

# Electrogenerated Chemiluminescence with Solvated Electrons in Hexamethylphosphoramide. 2

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**Abstract:** Electrogenerated chemiluminescence with solvated electrons of a number of compounds, including tosylates, halides, and aromatic amines, is demonstrated in HMPA. Relatively strong emission is observed from many systems with solvated electrons. The efficiency of electrogenerated chemiluminescence in the case of *N-p*-toluenesulfonylcarbazole is very large, 3.3%, which indicates that the excited singlet state of the carbazole anion is directly formed by the electron transfer reaction. In the case of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, the value is 0.2%. Possible mechanisms for the formation of excited states are discussed.

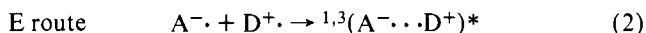
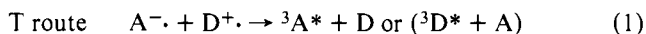
## Introduction

Numerous investigations about solvated electrons in various solvents have been reported since alkali metals were first noted to dissolve in liquid ammonia in 1863.<sup>1</sup> The physical and physicochemical properties of solvated electrons have been revealed by means of the electric conductivity, the optical absorption spectrum, ESR, NMR,<sup>2-4</sup> and electrode reactions.<sup>5-7</sup>

The electrochemical method seems to be very convenient for the generation of solvated electrons compared with the others such as the chemical preparations of the solutions of alkali metal, pulse radiolysis, and laser photolysis.

Solvated electrons are among the most powerful reducing agents that can exist in the liquid phase because the standard redox potential of the formation of solvated electrons is very negative. For example, the value of hexamethylphosphoramide (HMPA) is reported as  $-3.44$  V vs. Ag/AgClO<sub>4</sub> (0.1 M) at 5 °C by Kanzaki and Aoyagui.<sup>7</sup>

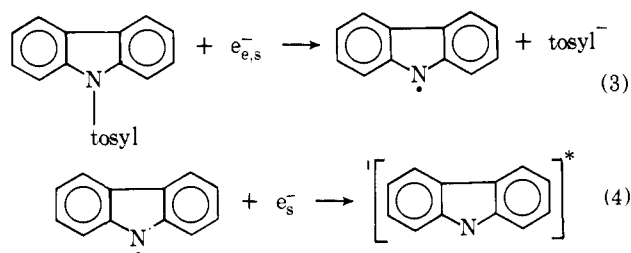
On the other hand, there have been many investigations concerning electrogenerated chemiluminescence (ecl)<sup>8-10</sup> and chemiluminescence (cl)<sup>11</sup> electron transfer reactions between the radical anions of aromatic hydrocarbons and the radical cations of aromatic amines such as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), tri-*p*-tolylamine (TPTA), and so on. The typical reactions are formulated as follows:



where  ${}^3\text{A}^*$ ,  ${}^3\text{D}^*$ , and  ${}^{1,3}(\text{A}^{\cdot-} \cdots \text{D}^{\cdot+})^*$  are the triplets of respective molecules and the singlet and triplet of intermolecular exciplex, respectively. In these reactions, the radical anions of aromatic hydrocarbons are frequently used as the electron donors in electron transfer luminescence. The most important point for the production of electronic excited states is the free energy change of the electron transfer reactions. In 1969, Chandross reported chemiluminescences of some organic compounds with solvated electrons in HMPA.<sup>12</sup> His prior work is of great interest in this area, but it is comparatively qualitative and is not electrochemical.

In this line, we reported ecl with solvated electrons in HMPA in a previous paper.<sup>13,14</sup> Emission was observed from *N-p*-toluenesulfonyl- (tosyl) carbazole (NTC), 9-chlorofluorene derivatives, and TMPD in the potential region of the electrochemical generation of solvated electrons.<sup>13</sup>

In the case of NTC, the reaction mechanism of ecl was formulated as eq 3 and 4, where  $e_{e,s}^-$ ,  $e_s^-$ , and tosyl represent the electron in the electrode, the solvated electron, and the *p*-toluenesulfonyl group, respectively. The first electron transfer (eq 3) is associated with the dissociation of a chemical



bond which is called "dissociative electron transfer". We proposed in the previous paper that the excited singlet state of the anion of carbazole seemed to be directly produced via the electron transfer reaction in eq 4.<sup>13</sup>

In this paper, we will report more details of ecl with solvated electrons.

## Experimental Section

**Materials.** HMPA was used as the solvent. The purification of HMPA was very difficult, but it was found that the following procedure was satisfactory for our experiments.

HMPA (Wako-Chemical Ind., Japan) was predried with CaH<sub>2</sub> for more than 1 week and was fractionally distilled over CaH<sub>2</sub> under a reduced pressure (7–5 mmHg) in a nitrogen atmosphere. Only the middle fraction was collected and was passed through a column of activated alumina (Woelm). That was poured into the vacuum tight flask (Figure 1A) with a small amount of pyrene and an equivalent amount of sodium metal, immediately forming a red solution of sodium pyrenide. It was allowed to stand for 1 day in order to remove the moisture and reducible impurities completely. The solution was degassed on a high-vacuum line and the tube was sealed off.

As shown in Figure 1B, the solvent was very gently transferred under vacuum by cooling the flask with liquid nitrogen. After this procedure was repeated twice, the solvent was collected in glass tubes with a break-seal (Figure 1C).

Pyrene which may be codistilled in the stage of the transfer (Figure 1B) could not be detected by means of fluorescence spectroscopy. The absorbance of HMPA purified by the above procedure was equal to less than 0.1 (light path length 10 mm) at 270 nm.

NTC was synthesized and was twice recrystallized from ethanol.<sup>15</sup>

Allyl chloride, benzyl chloride, diphenylmethyl chloride, and triphenylmethyl chloride were obtained commercially (Wako) and were purified by fractional distillation (the former three compounds) and by recrystallization (the last).  $\alpha$ -Chloromethylnaphthalene was synthesized and was twice recrystallized from petroleum ether.<sup>16</sup>

Tosylation of  $\alpha$ -naphthol,  $\beta$ -naphthol, 4-hydroxybiphenyl, and phenol was carried out by a conventional method and the compounds were recrystallized from ethanol.<sup>17</sup>

TMPD, tri-*p*-anisylamine (TPAA), *N,N*-dimethyl-*p*-anisidine (DMPA), and *N,N,N',N'*-tetramethyl-*p*-benzidine (TMBZ) were recrystallized from appropriate solvents and then vacuum sublimations were carried out.

Sodium perchlorate was used as the supporting electrolyte. It was

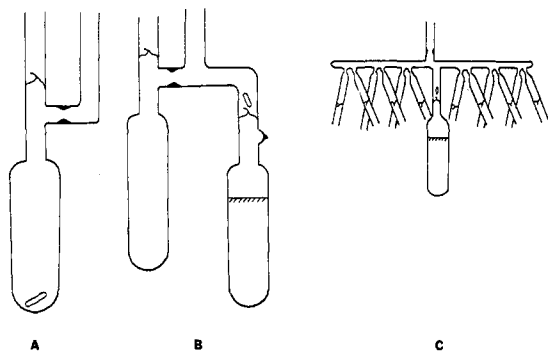


Figure 1. Apparatus for the purification of HMPA.

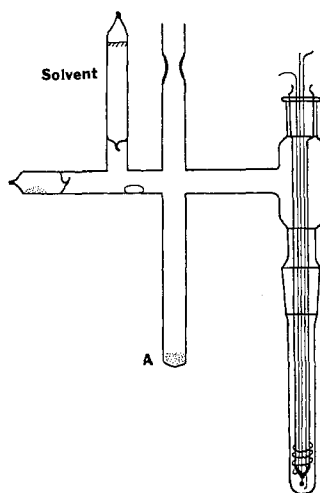


Figure 2. Cell used for the generation of luminescence at controlled potential. A, NaClO<sub>4</sub> salt.

triply recrystallized from an aqueous solution and then was dried in a vacuum oven at 180 °C for more than 24 h.

**Electrochemical Cell and Sample Preparation.** The preparation of sample solutions was carried out on a high vacuum line to eliminate moisture. The electrolytic cell used was described in Figure 2. Working and counter electrodes were platinum wires and a Ag wire was used as a quasi-reference electrode in most experiments. A Ag/0.1 M AgClO<sub>4</sub> reference electrode was also used when the correct potential was desired.<sup>14</sup> Sodium perchlorate (0.1 M) placed at A in Figure 2 was heated at 200 °C and the cell with ample solvent and the desired amount of sample (concentration 1–3 mM) was evacuated under high vacuum for more than 12 h. After the evacuation, the cell was sealed off and the test solution could be prepared by crushing break-seals with a magnetic hammer. Ecl spectra were taken with a Hitachi EPU-II spectrophotofluorometer. The integrating sphere used for the determinations of quantum efficiency has been described elsewhere.<sup>14</sup>

## Results and Discussion

**Electrochemical Generation of Solvated Electrons.** Figure 3 shows a typical cyclic voltammogram of the generation of solvated electrons in HMPA. Although the electrochemical behavior of solvated electrons has been recently published by Aoyagui and Kanzaki,<sup>7</sup> Avaca and Bewick,<sup>6</sup> and Krishtalik and Alpatova,<sup>5</sup> unresolved problems appear to remain. For example, Avaca and Bewick reported an unusual loop in which the cathodic current (generation of solvated electrons) during the initial part of the anodic sweep exceeded the corresponding current for the cathodic sweep.<sup>6</sup> The passivation of the electrode surface during cathodic polarization was pointed out by Krishtalik and Alpatova.<sup>5</sup> But it should be noticed that these phenomena were almost certainly due to the purification of solvent. We sometimes observed the loop and passivation in solvents that were not well purified and dried. They could never be observed in highly purified solvents.

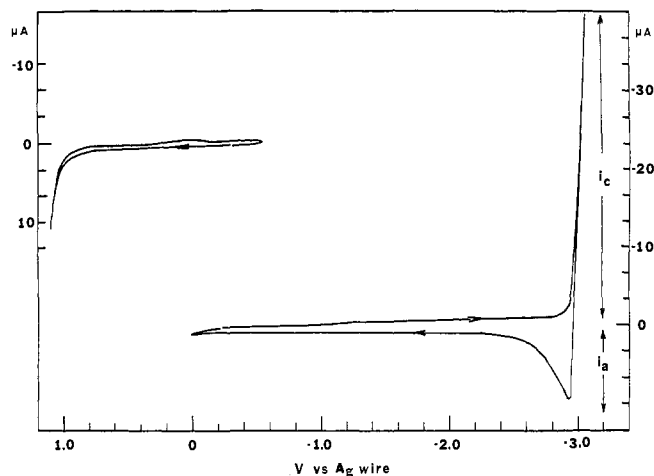


Figure 3. Current-potential characteristics for Pt electrode in HMPA. Scanning rate  $\nu = 0.15$  V/s; temp  $T = 20$  °C; supporting electrolyte, 0.1 M NaClO<sub>4</sub>.

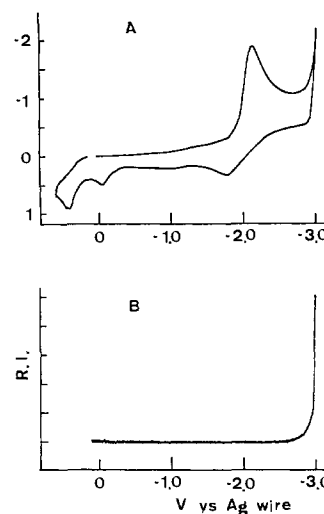
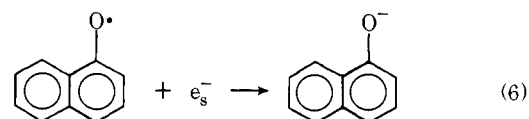
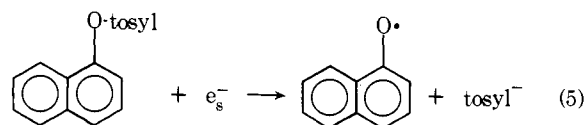


Figure 4. Cyclic voltammogram of  $\alpha$ -naphthyl tosylate (A) and emission-potential relationship (B). Concentration of the electroactive species was 2–3 mM. Scanning rate  $\nu = 0.2$  V/s. (Figure 4B is a record at a fixed wavenumber through spectrophotofluorometer.)

The Tafel slope for generation of solvated electrons was almost equal to 60 mV/decade which showed the reversible generation of solvated electrons as shown by Kanzaki and Aoyagui.<sup>7</sup> The ratio of  $i_a/i_c$  (see Figure 3) was equal to 0.19, which correlated with the theoretical value calculated by diffusion of solvated electrons.<sup>18</sup>

**Ecl of  $\alpha$ -Naphthyl Tosylate and Its Derivatives with Solvated Electrons.** Figure 4A shows the cyclic voltammogram of  $\alpha$ -naphthyl tosylate. The electrochemical reduction wave at about  $-2.2$  V vs. Ag wire is formulated as in eq 5 and 6, in which



$\alpha$ -naphthoxyl neutral radicals will have a more positive reduction potential, so that the second electron transfer reaction (eq 6) should occur spontaneously at potentials for reduction

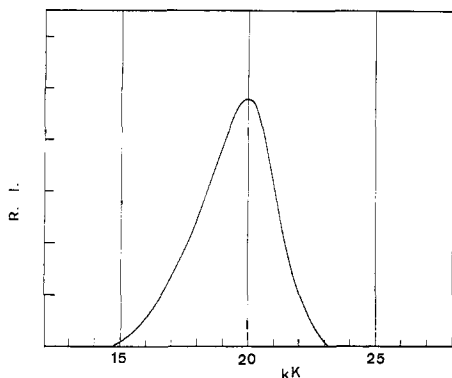


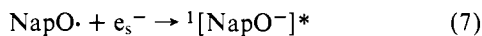
Figure 5. Electrogenerated chemiluminescence spectrum of  $\alpha$ -naphthyl-tosylate in HMPA. Spectra were obtained from the experiments shown in Figure 4B.

of parent. The electrochemical reduction mechanism can be classified as ECE, but side reactions such as dimerization and hydrogen transfer to the radicals may also be taking place. As shown in Figure 4, two waves appeared in the anodic region. The one with a peak potential at about +0.4 V is probably due to the oxidation reaction of the respective phenoxides. Although the origin of the other cannot exactly be interpreted, it should arise from side reactions.

The strong emission in the vicinity of electrode was observed at the same potential as the generation of solvated electrons except for phenyl tosylate. No ecl emission was detected before the generation of solvated electrons, though the "direct" ecl appeared in the reduction of some other compounds.<sup>19</sup>

Figure 5 shows the ecl emission spectrum from the above compound, which was obtained by plotting the intensity against wavenumber through a spectrometer. The spectra coincide with the fluorescence spectra of these phenoxides in HMPA. This coincidence clearly indicates that the excited singlet states of the phenoxides should be formed by the overall electron transfer reactions. Photochemical studies of  $\alpha$ -naphthol and its derivatives have been extensively carried out in various solvents and it is clear that the fluorescence spectra of phenoxides are remarkably shifted as a function of solvent.<sup>20,21</sup>

The electronic excited states of phenoxides will be produced via the electron transfer reaction as follows:



where  $\text{NapO}\cdot$  and  $\text{NapO}^-$  are the naphthoxyl neutral radical and its anion, respectively.

The free enthalpy changes of electron transfer reactions between neutral radicals and solvated electrons can be calculated by the differences of the standard redox potentials. The redox potentials of neutral radicals ( $\text{NapO}\cdot + e_s^- \rightleftharpoons \text{NapO}^-$ ) were calculated by the following equation which was reported previously.<sup>14,22</sup>

$$-E_{1/2} = -2.40m_1 + 1.02 (\pm 0.05) \text{ V vs. SCE} \quad (8)$$

in which  $m_1$  is the energy of the half-occupied orbital of the radical calculated by simple Hückel MO theory. Table I shows the molecular orbital energies ( $m_1$ ) and the calculated redox potentials. The oxidation peak potential of phenoxide ( $\text{PhO}^- \rightarrow \text{PhO}\cdot + e_s^-$ ) is reported as -0.3 V vs.  $\text{Ag}/\text{AgNO}_3$  (0.1 M) in acetonitrile by Mann et al.<sup>23</sup> The calculated value of phenoxide in the present paper is approximately equal to the experimental value because the potential of the reference electrode,  $\text{Ag}/\text{AgNO}_3$  (0.1 M), is equivalent to +0.320 V vs. SCE.<sup>24</sup> We can expect that the standard redox potential in HMPA will be nearly equal to that in acetonitrile because the solvation energy is not greatly changed in the two solvents. From the differences of the above value and the standard redox

Table I. Molecular Orbital Energies and Oxidation Potentials of the Phenoxides

phenoxide	$m_1$	$-E_{1/2}$ (vs. SCE)	$-\Delta G_i$ , eV <sup>a</sup>
	0.382	0.08	3.0
	0.265	0.34	2.75
	0.324	0.22	2.87
	0.34	0.18	2.91

<sup>a</sup> Free enthalpy changes of the electron transfer reaction are calculated by the equation  $-\Delta G_i = 3.09 + E_{1/2}$ .

potential of solvated electrons which is published by Kanzaki and Aoyagi,<sup>7</sup> we can estimate the free enthalpy changes of the electron transfer reaction. As shown in Table I, the changes are almost equal to -3.0 eV in all cases.

On the other hand, it is very difficult to estimate the energies of singlet states of phenoxides due to the extremely large Stokes shifts. But the excited singlets seem to be less than 3.0 eV in HMPA except for the phenoxyl anion ( $\text{PhO}^-$ ). Therefore, the excited singlet states of these anions should be formed directly via electron transfer reactions.

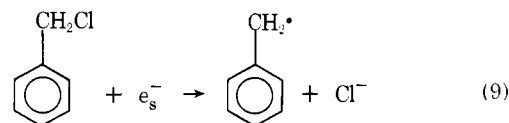
In the case of the phenoxyl anion, the excited singlet is located at 3.9 eV above the ground state in aqueous solution,<sup>25</sup> so the fluorescent states will not be produced directly by the electron transfer reaction. As mentioned above, the emission intensity from phenyl tosylate is too weak to obtain a well-resolved spectrum. But it was clear that the emission maximum existed in the vicinity of  $1.6 \mu\text{m}^{-1}$ . Therefore, the ecl emission does not correspond to fluorescence from the phenoxyl anion.

The recombination luminescences of phenoxides in a rigid organic matrix were examined by Linschitz et al.<sup>26</sup> The thermal bleached emission intensity of  $\alpha$ -naphtholate was very strong which is in fair accord with the present results. On the other hand, the intensity of phenolate caused by radical-electron recombination was reported to be weak.<sup>26</sup>

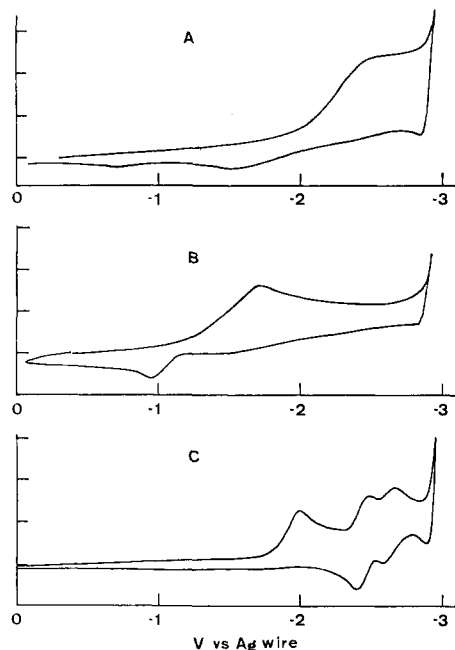
From energy considerations, the direct formation of the excited singlet of the phenolate anion cannot occur in HMPA. The low intensity emission from phenol tosylate remains a problem in the present research.

**Ecl from Benzyl Chloride and Its Derivatives.** For the investigation of the relationship between ecl and the energetics of electron transfer, we studied the following electron transfer reaction systems with solvated electrons.

Allyl and benzyl chloride and the others discussed in this section produce the neutral radicals via "dissociative electron transfer" which are characterized by "alternant hydrocarbon radicals with an odd number of carbon atoms". For example, when benzyl chloride reacts with a solvated electron, the benzyl neutral radical is formed as an intermediate as in eq 9. The



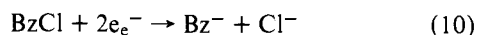
benzyl radical is a  $\pi$ -electron system with seven carbon atoms. We can expect that the standard redox potentials of these compounds ( $\text{AH}\cdot + e_s^- \rightleftharpoons \text{AH}^-$ ) will almost coincide with each other, because the above compounds have a nonbonding orbital whose energy is expressed as  $\alpha$  in the Hückel approxi-



**Figure 6.** Cyclic voltammograms of benzyl (A), triphenylmethyl (B), and  $\alpha$ -naphthylmethyl (C) chlorides in HMPA. Concentration of the electroactive species was 2–3 mM. Scanning rate  $v = 0.2$  V/s.

mation. Peover et al. proved that the monohydro alternant hydrocarbon anions had the same values of the redox potential which was equal to  $-1.15$  vs. SCE in DMF.<sup>27</sup> From the above discussion, we can calculate the free enthalpy changes of electron transfer between these neutral radicals and solvated electrons as a constant value of  $-1.95$  eV. Opposed to the constancy of the free enthalpy changes, the excited states are strongly dependent on molecular structure.

Figure 6 shows the cyclic voltammograms of benzyl, triphenylmethyl, and  $\alpha$ -naphthylmethyl chlorides in HMPA. The first reduction waves seem to be due to a two-electron transfer reaction from the electrode as:



$\text{BzCl}$  and  $\text{Bz}^-$  are benzylic chloride and its anion, respectively. In the case of  $\alpha$ -naphthylmethyl chloride, the additional reduction waves (reversible) appeared at more negative potential which should be due to products following the chemical reactions such as dimerization and proton transfer. The anodic waves which appeared at about  $-1.0$  V in diphenylmethyl and triphenylmethyl chlorides should be due to the oxidation of the respective carbanions (diphenylmethyl and triphenylmethyl carbanions). The appearance of the oxidation waves of the carbanions in the above two cases seem to be due to the high stability of the neutral radicals owing to the structural hindrance. In the other cases, the oxidation wave could not be observed in the cyclic voltammograms obtained with relatively slow scan rates.

Dimer formation during reactions of benzylic halides with lithium naphthalene was reported by Zieger et al.<sup>28</sup> It is proposed that the formation of dimer is followed via a reaction between benzylic halides and the respective carbanions. The details of the electrochemical reduction mechanism present an interesting problem, but we refrain from further discussion in this paper.

To obtain the ecl spectra with solvated electrons, the electrode potential was applied between  $-3.0$  and  $-0.5$  V as a square form in order to get a high intense ecl. Allyl and benzyl chlorides did not exhibit ecl, but the relatively strong emissions were observed from diphenylmethyl and triphenylmethyl chlorides. The ecl spectra are in accord with the fluorescences

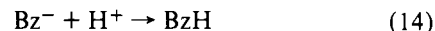
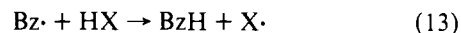
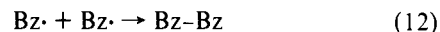
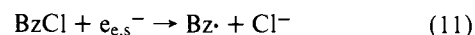
**Table II.** Absorption Maxima of Benzylic Carbanions

carbanion	$\lambda_{\text{max}}$ , nm	solvent
allyl	315	THF <sup>29</sup>
benzyl	355	THF <sup>30</sup>
diphenylmethyl	440	NH <sub>3</sub> <sup>31</sup>
triphenylmethyl	500	THF <sup>29</sup>
$\alpha$ -naphthylmethyl	498	THF <sup>32</sup>

of the carbanions. In the case of  $\alpha$ -naphthylmethyl chloride, very weak yellow emission occurred whose intensity was too weak to get a well-resolved spectrum.

Although there is not much fluorescence data to estimate the energies of excited states of carbanions, singlet energies can be estimated from the absorption maxima of benzylic carbanions as shown in Table II. The excited singlet states of diphenylmethyl and triphenylmethyl carbanions seem to be located at about 2.0 eV above the ground states which is nearly equal to the free enthalpy change of the electron transfer reaction as discussed above. On the other hand, the energies of the singlet states of allyl and benzyl carbanions are obviously larger than 2.0 eV. In these cases, it is impossible that the excited singlet states can be populated by the electron transfer reaction, which is an explanation for why the ecl from the above two compounds could not be detected. Consequently, it is clear that the formation of excited singlet states should occur only when the free enthalpy change of electron transfer exceeds the energy of the excited state. The same interpretation was drawn by Faulkner et al. from the ordinary ecl system<sup>37</sup> (eq 1).

Finally, it is necessary to point out that the intensity of ecl caused by "dissociation electron transfer reaction" with solvated electrons seems to be strongly dependent on the stability of neutral radicals and also of respective carbanions. A few possible side reactions following the dissociation of the carbon-halide bond can be written as follows:

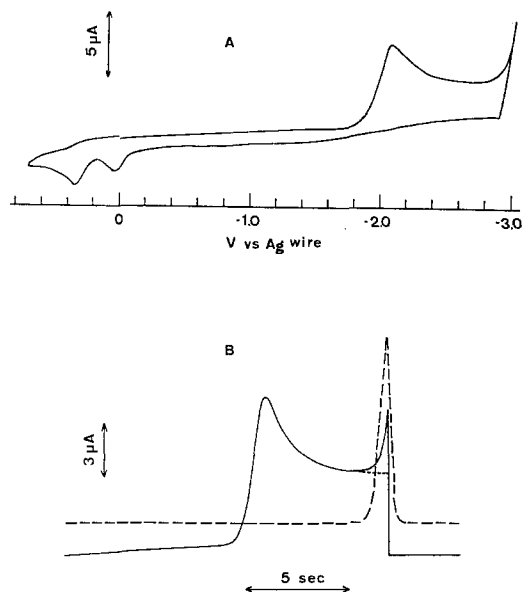


The dimerization (eq 12), hydrogen transfer (eq 13), and proton transfer (eq 14) seem to be most favorable paths of the ecl quenching reaction. Although the direct formation of the singlet state of  $\alpha$ -naphthylmethyl carbanion is possible based on energetic calculations, the intensity of ecl was very weak as mentioned above. In this case, the interferences of side reactions may diminish the intensity of ecl. The detailed investigation on the effect of the side reactions is still being carried out and will be published in the near future.

**Measurement of Quantum Yield of Ecl from NTC.** In the previous report,<sup>13</sup> we suggested from energy considerations that the excited singlet of the carbazole anion seemed to be produced directly via electron transfer (eq 4), because the free enthalpy change of reaction 4, estimated to be  $-3.1$  eV, is energetic sufficiently for the direct population of the first excited singlet state (2.92 eV in HMPA). If this discussion is correct, the efficiency of ecl can be expected to be relatively large.

The cyclic voltammogram of NTC is shown in Figure 7. The reduction wave at  $-2.0$  V is due to the electrochemical reduction of NTC to form the respective anion and *p*-toluenesulfonyl anion. The following procedure was applied to determination of the efficiency of ecl with solvated electrons.

When the electrode potential was swept linearly, the current flowing to the working electrode and the output of the integrating sphere were recorded at the same time as a function



**Figure 7.** Cyclic voltammogram of 3 mM *N*-tosylcarbazole (A) and current-time (—) and output of photon-time (---) relations (B) (see text).

**Table III.** Electrogenerated Chemiluminescence Efficiencies of *N*-*p*-Toluenesulfonylcarbazole with Solvated Electrons

$\int i_c(t) dt, \mu C^a$	$\int I(t) dt, \text{photons}^b$	$\phi_{ecl}$
1.32	$1.36 \times 10^{11}$	0.033
1.84	$1.65 \times 10^{11}$	0.029
4.44	$3.69 \times 10^{11}$	0.027
4.78	$3.58 \times 10^{11}$	0.014
16.0	$3.89 \times 10^{11}$	0.014
73.4	$2.39 \times 10^{12}$	0.0104

<sup>a</sup> Total charge consumed to the generation of solvated electrons.

<sup>b</sup> Total output of photons using an integrating sphere.

of time. After open circuiting the cell at an appropriate potential, the current suddenly drops to zero. On the other hand, the output of photomultiplier was continuously recorded. The total charge ( $Qe$ ) consumed by the generation of solvated electrons is calculated by integrating the corrected current (i.e.,  $i_c(t)$ ) for the tail of the preceding direct reduction current (---) vs. time curve (Figure 7) and the total output of photons is also found in a similar manner.

We can define the efficiency of ecl with solvated electrons as follows:

$$\phi_{ecl} = \frac{2 \int I(t) dt}{\frac{1}{F} \int i_c(t) dt} \quad (15)$$

The factor of 2 in the above equation is introduced by the following result. That is, the overall reaction of the production of the excited state can be formulated as eq 16, in which one molecule of NTC should consume two electrons.

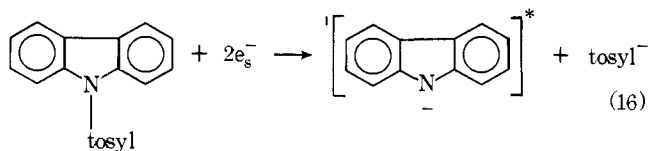
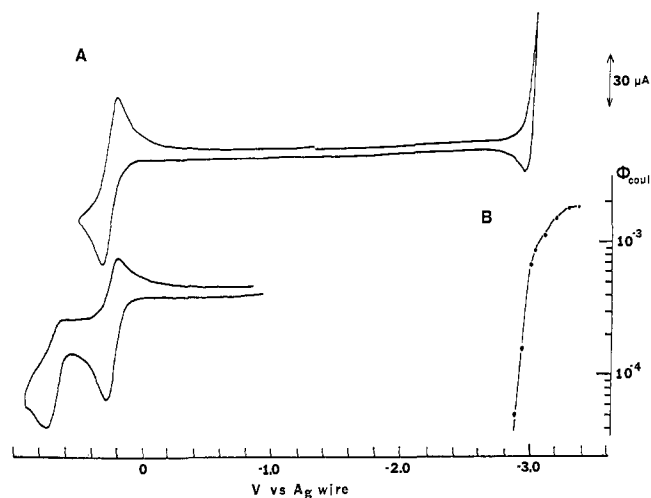


Figure 7 shows a few typical results for current-time and output of photon-time relations. Table III lists the experimental results obtained with various amounts of solvated electrons. The more solvated electrons were generated coulometrically, the less the efficiencies were obtained. The reason

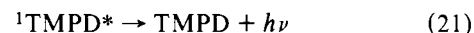
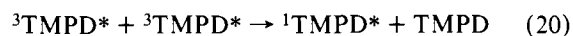
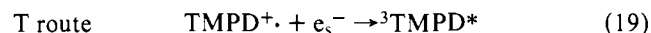
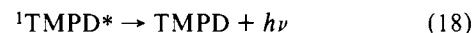
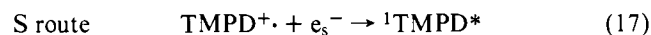


**Figure 8.** Cyclic voltammogram of 4 mM *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (A) and Coulombic efficiency of electrogenerated chemiluminescence-potential relation.

for this is not clear at present; however, there is only a slight change in  $\phi_{ecl}$  when the concentration of solvated electrons is varied over two orders of magnitude. The efficiency (3.3–1.0%) is an extremely large value, so that the triplet-triplet annihilation mechanism should not operate in ecl in this case. The excited singlet state of the carbazole anion should be produced directly via electron transfer between the neutral radicals and solvated electrons.

**TMPD<sup>+</sup>/e<sub>s</sub><sup>-</sup> and Other Systems.** Figure 8 shows the cyclic voltammogram of TMPD in HMPA. The first oxidation wave corresponds to the reversible formation of radical cations and the second one to the irreversible dication formation. When a rectangular electrode potential waveform was applied in the range between generation of solvated electrons and TMPD radical cations, blue emission corresponding to the fluorescence of TMPD was observed as mentioned in the previous paper.<sup>13</sup>

Two pathways of ecl mechanism were considered as follows:



Similar reactions have been extensively studied in the rigid organic matrices such as 2-methylpentane, EPA, and so on.<sup>34-36</sup> The delayed emission that was taken by excitation using infrared radiation is called "recombination luminescence". In the rigid matrix, however, the electrons are trapped in valley with various energy levels. It is very difficult to confirm the energy levels of the trapped electrons for the interpretation of the recombination process. Moreover, the trapped electrons have different characteristics for the production of excited states in rigid matrix, because the distance of recombination between the cation centers and the electrons is widely distributed which complicates the interpretation of the recombination luminescence in matrix media. On the other hand, we can know the energy released by the recombination reaction as the difference of the standard redox potentials in HMPA. An energy diagram of the above system is represented in Figure 9. The energy level of ion dissociation state ( $\text{TMPD}^{\cdot+} + e_s^-$ ) is located near the singlet state of TMPD. Although the direct formation of  ${}^1\text{TMPD}^*$  seems to be possible from energetic

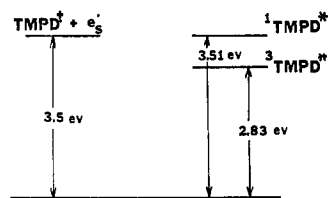


Figure 9. Energy diagram of  $\text{TMPD}^+/\text{e}_s^-$  system in HMPA.

Table IV. Electrogenerated Chemiluminescence Efficiencies of 4 mM  $N,N,N',N'$ -Tetramethyl-*p*-phenylenediamine with Solvated Electrons<sup>a</sup>

electrode potential, -V vs. Ag	$\int_{t_f}^{\infty} I(t) dt$ , photons	$\phi_{\text{coul}}^b$
2.87	$4.74 \times 10^9$	$5 \times 10^{-5}$
2.93	$1.52 \times 10^{10}$	$1.6 \times 10^{-4}$
2.99	$6.55 \times 10^{10}$	$6.9 \times 10^{-4}$
3.05	$8.08 \times 10^{10}$	$8.5 \times 10^{-4}$
3.10	$1.06 \times 10^{11}$	$1.12 \times 10^{-3}$
3.19	$1.48 \times 10^{11}$	$1.56 \times 10^{-3}$
3.30	$1.76 \times 10^{11}$	$1.86 \times 10^{-3}$
3.35	$1.77 \times 10^{11}$	$1.87 \times 10^{-3}$

<sup>a</sup> Time duration of the forward generation step ( $t_f$ ) was 0.2 s. Total charge given to reactant ion production in the forward step was 15.2  $\mu\text{C}$ . <sup>b</sup> Data were also plotted in Figure 8.

consideration, the detailed experimental results supporting this had not been included in the previous paper.<sup>13,14</sup>

Now, we used the sequence of the triple potential step method to get the efficiency of ecl similar to that previously employed by Faulkner et al.<sup>37</sup> in order to check the mechanism. The first step is applied to the electrode in the diffusion-limited region for the generation of the radical cations of TMPD which lasts for a time ( $t_f$ ). The electrode potential is shifted abruptly after the first step lasts for a time  $t_f$  (s) in a reverse step to a value in the appropriate potential range for the generation of solvated electrons.

We express the overall efficiency of ecl as a Coulombic efficiency,  $\phi_{\text{coul}}$ , which is defined as the ratio of the total photon output to the number of the radical cations of TMPD formed.

$$\phi_{\text{coul}} = \frac{\int_{t_f}^{\infty} I(t) dt}{\frac{1}{F} \int_0^{t_f} i_f(t) dt} \quad (22)$$

The efficiency of the ecl can be obtained at various potentials of the second step for the generation of solvated electrons, because there is no current maximum, as is usual in ecl systems, in the generation of solvated electrons. Table IV shows the ecl efficiencies obtained at the potential of the second step and Figure 8 also shows them plotted as a function of the potential of electrode. The efficiency increases rapidly with an increase in the generation of solvated electrons initially, and then saturation was observed as shown in Figure 8. The maximum value of the efficiency is about 0.2%. This value seems to be relatively small to support the direct formation of singlet of TMPD. However, the fluorescence quantum yield of TMPD is not so large, for example, which is reported as 0.09 in cyclohexane.<sup>38</sup> Consequently, the yield of the singlet state of TMPD via electron transfer may be large.

From these considerations, we can conclude that the singlet state of TMPD may be directly formed via electron transfer. That is, the main route of the ecl reaction is the S route.

The same ecl between radical cations and solvated electrons

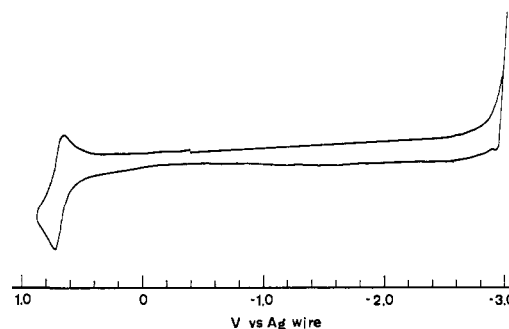


Figure 10. Cyclic voltammogram of tri-*p*-anisylamine in HMPA. Concentration of electroactive species was 2–3 mM. Scanning rate  $v = 0.2$  V/s.

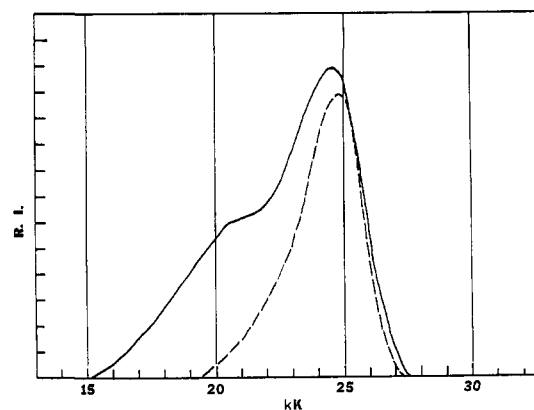


Figure 11. Electrogenerated chemiluminescence spectrum of tri-*p*-anisylamine in HMPA.

Table V. Spectroscopic and Electrochemical Data of Aromatic Amines

aromatic amine <sup>a</sup>	$-\Delta G_i$ , eV <sup>b</sup>	$^1E^*c$
TPAA	3.9	3.26 <sup>39</sup>
DMPA	3.8	3.6 <sup>d</sup>
TMBZ	3.8	3.4 <sup>d</sup>
	(3.55) <sup>e</sup>	

<sup>a</sup> TPAA, tri-*p*-anisylamine; DMPA, dimethyl-*p*-anisidine; TMBZ,  $N,N,N',N'$ -tetramethyl-*p*-benzidine. <sup>b</sup> Free enthalpy changes of the electron transfer reaction. <sup>c</sup> Singlet energy. <sup>d</sup> Estimated from the fluorescence spectrum. <sup>e</sup> Free enthalpy change of the reaction  $\text{TMBZ}^+ + \text{TMBZ}^- \rightarrow 2\text{TMBZ}$ .

can be expected. Figure 10 shows the cyclic voltammogram of TPAA, whose first oxidation potential is relatively low corresponding to the formation of the respective radical cations in acetonitrile.<sup>39</sup> The reduction waves of TPAA and DMPA could not be observed before the solvated electron was generated. In the case of TMBZ, the reduction wave which might be due to the formation of the radical anion of TMBZ was apparently observed as a shoulder of the wave corresponding to the formation of solvated electrons.

As in the case of TMPD, when the square electrode potential waveform was applied to form radical cations and solvated electrons, relatively strong emission in all cases was observed whose spectral distributions are shown in Figure 11. Generally, the ecl spectra consist of two bands. One of them (the band at higher wavenumber) is almost completely in accord with the fluorescence spectrum of the neutral molecule which is also represented in Figure 11 as dashed lines.

These preliminary results show that the excited singlet states should be formed by electron transfer with solvated electrons except for TMBZ, in which the electron transfer reaction be-

tween the radical anions and cations of TMBZ also takes place. The free enthalpy changes can be calculated as the differences of the standard redox potentials of solvated electrons and of the formation of radical cations. Table V lists these values including the free enthalpy change of the electron transfer reaction between the radical cations and anions of TMBZ ( $\text{TMBZ}^{\cdot+} + \text{TMBZ}^{\cdot-} \rightarrow 2\text{TMBZ}$ ) and the singlet energies. Energetically, all of the systems described above are fairly "energy sufficient" for the direct production of the excited singlet state.

As shown in Figure 11, however, there are additional emission bands in the eel spectra whose peak positions are located in the region  $2.0\text{--}2.2 \mu^{-1}$ . At present, the origin of these additional lower energy bands cannot be explained by the above preliminary experiments. There are several interpretations for these bands. One of them is that the lower wave-number bands are due to the formation of excimers. To check the above possibility we tried to measure the fluorescence of relatively high concentrations of TPAA solutions using a normal photoexcitation technique. Unfortunately, no additional band in the lower wavenumber region could be observed until the concentration of TPAA was 15 mM. The other possibility is that the additional band is caused by decomposition products of the radical anions. Although the reduction behavior of the above compounds is not clear at present, the oxidation peak of solvated electrons is diminished in the case of TPAA and DMPA as shown in Figure 10. Details will be published elsewhere.

**Acknowledgment.** We wish to thank Dr. William L. Wallace for his continuous interest in this work.

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## Kinetics of the Protolysis of Cryptands in Basic Aqueous Solution

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**Abstract:** The kinetics of the proton transfer reaction between hydroxide ions and the monoprotonated cryptands 2,1,1, 2,2,1, 2,2,2, and 2,2,2B have been investigated in aqueous solution, using the pressure-jump technique. Except for 2,2,1, the observed relaxation times for the cryptands are consistent with a simple rate-determining proton transfer step. The observed rate constants for the proton transfer to hydroxide are relatively low, varying from  $1.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for 2,1,1 to  $1.0 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for 2,2,2 (25 °C). The results for 2,2,1, however, require the postulation of a more complex reaction path. These relatively slow rates, together with the results for the 2,2,1 system, suggest that conformational changes within the ligands, associated with the inversion of the nitrogens, may play an important role in determining the overall kinetics of the reactions.

## Introduction

A variety of macrocyclic ligands synthesized in recent years, such as the polyethers (crown ethers)<sup>2</sup> and macrobicyclic ligands of the type 1–4 (cryptands, Cry),<sup>3</sup> display strong cation selectivity, comparable to that of naturally occurring metabolites such as nonactin and valinomycin.<sup>4</sup> This has resulted in

a number of kinetic<sup>5–9</sup> and thermodynamic studies<sup>10–13</sup> of their ion binding properties.

In aqueous solution, cryptands, in addition to their ability to form strong complexes with metal ions, may exist as monoprotonated and diprotonated derivatives because of the two basic nitrogen atoms. This then provides the opportunity for