with fall in temperature but decreases in the case of photoexcitation.

From Eqs. 7 and 9, Kihara *et al.*[3)] put

$$K'/K = (1+a^{-1})k_{DM}k_M, \tag{10}$$

$$K'/K'' = 1 + 1/[a^{-1} + (1+a^{-1})k_{MD}k_D], \tag{11}$$

and evaluated a from the data of k_M, k_D, k_{DM}, k_{MD} of pyrene in cyclohexane or 95% ethanol in substitution for them in acetonitrile. The value of K was estimated by extrapolation. The estimation seems erroneous for the following reasons: estimation of k values from the solutions different from the actual ones of ECL, and the erroneous extrapolation from the relationships I_D/I_M *vs.* concentration.

We postulate the following process for excimer formation in order to analyze the temperature effect on the concentration dependence of I_D/I_M.

From Eqs. 3, 4, 5, and 8, we have

$$\frac{d[M^*]}{dt} = k_{MD}[D^*] - (k_M + k_{DM}[M^*])[M^*]$$

$$\frac{d[D^*]}{dt} = k_{DM}[M][M^*] - (k_D + k_{MD})[D^*].$$

Let us consider the case in which the initial state is a monomer-state. Putting $[M^*]=[M^*]_0$, $[D^*]=0$ at $t=0$, we get

$$[M^*] = \frac{[M^*]_0}{\lambda_2 - \lambda_1}(c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t}),$$

$$[D^*] = \frac{k_{DM}[M][M^*]_0}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t}),$$

where

$$\lambda_1 = \frac{1}{2}\{k_M + k_{DM}[M] + k_D + k_{DM} - \sqrt{s}\},$$

$$\lambda_2 = \frac{1}{2}\{k_M + k_{DM}[M] + k_D + k_{MD} + \sqrt{s}\},$$

$$s = (k_D + k_{MD} - k_M - k_{DM}[M])^2 - 4k_{MD}k_{DM}[M],$$

$$c_1 = \lambda_2 - k_{\mathrm{M}} - k_{\mathrm{DM}}[\mathrm{M}],$$
$$c_2 = k_{\mathrm{M}} + k_{\mathrm{DM}}[\mathrm{M}] - \lambda_1.$$

Substituting them into the equation

$$\frac{I_{\mathrm{D}}}{I_{\mathrm{M}}} = \frac{k_{\mathrm{D}}\int[\mathrm{D}^*]\mathrm{d}t}{k_{\mathrm{M}}\int[\mathrm{M}^*]\mathrm{d}t},$$

we get

$$\frac{I_{\mathrm{D}}}{I_{\mathrm{M}}} = \frac{k_{\mathrm{D}}k_{\mathrm{DM}}[\mathrm{M}]}{k_{\mathrm{M}}(k_{\mathrm{D}}+k_{\mathrm{MD}})}. \qquad (12)$$

Putting $[\mathrm{M}^*]=0$, $[\mathrm{D}^*]=[\mathrm{D}^*]_0$ at $t=0$, we get

$$[\mathrm{M}^*] = \frac{[\mathrm{D}^*]_0(\lambda_2-y)(y-\lambda_1)}{k_{\mathrm{DM}}[\mathrm{M}](\lambda_2-\lambda_1)}(\mathrm{e}^{-\lambda_1 t}-\mathrm{e}^{-\lambda_2 t}),$$

$$[\mathrm{D}^*] = \frac{[\mathrm{D}^*]_0}{\lambda_2-\lambda_1}[(\lambda_2-y)\mathrm{e}^{-\lambda_1 t}+(y-\lambda_1)\mathrm{e}^{-\lambda_2 t}],$$

and

$$\frac{I_{\mathrm{D}}}{I_{\mathrm{M}}} = \frac{k_{\mathrm{D}}(k_{\mathrm{M}}+k_{\mathrm{DM}}[\mathrm{M}])}{k_{\mathrm{M}}k_{\mathrm{MD}}}, \qquad (13)$$

where

$$y = k_{\mathrm{D}} + k_{\mathrm{MD}}.$$

The decay parameters λ_1 and λ_2, obtained experimentally are given Figs. 5 and 6. The values of the rate constants k_{M}, k_{D}, k_{DM}, and k_{MD} can be obtained by use of the parameters. The constants in DMF at 20 °C, 0 °C, −20 °C, and −40 °C are given in Table 1. The temperature dependence of $k_{\mathrm{D}}k_{\mathrm{DM}}/k_{\mathrm{M}}(k_{\mathrm{D}}+k_{\mathrm{MD}})$ and $k_{\mathrm{D}}k_{\mathrm{DM}}/k_{\mathrm{M}}k_{\mathrm{MD}}$ is calculated by means of Eqs. 12 or 13 and the values given in Table 1. The results are shown in Fig. 7. By comparison of the curves in Figs. 4 and 7,

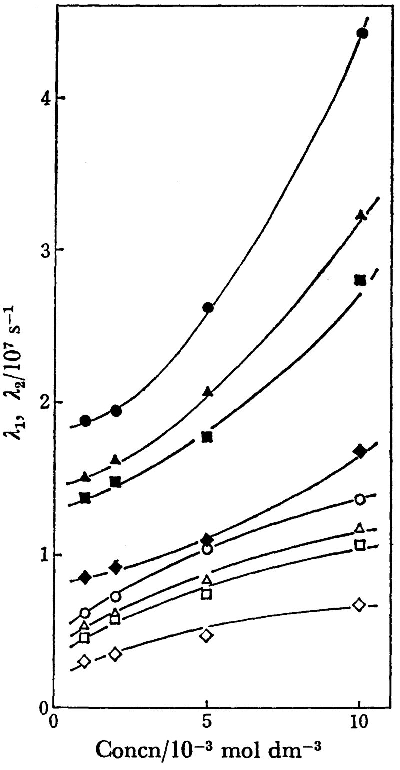

Fig. 5. Plots of decay parameters λ_1 and λ_2 against molar concentration, obtained by pulse excitation on the DMF solution of pyrene at various temperatures.
λ_1: ○ 20 °C, △ 0 °C, □ −20 °C, ◇ −40 °C.
λ_2: ● 20 °C, ▲ 0 °C, ■ −20 °C, ◆ −40 °C.

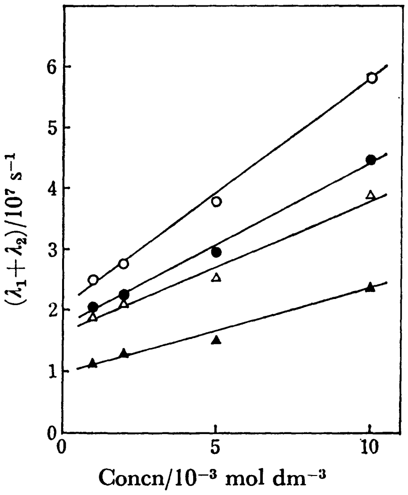

Fig. 6. Dependence of $\lambda_1+\lambda_2$ against molar concentration at various temperatures.
○: 20 °C, ●: 0 °C, △: −20 °C, ▲: −40 °C.

TABLE 1. RATE CONSTANTS OBTAINED BY PULSE EXCITATION OF THE DMF SOLUTION OF PYRENE AT VARIOUS TEMPERATURES

Temp/°C	k_{M} / 10^{-7} s^{-1}	k_{D} / 10^{-7} s^{-1}	k_{DM} / 10^{-9} M^{-1} s^{-1}	k_{MD} / 10^{-7} s^{-1}
20	0.5	1.4	3.8	0.4
0	0.4	1.2	2.6	0.4
−20	0.35	1.1	2.1	0.2
−40	0.25	0.7	1.4	0.1

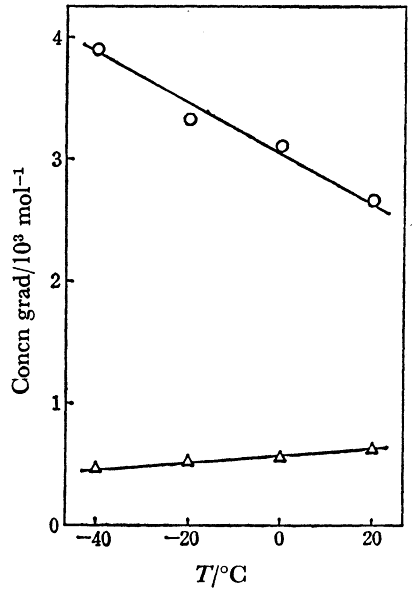

Fig. 7. Temperature dependence of concentration gradient calculated from Eqs. 12, 13, and Table 1.
○: Initial conditions [M*]=0, △: initial conditions [D*]=0.

we see that the curves for photoexcitation and for ECL (Fig. 4) correspond respectively to the curves for Eqs. 12 and 13. $[D^*]=0$ at $t=0$ in case of photoexcitation, and $[M^*]=0$ at $t=0$ (excimers are directly generated from anion-cation annihilation) in case of ECL. Mechanism of direct excimer formation is confirmed in ECL of pyrene through analysis of temperature and concentration dependence of I_D/I_M. The present approach is more advantageous than the conventional one, utilizing the value K of I_D/I_M at $[M]=0$, which is often erroneous.

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