

**Electrogenerated chemiluminescence. 39.  
Reactions of solvated electrons in liquid ammonia**

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triplet was produced as shown in Table I. The curve in Figure 6, which was adjusted to the data for  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Eu}^{3+}$ , does not fit the experimental points for the other metal ions. The failure in the fitting suggests that the electron-transfer mechanism does not hold for all metal ions. All experimental points that do not fit the curve are located above it, indicating efficient quenching mechanisms other than the electron transfer mechanism. From measurements of the fluorescence quantum yield of acridine and other water-soluble aromatic hydrocarbons, Kemlo and Shepherd<sup>7</sup> concluded that rapid dynamic quenching could take place in two cases. One of them is the charge-transfer mechanism discussed above, and the other is the so-called dipole-dipole mechanism.

In the dipole-dipole mechanism, the quenching rate relates to the spectral overlap. Pyrene fluorescence spectra had a maximum at about 390 nm. On the other hand, spin-allowed d-d transitions show absorptions at 395 and 530 nm for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ , respectively. Then the spectral overlap between pyrene fluorescence and  $\text{Ni}^{2+}$  absorption is greater than that for  $\text{Co}^{2+}$ . The experimental result shows that the quenching rate  $k_{1q}$  or  $k_q$  of  $\text{Ni}^{2+}$  is two times larger than that of  $\text{Co}^{2+}$ . Lanthanide ion absorption spectra show sharp peaks in the visible region,<sup>34</sup> which are assigned to f-f transitions. Among them,  $\text{Er}^{3+}$  has a large peak at 379 nm, suggesting that the quenching rate for simple deactivation  $k_{1q}$  is remarkably large for this ion. The spectrum of  $\text{Ho}^{3+}$  shows peaks at 361 and 416 nm, and

that of  $\text{Sm}^{3+}$  at 401 nm. These ions induce the less efficient quenching of pyrene fluorescence.

The dipole-dipole interaction of spin-allowed transitions cannot explain the triple-state formation, which cannot also be explained by the electron-transfer mechanism as mentioned above. Therefore, other mechanisms should be taken into consideration. Quenching by  $\text{Ag}^+$  produces a marked amount of triplet state. Although  $\text{Ag}^+$  forms a complex with pyrene at the ground state, the decay curve for pyrene fluorescence remains first order. The equilibrium constant for complex formation was  $\sim 2.3 \text{ M}^{-1}$ , which is calculated from the spectral change with graded amount of  $\text{Ag}^+$ . These facts suggest that the lifetime of the complex is shorter than the shortest observable fluorescence lifetime in the present experiments, i.e., about  $10^{-8} \text{ s}$ . The complexation causes distortion in the electron distribution on the pyrene molecules, since the absorption spectrum of pyrene shifts as shown in Figure 1. Consequently, it is probable that internal conversion and/or intersystem crossing of excited pyrene are accelerated by the electron distortion caused by complexation. If intersystem crossing is accelerated by metal ions, the value of  $k_{3q}$  becomes marked. Although the mechanism of these accelerations should differ from metal to metal, the same kind of metal ions would behave in the same way. This idea seems to be supported by the experimental facts; e.g., the values of  $k_{3q}$  for lanthanide ions are of same order in contrast with the difference in  $k_q$ .

*Acknowledgment.* We are grateful to Dr. H. Masuhara for helpful discussions and to Professor A. Henglein for suggestions on some values of redox potential.

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## Electrogenerated Chemiluminescence. 39. Reactions of Solvated Electrons in Liquid Ammonia

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Reaction of  $\alpha$ - and  $\beta$ -naphthol tosylates and *N*-tosylcarbazole (represented as R-Ts) with electrogenerated solvated electrons ( $e_s^-$ ) in liquid  $\text{NH}_3$ -tetrahydrofuran mixtures results in emission of light characteristic of  $\text{R}^-$  fluorescence. The following is the proposed reaction mechanism:  $\text{R-Ts} + e_s^- \rightarrow \text{R-Ts}^- \rightarrow \text{R}^- + \text{Ts}^-$ ;  $\text{R}^- + e_s^- \rightarrow {}^1\text{R}^*$ . The ecl quantum yield for these reactions is  $\sim 0.4$ - $0.8\%$ . Ecl reactions of diphenyl and dinaphthyl disulfide with  $e_s^-$  and of *N*-tosylcarbazole with radical anions are also described.

### Introduction

Solvated electrons can be generated electrochemically in a variety of solvents, such as liquid ammonia ( $\text{NH}_3$ ), hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide, and propylene carbonate. However, ammonia offers clear advantages in ease of purification, low viscosity, and its ability to stabilize solvated electrons for long periods of time.<sup>1</sup> The electrochemical behavior of solvated electrons in liquid  $\text{NH}_3$  has been investigated by cyclic voltammetry, coulometry, and the galvanostatic single pulse technique.<sup>1,2</sup> Additional information about excess electrons in liquid  $\text{NH}_3$  has been obtained from studies of the

photoejection of electrons from metal and semiconductor electrodes.<sup>3-7</sup> We recently briefly described the reactions of solvated electron with solutes like *N*-tosylcarbazole

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(NTC) in liquid  $\text{NH}_3$  to produce electronically excited states and the emission of light.<sup>5</sup> Previous studies of reactions of excess electrons with suitable substrates to produce excited states employing HMPA and HMPA-tetrahydrofuran (THF) mixtures were reported by Itaya et al.<sup>8,9</sup> and by Chandross.<sup>10</sup> Extension of such studies to liquid  $\text{NH}_3$  is of interest because solvated electrons have greater stability and their thermodynamic properties are known in this medium. Numerous studies of excited-state formation upon homogeneous electron transfer reactions of electrogenerated species (e.g., radical ions) have been reported.<sup>11</sup> These studies allow one to probe the details of the course of electron transfer reactions and can provide information about thermodynamic and kinetic properties of species involved in such reactions. We report here studies of electrogenerated chemiluminescence (ecl) with solvated electrons in liquid  $\text{NH}_3$ -THF mixtures. THF was added in these experiments to increase the solubility of the organic compounds studied here.

### Experimental Section

**Chemicals.** The ammonia (Matheson Gas, 99.9%) was purified by double distillation from sodium metal.<sup>15,3</sup> Potassium iodide was used for the supporting electrolyte (0.1 M). HMPA, which was also used as a solvent, was purified by the procedures described previously.<sup>9</sup> Sodium perchlorate (0.1 M) was used as the supporting electrolyte in experiments using HMPA. THF was purified by distillation from sodium benzophenone.

NTC was synthesized and was twice recrystallized from ethanol.<sup>12</sup>  $\alpha$ - and  $\beta$ -naphthol tosylates were synthesized and were twice recrystallized from ethanol.<sup>13</sup> Diphenyl disulfide and di-2-naphthyl disulfide were synthesized and were recrystallized from benzene and chloroform.<sup>14</sup> Allyl chloride, benzyl chloride, and triphenylmethyl chloride were obtained commercially and were purified. Tetraakis(dimethylamino)ethylene (TMAE) was purified by distillation. Spectrograde 9,10-dimethylanthracene and naphthalene were used as received. Carbazole used for the preparation of lithium carbazole solution was purified by recrystallization from ethanol. Lithium carbazole was made by the addition of *n*-butyllithium to the carbazole in THF.

**Apparatus.** The ecl cell contained a coiled Pt-wire counter electrode separated from the main compartment by a medium-porosity glass frit. The working electrode was a platinum disk with a projected area of 0.04 cm<sup>2</sup>. The quasi-reference electrode was a silver wire immersed in supporting electrolyte solution in a tube separated from the working electrode compartment by a fine-porosity glass frit. All potentials are reported vs. a Ag/AgNO<sub>3</sub> (0.1 M) reference electrode.<sup>16</sup> The cell was cooled in a 2-propanol/dry ice or a 2-propanol/liquid N<sub>2</sub> bath equipped with optical windows to  $\sim -60$  to  $-50$  °C. Electrochemical measurements were carried out with a Princeton Applied Research (PAR) Model 173 potentiostat and a PAR 175 universal programmer.

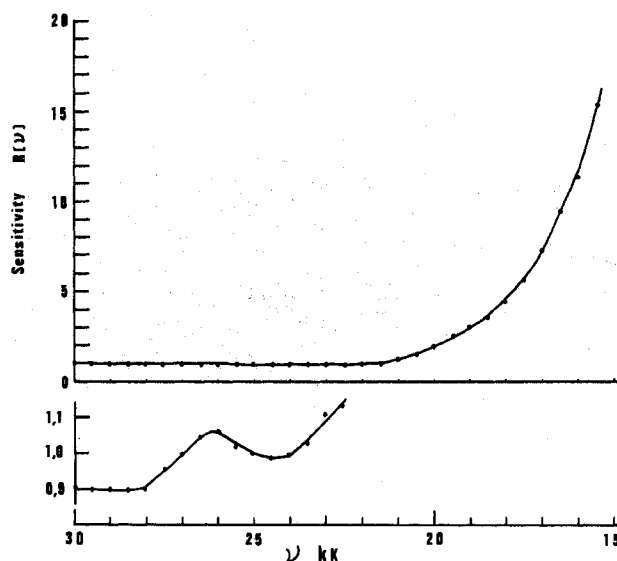


Figure 1. Relative sensitivity of the total photometric apparatus normalized to 415 nm. An expanded plot of the data from 330 to 440 nm is displayed in the lower curve.

An integrating sphere was used in this experiment for the determination of ecl efficiencies as first described by Bezman and Faulkner.<sup>15</sup> The cell and 2-propanol/liquid N<sub>2</sub> bath was enclosed by the integrating sphere made from a modified 5-L flask, which was coated on the inside with white reflectance paint (Eastman Kodak). The sample cell with the cooling apparatus entered the sphere and was held in position by a standard taper joint attached to the sphere. The sphere viewing port was connected to an Oriel monochromator with a photomultiplier (Hamamatsu TV R928). The apparatus described here did not use a rhodamine B quantum counter which has been frequently used in previous papers.<sup>9,11,15-17</sup> The calibration factors of a rhodamine B quantum counter-detector system have been measured by Faulkner et al.<sup>11,15,16</sup> The factors for  $\lambda \leq 600$  nm only varies from 0.95 to 1.10. However, for  $\lambda > 600$  nm, the sensitivity of the apparatus rises sharply, because incident light passes directly through the quantum counter solution. This is a serious problem for the measurement of absolute light levels for light sources with a spectral component at wavelengths longer than 600 nm, even if this component is very small. In the experiments described here, the spectral sensitivity of the whole apparatus with a monochromator-photomultiplier detector system was measured by employing as references standard fluorescent solutions of 2-aminopyridine,<sup>18</sup> quinine, and *m*-(dimethylamino)nitrobenzene.<sup>19</sup> In Figure 1 the relative

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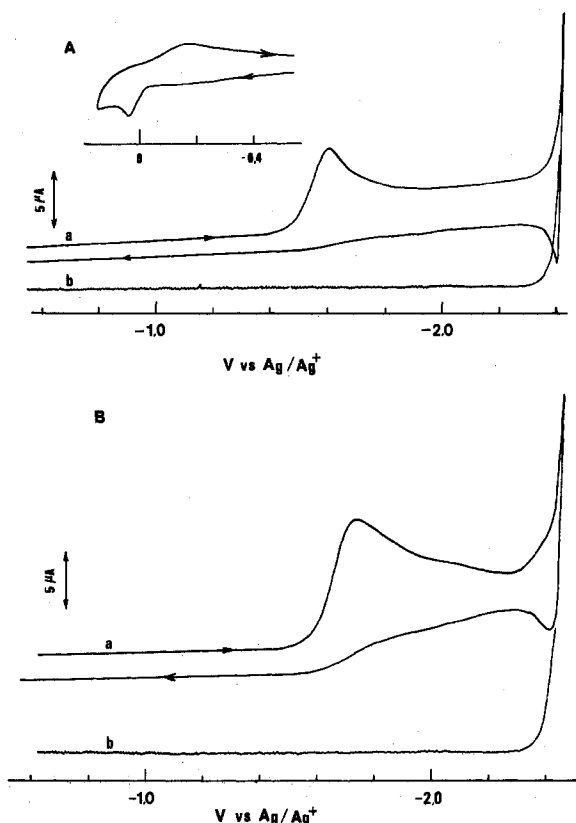
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**Figure 2.** Cyclic voltammograms of  $\alpha$ -naphthol tosylate (A-a) and of  $\beta$ -naphthol tosylate (B-a) in  $\text{NH}_3$ -THF mixtures (2:1 by volume) at  $-40^\circ\text{C}$ . Concentration of the electroactive species was 1–3 mM; scan rate, 200 mV/s. A-b and B-b are records of light emission at a fixed wavelength.

sensitivity of the photometric apparatus normalized at 415 nm is shown. An absolute calibration of the apparatus was carried out by a standard actinometric procedure with 0.15 M ferrioxalate actinometer. The light source used for the actinometric procedure was made monochromatic with glass filters whose spectral distribution was measured by the calibrated monochromator-detector system. The absolute calibration factor at 415 nm was  $(0.610 \pm 0.014) \times 10^{10}$  photons  $\text{cm}/(\mu\text{A s})$ . The integrated intensity of any other light source ( $I$ ) could be calibrated by use of 1, where  $I(\text{photons}) =$

$$(0.610 \times 10^{10}) \left[ \int F(\nu) d\nu / F(\nu_{\text{meas}}) \right] [R(\nu_{\text{meas}})] [Q(\mu\text{A s})] \quad (1)$$

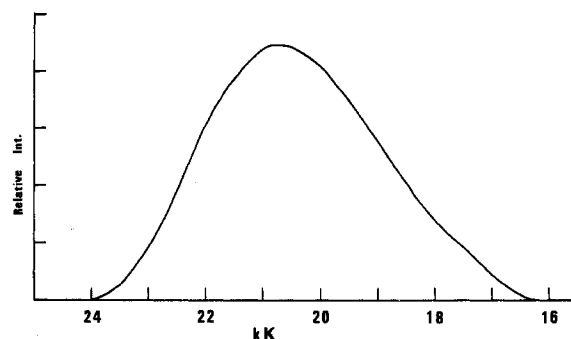
the factor  $\int F(\nu) d\nu / F(\nu_{\text{meas}})$  is the ratio of the integrated corrected spectral distribution of a light ( $\int F(\nu) d\nu$ ) to the intensity at the calibration wavelength ( $F(\nu_{\text{meas}})$ ), and  $R(\nu_{\text{meas}})$  is the relative sensitivity of the apparatus at  $\nu_{\text{meas}}$ . The output of the apparatus at  $\nu_{\text{meas}}$  was measured as  $Q(\mu\text{A s})$ .

To probe the reliability of the calibration procedure presented here, we carried out measurements of  $\phi_{\text{ecl}}$  of 9,10-diphenylanthracene and of  $\text{Ru}(\text{bpy})_3^{2+}$  in acetonitrile (0.1 M TBAP) at room temperature. The factors of  $F(\nu) d\nu / F(\nu_{\text{meas}})$  in eq 1 are 3.19 at 428 nm and 3.56 at 630 nm

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**Figure 3.** Corrected electrogenerated chemiluminescence spectrum of  $\alpha$ -naphthol tosylate in a  $\text{NH}_3$ -THF (2:1) mixture at  $-40^\circ\text{C}$ .

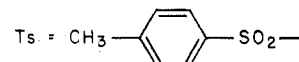
for 9,10-diphenylanthracene and for  $\text{Ru}(\text{bpy})_3^{2+}$ , respectively. The average values of  $\phi_{\text{ecl}}$  were  $0.3 \pm 0.1\%$  and  $3.0 \pm 0.5\%$  for 9,10-diphenylanthracene and for  $\text{Ru}(\text{bpy})_3^{2+}$ , respectively, in agreement with values previously reported.<sup>11,31,32</sup> These results indicate that the described procedure is a reliable one even for the measurement of  $\phi_{\text{ecl}}$  of  $\text{Ru}(\text{bpy})_3^{2+}$  where the emission band extends over wavelengths longer than 600 nm. In this case, a rhodamine B quantum counter detector system cannot be used in the measurement of  $\phi_{\text{ecl}}$ .

## Results and Discussion

**Electrochemical and Ecl Studies.** The cyclic voltammetry (CV) of  $\alpha$ - and  $\beta$ -naphthol tosylates in a  $\text{NH}_3$ -THF mixture (2:1 by volume) (Figure 2) showed cathodic waves at  $-1.6$  and  $-1.7$  V vs.  $\text{Ag}/\text{Ag}^+$  (0.1 M  $\text{AgNO}_3$ ) corresponding to the reduction of the tosylates, as proposed in a previous paper.<sup>9</sup> The electrode reaction is an overall two-electron reduction



where  $\text{Naph}^-$  is the anion of naphthol and



The oxidation wave at 0.1 V can be attributed either to the oxidation of the anions of naphthol or to products of side reactions. Itaya et al. assumed that the oxidation wave which appeared at  $+0.4$  V in HMPA was due to the oxidation of the respective naphtholate.<sup>9</sup> This wave could not be investigated in the  $\text{NH}_3$ -THF mixture because of the large background current at these potentials. As shown in Figure 2 (line b), a strong emission was observed at the same potential as the generation of solvated electrons ( $e_s^-$ ) ( $-2.4$  V vs.  $\text{Ag}^+$ ). Note that the cyclic voltammogram in the potential region where solvated electrons are generated at the Pt electrode in  $\text{NH}_3$ -THF (2:1) is almost identical with that observed in liquid  $\text{NH}_3$  alone.<sup>1b,5</sup> This indicates that the reducing power of solvated electrons in  $\text{NH}_3$ -THF (2:1) is almost the same as in pure  $\text{NH}_3$ . No ecl emission was obtained during the direct electrochemical reductions of the tosylates themselves. This strongly suggests that excited states are produced by electron transfer reactions of solvated electrons.

The ecl spectrum of  $\alpha$ -naphthol tosylate (Figure 3) is completely in accord with the fluorescence spectrum of the respective phenoxide in the same solvent. The same result was obtained with  $\beta$ -naphthol tosylate. This agreement clearly shows that the excited states of the phenoxides are

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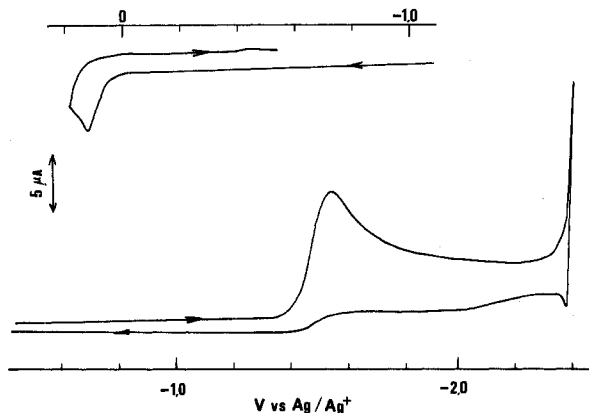


Figure 4. Cyclic voltammogram of *N*-tosylcarbazole in a  $\text{NH}_3$ -THF (2:1) mixture at  $-40^\circ\text{C}$ ; scan rate, 200 mV/s.

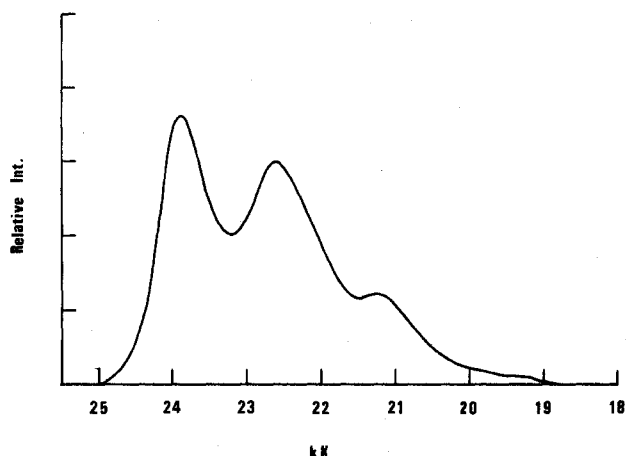
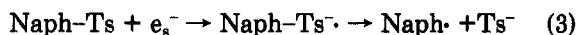


Figure 5. Corrected electrogenerated chemiluminescence spectrum of *N*-tosylcarbazole in a  $\text{NH}_3$ -THF (2:1) mixture at  $-40^\circ\text{C}$ .

directly responsible for the emission in the ecl processes. The mechanism of the reaction thus involves the diffusion of the electrogenerated  $e_s^-$  away from the electrode surface. Upon encountering  $\text{Naph-Ts}$ , a one-electron reaction occurs (eq 3), where  $\text{Naph}\cdot$  is the naphthoxyl radical. The



electronic excited singlet states of the phenoxides are produced via the reaction of  $\text{Naph}\cdot$  with  $e_s^-$  (eq 4). Any



$\text{Naph}\cdot$  which reaches the electrode surface will be reduced directly to ground-state  $\text{Naph}^-$  so that no emission is observed for the direct reduction of  $\text{Naph-Ts}$ . If we assume that the standard potential of the solvated electron in a  $\text{NH}_3$ -THF is the same as that in liquid  $\text{NH}_3$  ( $-2.74$  V vs.  $\text{Ag}/\text{AgNO}_3$  (0.1 M))<sup>5</sup> and the potential for oxidation of the naphtholate ( $\text{Naph}\cdot + e^- \rightleftharpoons \text{Naph}^-$ ) is  $\sim +0.1$  V, a value of  $-2.84$  eV is obtained for the free enthalpy change of the reaction between the neutral radical and the solvated electron.

A cyclic voltammogram of *N*-tosylcarbazole (NTC) in a  $\text{NH}_3$ -THF mixture (2:1) is shown in Figure 4. Again a strong emission was observed at the potential for generation of solvated electrons. An oxidation wave occurs at  $+0.1$  V, which is ascribed to the oxidation of the carbazole anion. An ecl spectrum, obtained by stepping the electrode potential between  $-0.5$  and  $-2.4$  V, is shown in Figure 5. The fluorescence spectrum of a solution of the carbazole anion agrees very well with the observed ecl spectrum. The peak position of the 0-0 band in  $\text{NH}_3$

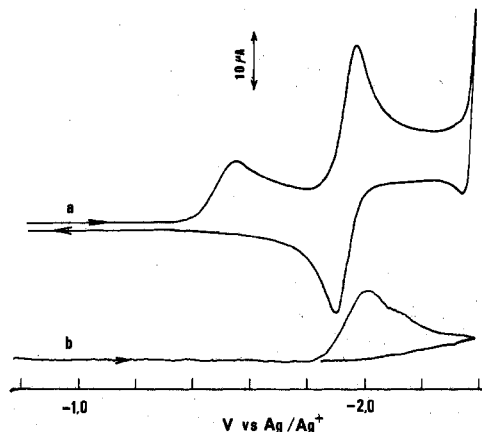


Figure 6. (a) Cyclic voltammogram of *N*-tosylcarbazole and naphthalene in a  $\text{NH}_3$ -THF (2:1) mixture at  $-40^\circ\text{C}$ ; concentration of naphthalene,  $\sim 5$  mM; scan rate, 200 mV/s. (b) Light emission during scan.

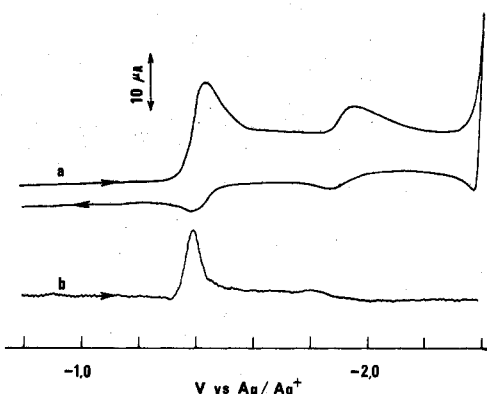
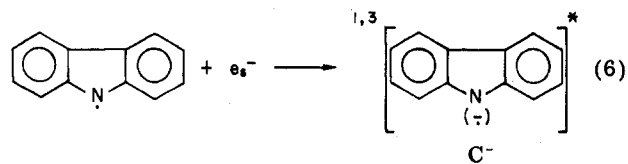
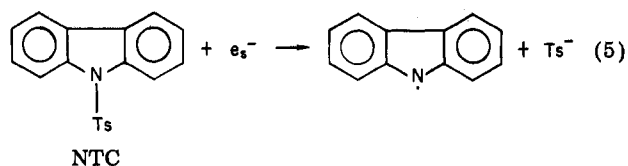
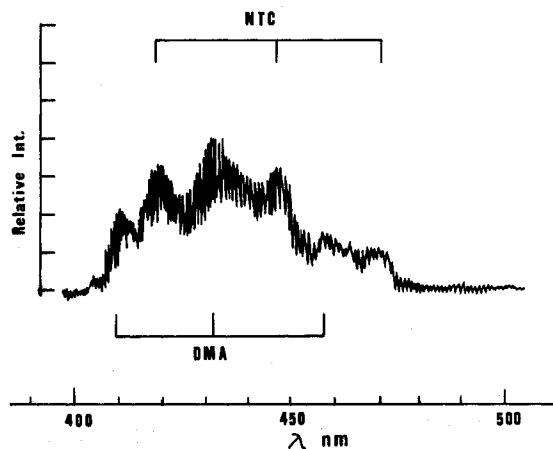


Figure 7. (a) Cyclic voltammogram of *N*-tosylcarbazole and 9,10-dimethylanthracene in a  $\text{NH}_3$ -THF (2:1) mixture at  $-40^\circ\text{C}$ ; concentration of 9,10-dimethylanthracene,  $\sim 1$  mM; scan rate, 200 mV/s. (b) Light emission during scan.

occurred at 418 nm, whereas 427 nm has been observed in HMPA.<sup>8</sup> The proposed mechanism for the reaction is as follows:<sup>5,8</sup>

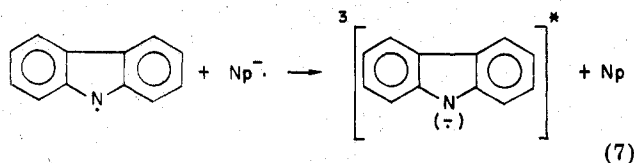


To test the possibility of excited-state formation on reaction of the carbazole radical with reductants that are weaker than  $e_s^-$ , we investigated reactions with the radical anions of naphthalene (Np) and 9,10-dimethylanthracene (DMA). Cyclic voltammograms of mixtures of NTC and Np and NTC and DMA are shown in Figures 6 and 7, respectively. The observed emissions in both cases were much weaker than that found with  $e_s^-$ ; for example, the relative ecl intensity for the simultaneous reduction of NTC and Np was  $\sim 2\%$  of that found with  $e_s^-$ . The ecl spectrum of the NTC-Np system was again the same as the fluorescence spectrum of the carbazole anion; no component of emission ascribable to naphthalene fluorescence was seen. This strongly indicates that only the triplet state



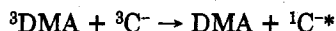
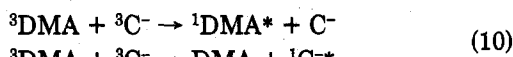
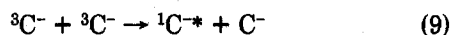
**Figure 8.** Uncorrected electrogenerated chemiluminescence spectrum of *N*-tosylcarbazole with 9,10-dimethylantracene. The six major bands can be assigned to the fluorescence bands of *N*-tosylcarbazole (NTC) and 9,10-dimethylantracene (DMA).

of the carbazole anion can be formed by the electron transfer reaction (eq 7). Formation of the triplet state

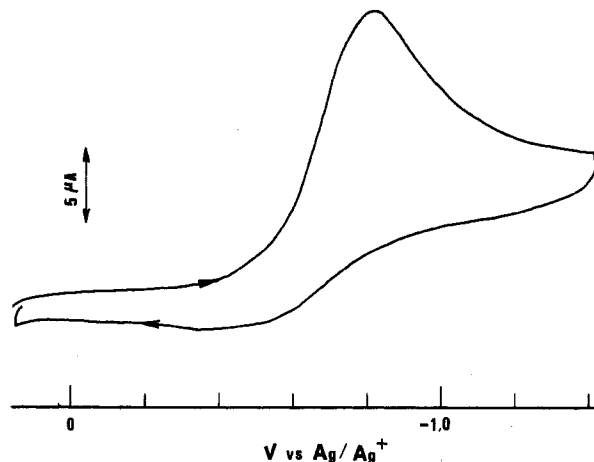


of naphthalene is not possible by this electron transfer reaction (eq 7), because the triplet-state energy of naphthalene, 2.63 eV,<sup>20</sup> is much greater than the free enthalpy change of the electron transfer reaction (~2.0 eV, as estimated from the cyclic voltammogram). The observed carbazole anion emission in the  $\text{Np}^-$  reaction suggests that the energy level of the triplet state of the carbazole anion is less than 2.0 eV.

The ecl spectrum observed during the simultaneous reduction of NTC and DMA (Figure 8), however, shows two components which correspond to the fluorescence of DMA and that of  $\text{C}^-$ . In this case the reaction between  $\text{C}^-$  and  $\text{DMA}^-$  can yield both triplet  $\text{C}^-$  and triplet DMA. This is then followed by triplet-triplet annihilation reactions as follows:



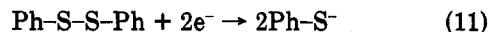
The energy level of triplet DMA lies at 1.80 eV, and the triplet state of the carbazole anion is probably near this value.<sup>20</sup> If the  $\text{C}^-$  triplet energy were larger than that of DMA, energy transfer to ground-state DMA could occur readily and this would result in a predominance of DMA emission in the ecl spectra. An estimate of the free enthalpy change for the  $\text{C}^-/\text{DMA}^-$  reaction based on the CV oxidation wave of  $\text{C}^-$  yields ~1.5 eV. This estimated value is obviously less than the energy of the triplet states of NTC and DMA. This discrepancy suggests that the actual standard potential of  $\text{NTC}^-/\text{NTC}$  couple is more positive than the observed peak potential of the irreversible oxidation wave and is at least +0.4 V vs.  $\text{Ag}^+$ . If we take the standard potential of  $\text{NTC}^-/\text{NTC}$  as +0.4 V vs.  $\text{Ag}^+$ , the free enthalpy change of the reaction of NTC with solvated electron (eq 6) is -3.1 eV. The energy of the excited singlet state of carbazole anion is estimated to be 3.00 eV ( $\pm 0.01$ )



**Figure 9.** Cyclic voltammogram of diphenyl disulfide in a  $\text{NH}_3$ -THF (3:2) mixture at  $-40^\circ\text{C}$ ; concentration of the disulfide, ~2-3 mM; scan rate, 200 mV/s.

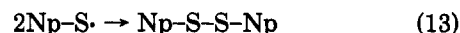
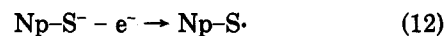
from the position of the 0-0 bands of the absorption and fluorescence spectra. Thus the reaction between  $\text{C}^-$  and  $\text{e}_s^-$  probably leads to the direct population of the excited singlet state by the electron transfer reaction (i.e., is an S-route system).

A cyclic voltammogram of diphenyl disulfide in a  $\text{NH}_3$ -THF mixture (3:2 by volume) is shown in Figure 9. The wave at -0.8 V is ascribed to reaction 11, where Ph-



S-S-Ph and  $\text{Ph-S}^-$  are the disulfide and the thiolate anion, respectively. Previous studies on the electrochemistry of disulfides have also shown that the reduction waves were totally irreversible.<sup>21,22</sup>

Although the emission intensity was very weak, an emission spectrum for ecl was obtained during generation of  $\text{e}_s^-$  which showed a single peak at 470-480 nm. The solubility of dinaphthyl disulfide ( $\text{Np-S-S-Np}$ ) in  $\text{NH}_3$ -THF, even in a 1:1 mixture, was too low to obtain a well-resolved voltammogram. However an ecl spectrum could be obtained during  $\text{e}_s^-$  generation, as shown in Figure 10A. Two bands are observed in the ecl spectrum, at ca. 490 and 590 nm. To solve the solubility problem with  $\text{NH}_3$ -THF mixtures, we used HMPA as a solvent for an ecl experiment with dinaphthyl disulfide. A cyclic voltammogram of  $\text{Np-S-S-Np}$  in 0.1 M  $\text{NaClO}_4/\text{HMPA}$  shows a totally irreversible reduction wave at -1.8 V vs. a  $\text{Ag}$  quasi-reference electrode (Figure 11). The oxidation wave at ~0 V can be identified with the oxidation of  $\text{Np-S}^-$ , leading to regeneration of the original disulfide (eq 12 and 13). The dimerization of thiny radicals has been



extensively studied by Ito and Matsuda<sup>23</sup> by a flash photolytic technique, so that electrochemical  $\text{Np-S}^-$  oxidation probably produces predominantly the disulfide. On the basis of this reaction mechanism, the disulfides (unlike the carbazole and naphthol tosylates) involve a kind of regeneratable ecl system. With NTC and the naphthol tosylates, the compounds are always consumed in the reactions. Ecl and fluorescence spectra of a solution of  $\text{Np-S}^-$  in HMPA are shown in Figure 10. The solution of  $\text{Np-S}^-$  was obtained in HMPA by a direct reduction of the disulfide by a solution of sodium in HMPA. The concentration of the disulfide was less than  $10^{-5}$  M. Both the ecl and fluorescence spectra showed the same two bands as

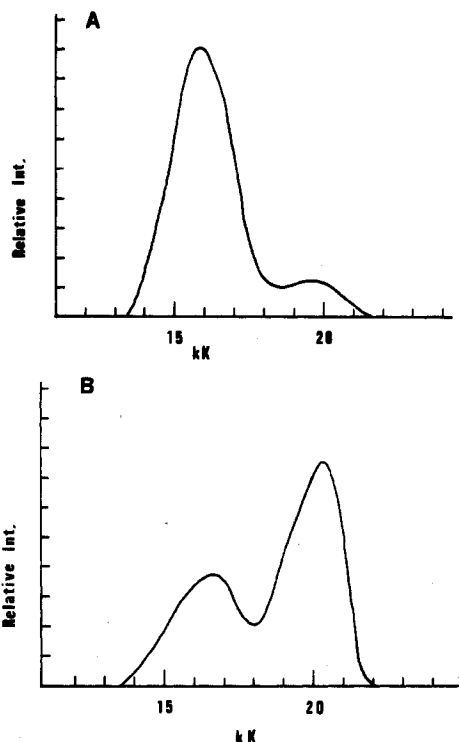


Figure 10. Uncorrected electrogenerated chemiluminescence spectrum of 2-dinaphthyl disulfide (A) and fluorescence spectrum of 2-naphthylthiolate anion (B) in HMPA. An identical ecl spectrum was obtained in a  $\text{NH}_3$ -THF (1:1) mixture at  $-40^\circ\text{C}$ .

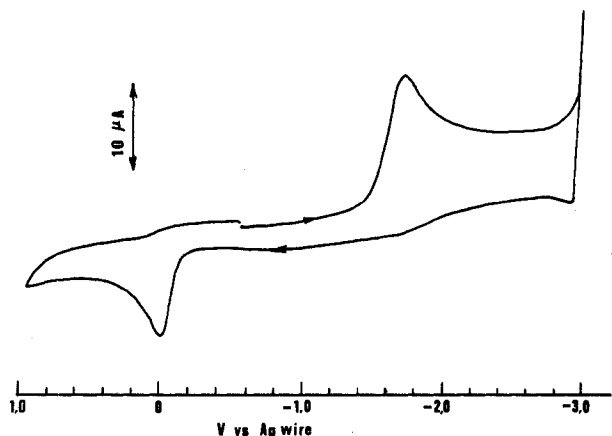


Figure 11. Cyclic voltammogram of 2-dinaphthyl disulfide in HMPA at  $20^\circ\text{C}$ ; concentration of the disulfide,  $\sim 2$ - $3$  mM; scan rate,  $100$  mV/s; supporting electrolyte,  $0.1$  M  $\text{NaClO}_4$ ; a Ag-wire quasi-reference electrode was employed.

observed with  $\text{NH}_3$ -THF mixtures. However, the band at  $590$  nm was the main component in ecl, but not in the fluorescence. In the fluorescence experiment, no change in the relative intensities of the two bands was observed regardless of the degree of reduction of the disulfide with a sodium solution of HMPA (i.e., for 5-100% reduction). The nature of the species producing the two bands was not investigated further, but they may be due to formation of dimers in the excited state (excimers) or due to products of side reactions.

Several other compounds were examined: allyl chloride, benzyl chloride, triphenylmethyl chloride, and tetrakis(dimethylamino)ethylene. No appreciable ecl emission was detected for these in  $\text{NH}_3$ -THF. Cyclic voltammograms are shown in Figure 12. Triphenylmethyl chloride exhibited a relatively strong red emission in HMPA,<sup>9</sup> but it could not be examined in  $\text{NH}_3$ -THF mixtures because of

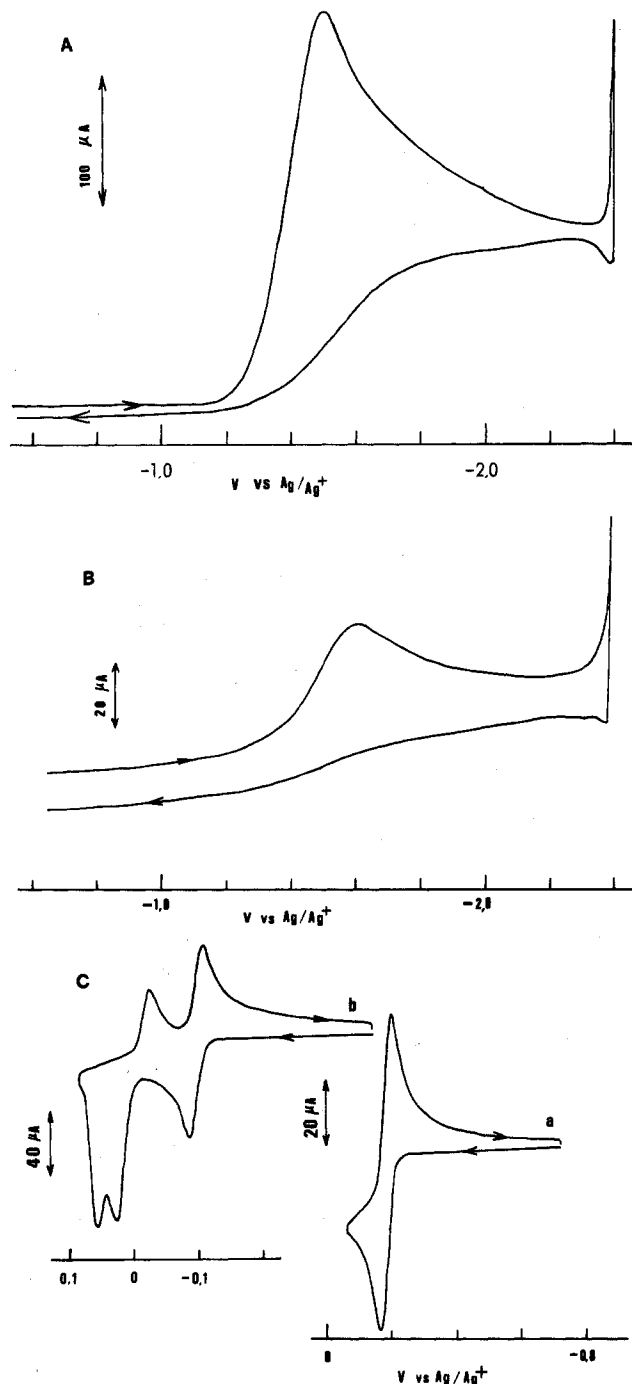


Figure 12. Cyclic voltammograms of (A) allyl chloride ( $10$ - $30$  mM), (B) benzyl chloride ( $5$  mM), and (C) tetrakis(dimethylamino)ethylene ( $7$  mM) in  $\text{NH}_3$ -THF (2:1) mixtures at  $-40^\circ\text{C}$ .

its low solubility. Tetramethyl-*p*-phenyldiamine and aromatic amines have also been examined in HMPA.<sup>9</sup> Although tetrakis(dimethylamino)ethylene, which has been shown to produce a radical cation on electrochemical oxidation in MeCN and DMF,<sup>24a</sup> showed clean cyclic voltammetric behavior (Figure 12C), no ecl was obtained by generation of  $e_s^-$ . Nakato et al. have studied the photoionization of tetraaminoethylenes in organic solvents and have estimated that the energies of the solvated ionized state ( $M_s^+ + e_s^-$ ) and the fluorescent states were almost the same in ether.<sup>24b</sup> In  $\text{NH}_3$ -THF mixtures, the energy level of the solvated ionized state is probably lower than that of the fluorescence state.

**Measurement of Ecl Yield.** The procedure described in a previous paper<sup>9</sup> was applied to determine the ecl ef-

**TABLE I: Electrogenerated Chemiluminescence Efficiencies of  $\alpha$ -Naphthol Tosylate with Solvated Electrons in a  $\text{NH}_3$ -THF Mixture (2:1 by Volume) at  $-40^\circ\text{C}$ <sup>a</sup>**

run	$\int i_e(t) dt, \mu\text{C}$	$\int I(t) dt, \text{photons}$	$\phi_{\text{ecl}}, \%$
1	9.17	$2.1 \times 10^{11}$	0.75
2	11.28	$2.8 \times 10^{11}$	0.8
3	15.8	$3.4 \times 10^{11}$	0.7
4	21.5	$3.7 \times 10^{11}$	0.56
5	43.6	$6.5 \times 10^{11}$	0.48
6	190	$26.0 \times 10^{11}$	0.44

<sup>a</sup> Emission was monitored at 475 nm. At this wavelength, the factor  $\int F(\nu) d\nu / F(\nu_{\text{meas}})$  was  $3.85 \times 10^3 \text{ cm}^{-1}$ .

**TABLE II: Electrogenerated Chemiluminescence Efficiencies of *N*-Tosylcarbazole with Solvated Electrons in a  $\text{NH}_3$ -THF Mixture (2:1 by Volume) at  $-40^\circ\text{C}$ <sup>a</sup>**

run	$\int i_e(t) dt, \mu\text{C}$	$\int I(t) dt, \text{photons}$	$\mu_{\text{ecl}}, \%$
1	24.5	$3.5 \times 10^{11}$	0.46
2	25.5	$3.4 \times 10^{11}$	0.43
3	29.0	$4.9 \times 10^{11}$	0.54
4	32.0	$5.2 \times 10^{11}$	0.52
5	33.7	$5.0 \times 10^{11}$	0.48
6	38.12	$7.3 \times 10^{11}$	0.62

<sup>a</sup> Emission was monitored at 419 nm. At this wavelength the factor  $\int F(\nu) d\nu / F(\nu_{\text{meas}})$  was  $2.31 \times 10^3 \text{ cm}^{-1}$ .

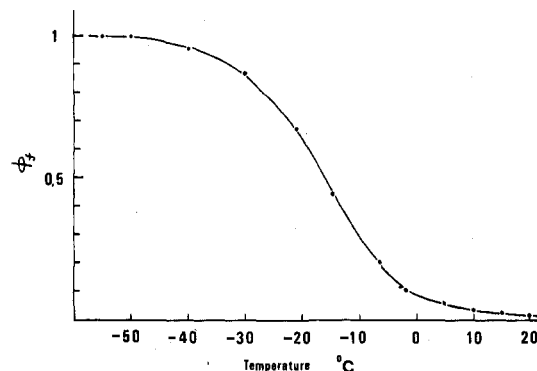
efficiencies of  $\alpha$ -naphthol tosylate and of *N*-tosylcarbazole. The electrode potential was swept linearly, and the current flowing to the working electrode for  $e_s^-$  generation,  $i_e(t)$ , and the output of the integrating sphere-detector system ( $I(t)$ ) were recorded at the same time as a function of time. The total change ( $Q_e$ ) consumed by the generation of solvated electrons was calculated by integrating the current ( $i_e(t)$ ) corrected for the tail of the preceding electrochemical reduction of the compounds vs. time (see Figure 7 in ref 9). The efficiency of ecl with solvated electrons can be defined as follows:

$$\phi_{\text{ecl}} = 2 \int I(t) dt / (1/F) \int i_e(t) dt \quad (14)$$

The factor of 2 arises because one electron is required for parent-compound reduction and a second for excited-state production (see eq 3 and 4). We assume no loss of  $e_s^-$  by other routes.

Table I lists the experimental results for  $\alpha$ -naphthol tosylate obtained with different quantities of generated solvated electrons. The factors of  $F(\nu) d\nu / F(\nu_{\text{meas}})$  in eq 1 are 0.85 at 475 nm and 2.31 at 419 nm for  $\alpha$ -naphthol tosylate and for *N*-tosylcarbazole, respectively. The greater the amount of solvated electrons generated coulometrically, the smaller were the efficiencies obtained. The same trend was observed in a previous paper.<sup>9</sup> Clearly solvated electrons would be potent quenchers of the excited states (just as radical ions are in the other ecl reactions). Their effectiveness would depend upon the excited-state lifetime and the concentration of  $e_s^-$  in the reaction zone. The efficiency (0.4–0.8%) seems to be sufficiently high that the direct formation of the excited singlet state of the naphthol anion as the dominant route in ecl appears reasonable.

Table II lists the experimental results for NTC obtained with different quantities of solvated electrons. The average value of  $\phi_{\text{ecl}}$  was  $\sim 0.5\%$ . In HMPA, an efficiency of 1–3.3% as reported.<sup>9</sup> Since totally different methods were applied for the measurement of  $\phi_{\text{ecl}}$  in these papers and absolute ecl efficiency measurements always involve considerable uncertainties,<sup>11</sup> we feel that the efficiencies in  $\text{NH}_3$ -THF and HMPA are virtually the same within ex-



**Figure 13.** Temperature dependence of the fluorescence quantum yield ( $\phi_f$ ) of carbazole anion in a  $\text{NH}_3$ -THF (2:1) mixture.

perimental error. Such high values suggest that reaction 6 leads mainly to the direct formation of excited singlet states (S route). The strong decrease of  $\phi_{\text{ecl}}$  found in the simultaneous reduction of NTC and naphthalene described above also suggests that the dominant path of the  $e_s^-$  electron transfer reaction is S route, because a pure T route is probably operating in the NTC and naphthalene system.

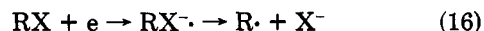
*Temperature Dependence of Fluorescence Yield of Carbazole Anion.* To estimate the yield of excited states formed by the electron transfer reaction from  $\phi_{\text{ecl}}$ , one needs a value of the fluorescence quantum yield, since<sup>11</sup>

$$\phi_{\text{ecl}} = \phi_f \phi_s \quad (15)$$

where  $\phi_f$  and  $\phi_s$  are the fluorescence quantum yield and the yield of excited singlet states by the electron transfer reaction, respectively. To measure  $\phi_f$  for NTC, we used a solution of 9,10-diphenylanthracene in degassed cyclohexane as a reference solution.<sup>20</sup> The result is shown in Figure 13. The quantum yield at temperatures below  $-40^\circ\text{C}$  was almost unity. At higher temperatures  $\phi_f$  decreased, attaining the rather low value of 0.016 at  $+20^\circ\text{C}$ . This large temperature dependence is of interest, since it suggests either a significant structural change in the excited state or an energy level near the excited singlet which undergoes a rapid radiationless transition to the ground state. A similar large temperature dependence of the emission quantum yield has been observed in  $\text{Ru}(\text{bpy})_3^{2+}$  in acetonitrile.<sup>25</sup> The temperature employed for the measurement of  $\phi_{\text{ecl}}$  of NTC was  $-40^\circ\text{C}$ , as mentioned above. Thus, at this temperature, the yield of the excited singlet state,  $\phi_s$ , is less than 0.01, so that 99% of the electron transfer reactions do not lead to excited singlets. The large temperature dependence of  $\phi_f$  and the small value of  $\phi_s$  suggest that the existence of the other states (e.g., ion pair<sup>26,27</sup> or higher excited states) must be taken into account for a better understanding of the mechanism of the electron transfer reaction.

## Conclusions

The reactions of the naphthol and carbazole tosylates and diphenyl disulfides are further examples of "oxidative reductions" where the compound formed on reduction undergoes a reaction involving bond breaking which produces a stronger oxidant than the original starting material, i.e., the sequence



followed by reaction of  $\text{R} \cdot$  with solvated electrons or with a strong reductant to produce an excited state. Analogous reactions have been reported previously with various organic halo compounds (e.g., 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene).<sup>28</sup> The light emission during these reactions provides evidence of this ECE reaction sequence



(e.g., in electrochemical reactions) and is useful in identifying intermediates. Note also that parallel "reductive oxidations" occur, for example, during the oxidation of oxalate, where the strong reductant  $\text{CO}_2\cdot^-$  is formed and ecl is observed.<sup>29</sup> Similar mechanisms have also been

proposed for chemiluminescence of diphenyl peroxide and related compounds.<sup>30</sup>

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## Flash Photolysis Study on Initiation of Radical Polymerization. Addition Rates of Benzothiazole-2-thiyl Radical to Vinyl Monomers

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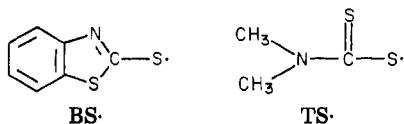
Rate constants for addition ( $k_a$ ) of benzothiazole-2-thiyl radical (BS·) to vinyl monomers ( $\text{CH}_2=\text{CHY}$ ) have been determined by means of flash photolysis. Reversibility of the reaction has been shown to be important in the decay process of BS·. Rate constants for the reverse reaction ( $k_{-a}$ ) and equilibrium constants ( $K = k_a/k_{-a}$ ) have been estimated as ratios of the rate constants for the reaction between  $\text{BSCH}_2\text{CHY}$  and oxygen; oxygen was used as a scavenger for  $\text{BSCH}_2\text{CHY}$  because of the low reactivity of BS· toward oxygen. The  $k_a$  values estimated in this work were in the range of  $6.3 \times 10^5$  (vinyl acetate)– $2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (styrene); the addition rates depend on both the resonance effect and the polar effect of vinyl monomers. On the other hand, the reactivity of the dimethylthiuramthiyl radical toward vinyl monomers is too low to be determined by flash photolysis.

### Introduction

Some organic disulfides have been found to serve as excellent photoinitiators for radical polymerization of vinyl monomers.<sup>1</sup> The mechanism of the initiation reaction has been investigated by the rotating sector method<sup>2,3</sup> and the spin trapping method.<sup>4,5</sup> Recently we have applied the flash photolysis technique to evaluate kinetic parameters of the addition reaction of thiyl radicals to vinyl monomers.<sup>6-8</sup> An advantage of this method is that it allows one to determine the absolute rate constants for the initiation reactions.

The compounds 2,2'-dibenzothiazolyl disulfide (BSSB) and tetramethylthiuram disulfide (TSST) were studied as thermal or photochemical initiators for polymerization of vinyl monomers.<sup>1,9</sup> Upon photolysis, radical polymerization of acrylonitrile or methyl methacrylate is initiated by BSSB but not by TSST.<sup>9</sup> The flash photolysis method should be useful to clarify this difference.

The photochemistry of BSSB has been studied; the benzothiazole-2-thiyl radical (BS·) was suggested as an



intermediate in the photolysis of BSSB in ethanol yielding

the corresponding mercaptan (BSH).<sup>10</sup> A transient absorption band around 350 nm was observed by flash photolysis and was attributed to BS·.<sup>10</sup> However, analysis of decay kinetics of the transient band was not reported because of the overlap with the band of BSSB. In this work, another transient band attributable to BS· was found in the visible region; thus the rates of addition of BS· toward vinyl monomers were estimated. A similar experiment was carried out for dimethylthiuramthiyl radical (TS·).

### Experimental Section

*Materials.* 2,2'-Benzothiazolyl disulfide (BSSB) was recrystallized from benzene below 40 °C. Bis(2-benzothiazolyl) sulfide (BSB) was prepared by the method described in the literature.<sup>11</sup> Tetramethylthiuram disulfide (TSST) and the monosulfide (TST) were used after purification. Vinyl monomers were distilled in the usual way before use. Cumene was distilled under reduced pressure over a stable free radical, 1,1-diphenyl-2-picrylhydrazyl. The cyclohexane used as solvent was of spectrophotometric grade.

*Methods.* The flash photolysis apparatus was of standard design; the half-duration of the xenon flash lamps (Xenon Corp. N-851) was ca. 10  $\mu\text{s}$ , and first-order rate constants less than  $5 \times 10^4 \text{ s}^{-1}$  were measurable. The flash photolysis measurements were performed in a cylindrical cell (optical path = 10 cm) at room temperature controlled at  $23 \pm 1$  °C. The oxygen concentration in cyclohexane was determined in the following way. After the solution was degassed up to ca.  $10^{-4}$  torr, oxygen was dissolved in the solution under an appropriate pressure of oxygen which

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