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Chemiluminescence Induced by Mediated Oxidation of 1,2-Diols

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The electrooxidation of iodide ions (I^-) induces chemiluminescence from1,2-diols in an alkaline solution. The induced chemiluminescence occurs slightly after the electrooxidation of I^-. The anodically generated hypoiodite ions (IO^-) seem to be a mediator-oxidant responsible for the mediated oxidation of 1,2-diols, resulting in the induced chemiluminescence.

As reported previously, various polyhydric alcohols including 1,2-diols and some monoalcohols, such as methanol and ethanol, emit light peaking at approximately 550 nm, when electrooxidized in an alkaline solution.1) A cyclic voltammetric study showed that the light emission occurred at potentials more positive than + 1.1 V (vs. Ag/AgCl, 3 M NaCl), slightly after the electrooxidation of alcoholic hydroxyl groups. Aldehyde and its corresponding carboxylic acid were found to be generated in the reaction sequence and such carbonyl fragments seemed to be generated in the electronically excited state responsible for the light emission. The present study showed that the mediated oxidation of 1,2-diols also causes light emission. This light emission is referred to herein as the induced chemiluminescence. The electrooxidation system of I^- was employed to give a mediator-oxidant because the oxidized derivatives of I^- possess useful electrophilicity to oxidize organic compounds and are easily generated anodically.2) For instance, iodonium ions (I^+) are such potent electrophiles that they oxidize even monoalcohols to corresponding ketones.3) Shono et al. developed the mediated oxidation of monoalcohols to ketones and esters using anodically generated I^+ as an electron carrier.4)

The electrolytic cell employed has a glassy carbon working electrode (6 mm in diameter) and a quartz window, facing the working electrode. Both are embedded in two Teflon plates and a silicone rubber spacer (5mm in thickness) is placed between them. The counter electrode was a Pt wire. The electrode potential was monitored with respect to an Ag/AgCl, 3 M NaCl, electrode (BAS Co.). The sample size was kept at 1.4 ml at each measurement. The photo-tube output for the light emission was expressed in nano ampere (nA). The apparatus for measurements has been described previously.1, 5) The I^- solution was prepared from NaI (Wako Pure Chemical Industries). Glycols were of the best commercial grade (Tokyo Chemical Industries). Monoalcohols were of spectral grade. NaOH was Merck's Suprapur®. Every sample solution was prepared using deionized and distilled water. All measurements were conducted at 25 ± 1 °C.

Figure 1 shows the cyclic voltammograms of 1,2-ethanediol in 2.0 M NaOH in the presence and absence of I^- and the corresponding light emission profiles as a function of the applied potential. In the absence of I^-, the light emission wave around + 1.4 V, due to the direct electrooxidation of 1,2-ethanediol,1) was observed; while in its presence another light emission wave around + 1.1 V was observed. The light emission wave around +1.1 V occurred slightly after the anodic wave of I^-. This implies that a certain oxidant anodically derived from I^- induces the chemiluminescence from 1,2-ethanediol. However, the light emission wave around + 1.4 V decreased as compared to that observed in the absence of I^-. As shown in Fig. 2, 1,2-diols other than 1,2-ethanediol also showed the induced chemiluminescence, although the intensity was weaker. Unlike 1,2-diols, the electrooxidation of I^- did not induce the chemiluminescence from monoalcohols tested (methanol, ethanol, 2-propanol and *t*-butyl alcohol) or from 1,3-diols tested (1,3-propanediol and 1,3-butanediol). There was no difference in the anodic wave for I^- between the systems, one produced the induced chemiluminescence and the other did not. In contrast to the electrooxidation of I^-, that of either Br^- or Cl^- did not induce chemiluminescence.

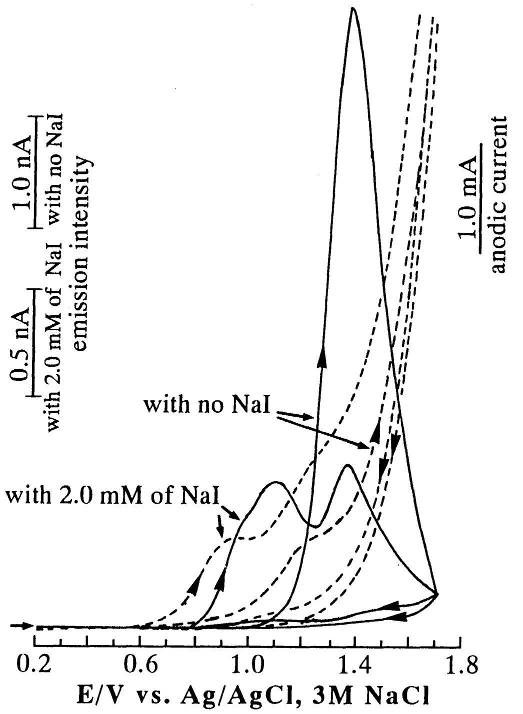

Fig. 1. Light emission profiles (——) of 1,2-ethanediol (5.0 mM) in 2.0 M NaOH in the presence and absence of I^- and corresponding cyclic voltammograms (-----). Potential scan starts from + 0.3 V at 200 mV/s. Zero emission is indicated by an arrow.

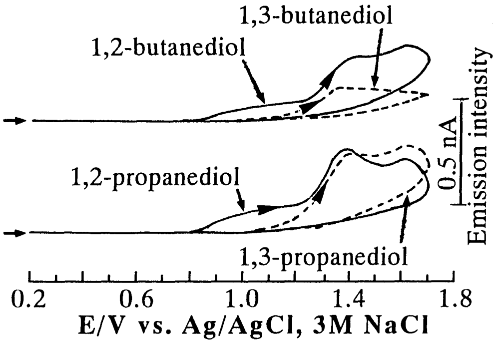

Fig. 2. Comparison of light emission profiles between 1,2-diol (5.0 mM) and 1,3-diol (5.0 mM) in 2.0 M NaOH containing 2.0 mM of NaI. Potential scan starts from + 0.3 V at 200mV/s. Each zero emission is indicated by an arrow.

On the assumption that the electrooxidation of I^- induces the chemiluminescence from 1,2-diols, it was expected that an increase in the anodic current of I^- would increase the intensity of the induced chemiluminescence. To test this, the relationship between the anodic current of I^- and the induced chemiluminescence intensity was studied by cyclic voltammetry in the system of 1,2-ethanediol containing various concentrations of NaOH and NaI. As shown in Fig. 3, the induced chemiluminescence intensity increased with the anodic current of I^-. These findings support that the electrooxidation of I^- triggers the induced chemiluminescence. However, at NaI concentrations over 4 mM, the induced chemiluminescence decreased.

As stated above, the direct electrooxidation of monoalcohols and polyhydric alcohols, resulting in the light emission, gave aldehyde and then corresponding carboxylic acid.1) For instance, both the direct electrooxidations of 1,2-ethanediol and methanol gave formaldehyde and formic acid. Therefore, to characterize the induced chemiluminescence, it is important to see if aldehyde and carboxylic acid are generated via the mediated oxidation linked with the electrooxidation of I^-. This was tested in the systems of 1,2-ethanediol and of methanol in various concentrations of NaOH solution. For the detection of formaldehyde, the color reaction using 2-amino-5-naphthol-7-sulfonic acid (referred to as J acid) was conducted against the reaction

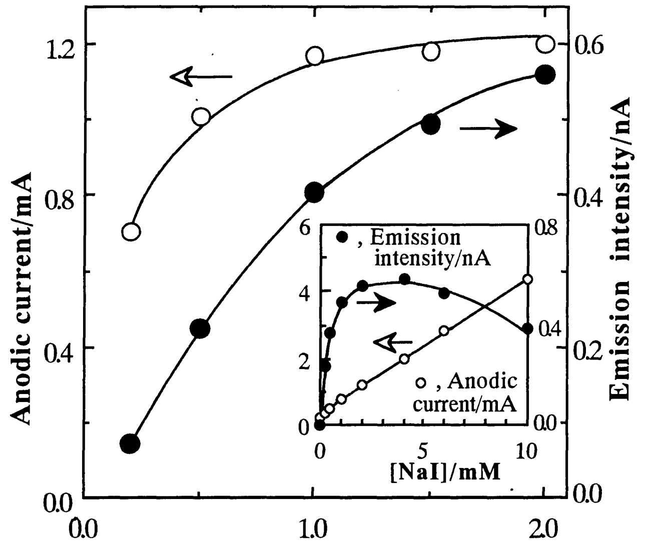

Fig. 3. Plots of anodic current at + 0.9 V and of induced chemiluminescence intensity at + 1.0 V at various concentrations of NaOH in the presence of 2.0 mM of NaI. Inset shows the same plots with the changes in concentration of NaI in 2.0 M NaOH. Plotted data were obtained as in Figs. 1 and 2.

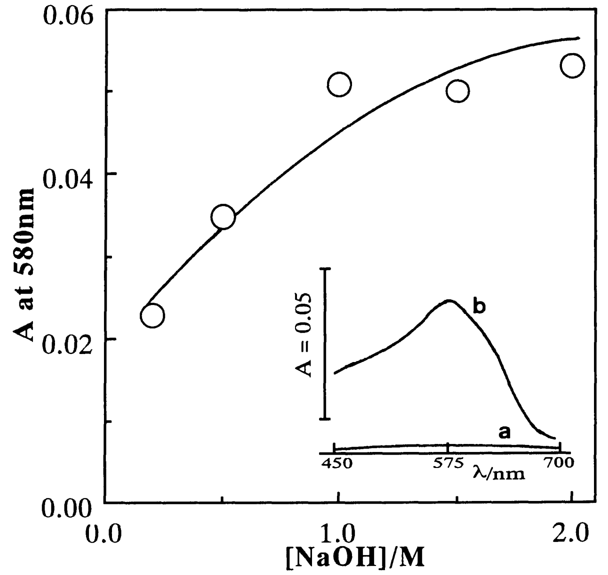

Fig. 4. Formation of formaldehyde upon the mediated oxidation of 1,2-ethanediol (5.0 mM) at various concentartions of NaOH. Inset shows the typical absorption spectra for the color product resulting from the reaction of J acid with the mediator oxidated 1,2-ethanediol (5.0 mM) in 2.0 M NaOH in the absence (a) and presence (b) of 2.0 mM of NaI.

product obtained by the electrooxidation at + 0.9 V of the constant potential with agitation for 5 min.[6] If formaldehyde is generated, then the specific absorption, peaking at 580 nm, is observed and is proportional to the formaldehyde concentration. As shown in Fig. 4, the mediated oxidation of 1,2-ethanediol also yielded formaldehyde and that the amounts increased with the NaOH concentration. The latter finding agrees with the cyclic voltammetric results shown in Fig. 3. Formic acid was not detected in the reaction product.[7] Upon the electrooxidation of 1,2-ethanediol in the absence of I^- at + 0.9 V, no formaldehyde was detected in the reaction product. This is in agreement with the finding that no light emission was observed at + 0.9 V in the system with no I^-. In contrast to 1,2-ethanediol, formaldehyde was not detected in the reaction product of the electrooxidation of methanol in the presence of I^-. This also agrees with the finding that the induced chemiluminescence was not observed in the system of methanol with I^-.

In the reaction sequence for the induced chemiluminescence, it is important to consider the anodical behaviors of I^-. Only one anodic wave attributed to the formation of iodine (I_2), ($2I^- - 2e^- \longrightarrow I_2$), is observed in an alkaline solution and then I_2 reacts with hydroxide ions, resulting in the formation of hypoiodous acid (IOH or HIO), ($I_2 + OH^- \longrightarrow HIO + I^-$), as a first parallel reaction of the electrooxidation of I^-.[8] HIO gives IO^- in an alkaline solution because of its amphoteric property. Since IO^- is a strong electrophile and relatively stable in an alkaline solution, it may be a possible mediator-oxidant for 1,2-diols. In the case of 1,2-ethanediol, the following reaction (1) is proposed as the mediated oxidation. Unlike 1,2-diols,

$$IO^- + C_2H_2(OH)_2 \rightarrow\rightarrow\rightarrow 2HCHO + I^- + H_2O \qquad (1)$$

monoalcohols and 1,3-diols are considered not to be oxidized by IO^- probably because the electrophilicity of IO^- is not strong enough to oxidize monoalcohols or 1,3-diols as compared to that of I^+.

In the reaction (1), fluorescent species is not contained. If formaldehyde is generated in the triplet excited state, then it could emit light in the visible region. Such visible chemiluminescence attributed to non fluorescent carbonyl compounds populated to the triplet excited state was found in the oxidation of hydrocarbon in the liquid phase.9) However, another possibility that intermediate and/or by-product formed in the reaction (1) emitts light should be also taken into account. The coulombic efficiency of the induced chemiluminescence from 1,2-ethanediol was found to be very low (10^{-6} to 10^{-7}).10) The spectrum of the induced chemiluminescence from 1,2-diols was not obtained in the present study because of insufficient intensity. The decreases in the light emission intensity due to the direct electrooxidation of 1,2-ethanediol (see Fig. 1) and in the induced chemiluminescence when the NaI concentration is greater than 4 mM (see Fig. 3) can not be explained at present. Further studies on the induced chemiluminescence including the improvement of the reaction conditions to increase the coulombic efficiency of the induced chemiluminescence are in progress.

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6) Formaldehyde was detected as reported previously (O. M. Aly and S. D. Faust, *Anal Chem.*, **36**, 2200 (1964)). To 1ml of the reaction product resulting from the electrooxidation of 6 ml a sample solution at + 0.9 V (vs. Ag/AgCl, 3 M NaCl) with agitation, 3 ml of 0.3 w/v% J acid prepared with 36 N H_2SO_4 was added and then placed in an oven set at 165 ℃ for 5 min. After the resulting mixture was cooled to room temperature, it was brought to 25 ml solution with acetic acid. Then, the absorption spectrum was recorded ranging between 450 nm and 700 nm with respect to the sample blank, prepared with 1 ml of 2.0 M NaOH instead of 1 ml of the reaction product.
7) Detection of formic acid was attained in accordance to the protocol reported previously (R. Horikawa and T. Tanimura, *Anal. Lett.*, **15**, 1629 (1982) with some changes.
8) W. Geissler, R. Nitzsche, and R. Landsberg, *Electrochim. Acta*, **11**, 389 (1966).
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10) To measure the the coulombic efficiency of the induced chemiluminescence($ø_{ic}$) from 1,2-ethanediol (5mM in 2.0 M NaOH in thepresence of 2.0 mM of NaI), luminol (1 mM in 0.1 M NaOH) was used as a relative standard. The $ø_{ic}$ was calculated according to the following equation; $ø_{ic} = ø_{ecl}(I_{ic}Q_{ecl} / I_{ecl} Q_{ic})$, where $ø_{ecl}$ is the coulombic efficiency of the electrogenerated chemiluminescence of luminol (= 0.0003 (B. Epstein and T. Kuwana, *Photochem. Photobiol.*, **4**, 1157 (1965)). I_{ic} and I_{ecl} are photo-tube outputs, and Q_{ic} and Q_{ecl} are the charges during the electrooxidation of I^- at + 0.9 V and that of luminol at + 0.29 V, respectively. The electrooxidation was conducted with agitation and both I and Q were integrated for 10 s after the application of the potential.

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