

**Electrochemical and photoelectrochemical  
studies of excess electrons in liquid ammonia**

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ciated with a quasi-free extended state or with a localized state of the excess electron? The completely solvated state can be excluded both on time scale and energetic grounds. Electron localization in polar liquids has been thoroughly analyzed and the role of preexisting density fluctuations or preexisting clusters has been considered as crucial.<sup>9,26,27</sup> The depth of such localization sites is, however, difficult to assess, as well as the time required for localization, and the present results are unable to elucidate these questions.

From a pragmatic point of view, it is, however, striking and significant that the same final energy state is attained from quite different experimental conditions, i.e., when the excess electron is emitted from a metallic electrode into a concentrated electrolyte solution or when ejected from a solute molecule diluted in the pure solvent.

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## Electrochemical and Photoelectrochemical Studies of Excess Electrons in Liquid Ammonia

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The applications of electrochemical techniques (voltammetry, coulometry, current step) to studies of the generation and properties of excess electrons in liquid ammonia are discussed. A study of the variation of the equilibrium potential with total concentration of solvated electrons placed the standard potential at  $-2.74$  V vs.  $\text{Ag}/\text{Ag}^+$  (0.1 M) and provided evidence for a dimeric electron species. Studies of the photoemission of electrons from a platinum electrode under laser irradiation are also described and the existence of an "injection level" at  $-2.91$  V vs.  $\text{Ag}/\text{Ag}^+$  (0.1 M) is reported. The reaction of excess electrons with *N*-tosylcarbazole which leads to strong emission of light (electrogenerated chemiluminescence) characteristic of carbazole anion fluorescence is also discussed.

### Introduction

Electrochemical experiments involving reductions in liquid ammonia with the probable generation of solvated electrons date back to at least the 1890's.<sup>1,2</sup> Although several later studies which involved the cathodic generation of excess electrons ( $e_s^-$ ) at mercury and solid metal electrodes were reported,<sup>3-7</sup> there have been surprisingly few studies on such Faradaic reactions employing modern electrochemical techniques with  $\text{NH}_3$  solutions prepared and examined under rigorously pure and dry conditions.<sup>8,9</sup> The electrochemical generation (and oxidation) of excess electrons is especially convenient because solutions with

known concentrations of  $e_s^-$  can be prepared coulometrically and then investigated without opening the system or adding additional reactants. Moreover, electrochemical techniques are very well suited to the collection of accurate data which can provide information about the thermodynamics, kinetics, and transport properties of excess electrons. Additional information can be obtained from studies of the photoejection of electrons from metal and semiconductor electrodes into liquid ammonia solutions. In this paper we briefly review the results of recent work in our laboratory on electrochemical studies of excess electrons in ammonia, highlighting, as appropriate, the

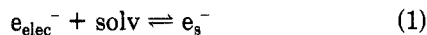
TABLE I: Concentrations (M) of Species Present in Liquid Ammonia Solutions of Solvated Electrons Containing 0.1 M KI at  $-55^\circ\text{C}$ 

| $C_T$ , M             | $[e_s^-]$             | $[K^+e^-]$            | $[K^+]$               | $[KI]$                | $[I^-]$               | $[(K^+e^-)_2]$        |
|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| $9.16 \times 10^{-5}$ | $4.78 \times 10^{-6}$ | $4.55 \times 10^{-5}$ | $9.52 \times 10^{-3}$ | $9.05 \times 10^{-2}$ | $9.51 \times 10^{-3}$ | $2.07 \times 10^{-5}$ |
| $2.24 \times 10^{-4}$ | $8.59 \times 10^{-6}$ | $8.18 \times 10^{-5}$ | $9.52 \times 10^{-3}$ | $9.05 \times 10^{-2}$ | $9.51 \times 10^{-3}$ | $6.69 \times 10^{-5}$ |
| $5.20 \times 10^{-4}$ | $1.43 \times 10^{-5}$ | $1.36 \times 10^{-4}$ | $9.52 \times 10^{-3}$ | $9.05 \times 10^{-2}$ | $9.51 \times 10^{-3}$ | $1.85 \times 10^{-4}$ |
| $2.37 \times 10^{-3}$ | $3.33 \times 10^{-5}$ | $3.17 \times 10^{-4}$ | $9.53 \times 10^{-3}$ | $9.05 \times 10^{-2}$ | $9.50 \times 10^{-3}$ | $1.00 \times 10^{-3}$ |
| $1.00 \times 10^{-2}$ | $7.13 \times 10^{-5}$ | $6.81 \times 10^{-4}$ | $9.55 \times 10^{-3}$ | $9.05 \times 10^{-2}$ | $9.48 \times 10^{-3}$ | $4.64 \times 10^{-3}$ |

difficulties and unanswered questions in this area. Recent work on reactions of solvated electrons with solutes in ammonia to produce excited states and the emission of light (electrogenerated chemiluminescence or ECL) will also be described.

### Electrogeneration of Solvated Electrons

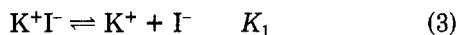
A recent paper from this laboratory<sup>10</sup> described an investigation of the electrochemical behavior of excess electrons in liquid ammonia containing 0.1 M KI as supporting electrolyte by cyclic voltammetric, coulometric, and single pulse galvanostatic techniques. The coulometric measurements demonstrated the excellent stability of the electrons over a time period of hours under our experimental conditions for total concentrations of  $10^{-4}$  to  $2.5 \times 10^{-2}$  M. This stability permitted the study of the effect of excess electron concentration on the potential of a platinum electrode (with respect to a  $\text{Ag}/\text{AgNO}_3$  (0.1 M) reference electrode) with the aim of determining the standard potential for the half-reaction



[For previous studies of the standard potential of  $e_s^-$ , see ref 3, 6, 11, and 12.] If  $e_s^-$  is the predominant excess electron species in the solution the observed response should follow the Nernst equation:

$$E = E^\circ - (RT/F) \ln (\gamma_e [e_s^-]) = E^{\circ'} - (RT/F) \ln [e_s^-] \quad (2)$$

where  $E^\circ$  and  $E^{\circ'}$  are the standard and formal potentials, respectively,  $\gamma_e$  is the activity coefficient of  $e_s^-$ , and  $[e_s^-]$  is its concentration. A plot of  $E$  vs.  $\log C_T$  (where  $C_T$  is the total concentration of generated solvated electrons) should thus be linear with a slope of 43 mV (at  $-55^\circ\text{C}$ ), if  $[e_s^-] = C_T$ . However, the experimental results (Figure 1) showed considerable curvature and a slope at low concentrations of  $35 \pm 2$  mV. This can be rationalized by including the possibility of ion pair formation and dimerization, i.e.



(It is also possible that ion triplets of the form  $e_s^-K^+e_s^-$  are present, but such species were not considered in the following calculation.) By taking<sup>13,14</sup>  $K_1 = K_1' = 10^{-3}$  and  $K_2 = 10^4$  (all concentrations in mole liter<sup>-1</sup>) and  $C_T = \{[e_s^-] + [K^+e_s^-] + 2[(K^+e_s^-)_2]\}$ , one can plot the experimental results as shown by the dashed line in Figure 1. The calculated concentrations of the different species are given in Table I. A plot of  $E$  vs.  $\log [e_s^-]$  produced a straight line over the whole  $C_T$  region with a slope of 43 mV and yielded an  $E^{\circ'}$  value for eq 1 of  $-2.74 \pm 0.01$  V vs.  $\text{Ag}/\text{AgNO}_3$  (0.1 M). The data obtained in these studies are clearly insufficient to obtain accurate independent measurements of  $K_1$ ,  $K_1'$ , and  $K_2$ . However, the results suggest that measurements of the electrode potential for electrogeneration of  $e_s^-$  with different concentrations of KI and

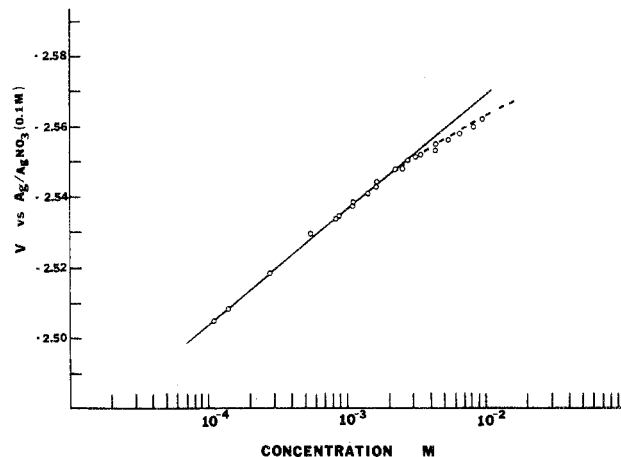
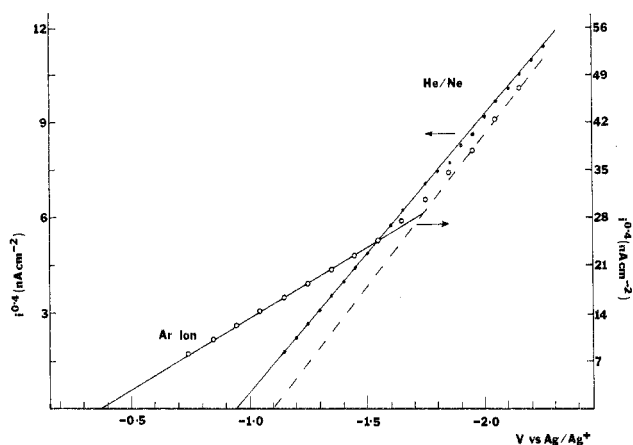


Figure 1. The equilibrium potential of solvated electrons vs. concentration. Supporting electrolyte, 0.1 M KI; reference electrode,  $\text{Ag}/\text{AgNO}_3$  (0.1 M); temperature,  $-55^\circ\text{C}$  (solid line). The theoretical electrode potential vs.  $C_T$  (dashed curve).

different supporting electrolyte salts can supplement other physical measurements in studying the thermodynamic properties of dilute metal-ammonia solutions.<sup>15</sup>

Electrochemical measurements of the collection of solvated electrons (in the form of the ion paired species) at an inert electrode are also useful in obtaining information about the transport properties and rates of reaction of  $e_s^-$ . Thus chronocoulometric experiments, for solutions with  $C_1 = 1.12 \times 10^{-3}$  M, where the potential of a platinum electrode was stepped to a value where the oxidation (collection) of  $e_s^-$  [the reverse of eq 1] occurred at the diffusion limited rate and the integrated current, determined as a function of time, lead to the following value for diffusion coefficient,  $D$ , and mobility ( $\mu$ ) ( $T = -55^\circ\text{C}$ ):<sup>10</sup> for 0.1 M KI,  $D = 4.47 (\pm 0.08) \times 10^{-5}$  cm<sup>2</sup>/s,  $\mu = 2.38 \times 10^{-3}$  cm<sup>2</sup>/V s; for 0.4 M KI,  $D = 2.5 (\pm 0.1) \times 10^{-5}$  cm<sup>2</sup>/s,  $\mu = 1.33 \times 10^{-3}$  cm<sup>2</sup>/V s. These values of  $D$  for associated  $e_s^-$  are in reasonable agreement with a previously reported  $D$  value obtained by chronopotentiometry<sup>16</sup> and estimates of  $\mu$ . Precise measurements of  $D$  and  $\mu$  for  $e_s^-$  as functions of temperature and  $C_T$  and comparisons with chronocoulometric determinations of  $D$  values for other electroactive species in  $\text{NH}_3$  should be of value in describing any special features governing the mobility of electrons in liquid  $\text{NH}_3$ . The  $D$  for the solvated electron system in 0.1 M KI at this  $C_T$  value is not much larger than that found for nitrobenzene in this solvent,  $2.8 \times 10^{-5}$  cm<sup>2</sup>/s.<sup>9</sup> The limiting value obtained by extrapolation from solutions with lower concentrations of KI and  $C_T$ , where unassociated  $e_s^-$  is the predominant species, would clearly be of interest. Measurements of the oxidation of  $e_s^-$  in liquid ammonia by a galvanostatic pulse method have also been attempted.<sup>10</sup> The exchange current density for this process for  $C_T = 0.12 \times 10^{-3}$  M was relatively large,  $6 (\pm 2)$  mA/cm<sup>2</sup>.<sup>34</sup> The measured values in this case were somewhat uncertain because of solution resistance problems and the 8- $\mu\text{s}$  rise time of the applied current pulse. Under improved experimental conditions measurements of the rate constant of electron transfer with different electrolytes should be



**Figure 2.** Dependence of photocurrent ( $i^{0.4}$ ) on electrode potential for irradiation with Ar ion (O) and He-Ne (●) lasers. Solution contained 60 mM *n*-butyl chloride. Dashed line indicates extrapolation from more negative potentials in Ar-ion laser experiment. Temperature,  $-55^\circ\text{C}$ .

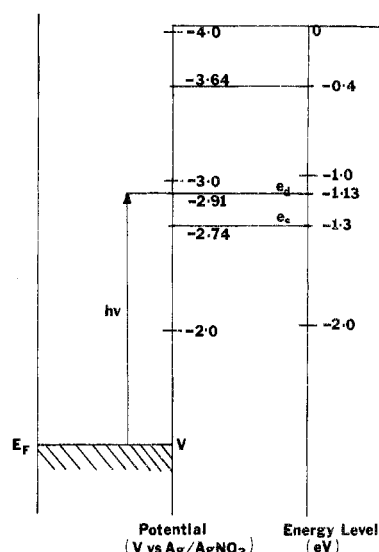
possible. Studies of such heterogeneous electron transfer rates at electrodes in aqueous and aprotic solutions have previously been correlated with inner- and outer-sphere reorganization energies and reaction rates of homogeneous chemical reactions.<sup>17-19</sup> Similar studies in liquid ammonia could help in a description of the state of  $e_s^-$ .

### Photoemission of Electrons from Metal Electrodes

Numerous studies of photoelectron emission from metal electrodes into electrolyte solutions have been undertaken with a view to obtaining information about the energies of nonthermalized excess electrons.<sup>20</sup> Most of these studies have involved aqueous solutions containing scavengers for the photoinjected solvated electron. We have recently carried out experiments on the photoinjection of electrons into liquid ammonia-0.1 M KI from a platinum electrode under illumination with either a He/Ne or Ar ion laser at  $-55^\circ\text{C}$ .<sup>21</sup> In these experiments *n*-butyl chloride, which reduces at  $-2.4$  V [vs.  $\text{Ag}/\text{AgNO}_3$  (0.1 M)], was employed as an electron scavenger. Plots of the experimental photocurrent as a function of electrode potential are given in Figure 2. The experimental plots show excellent linearity of  $i^{0.4}$  vs.  $V$ , suggesting that the "five-halves law" predicted for photoemission at the metal-electrolyte interface<sup>20,22</sup>

$$i = A(h\nu - h\nu_0 - eV)^{5/2} \quad (6)$$

is followed ( $V$  is the electrode potential;  $\nu$ , the frequency of the excitation source;  $\nu_0$ , the threshold frequency at  $V = 0$  vs. the reference electrode, and  $A$ , a proportionality constant). The intercept of these plots with the  $V$  axis yields the following values of the "threshold potential" for photoemission of electrons: He/Ne laser ( $\lambda = 632.8$  nm,  $E = 1.96$  eV),  $-0.95$  V; Ar ion laser ( $\lambda = 488.0$  nm,  $E = 2.54$  eV),  $-0.37$  V (vs.  $\text{Ag}/\text{AgNO}_3$ ). Note that the difference in these values exactly equals the difference in laser photon energy. This places the energy level of the emitted photons, calculated from the sum of the threshold potential and the laser energy, at  $-2.91$  ( $\pm 0.03$ ) V vs.  $\text{Ag}/\text{AgNO}_3$  (0.1 M), or 0.2 V above the  $E^\circ$  value for  $e_s^-$ . It is usually assumed that the emitted photon is "quasi-free", i.e., that the photoemission process occurs so rapidly that only electronic polarization but not orientational polarization of the ammonia can occur.<sup>20,23</sup> In this case, the injection level,  $e_d$ , on the proposed excess electron energy level diagram shown in Figure 3 can be assigned to the conduction band edge.<sup>21</sup> These levels have been related to the vacuum level by intercomparison of the  $\text{Ag}/\text{AgNO}_3$ , ferrocene, and naphthalene potentials in  $\text{NH}_3$  and  $\text{CH}_3\text{CN}$ ,<sup>24</sup> with the



**Figure 3.** Proposed energy levels of electron states in liquid  $\text{NH}_3$  in  $V$  vs.  $\text{Ag}/\text{Ag}^+$  reference electrode and estimated vs. vacuum.

assumption that the formal potential of the  $\text{Ag}/\text{AgNO}_3$  (0.01 M) couple in  $\text{CH}_3\text{CN}$  corresponds to  $-4.7$  eV (with respect to vacuum).<sup>25</sup> The difference in energies between the injection level and the solvated electron level in ammonia is very near the value found in aqueous solutions ( $\sim 0.2$  eV) for photoinjection from a number of different materials.<sup>23</sup> Krohn and Thompson<sup>26</sup> have pointed out that the assignment (in both  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ) of the injection level to that of the quasi-free electron appears inconsistent with theoretical estimates of the location of this level with respect to vacuum, as well as the observed experimental mobility and optical properties of  $e_s^-$ . They consider the injection level as corresponding to trap states either in the bulk solvent or at the electrode/solvent interface. The actual conduction band edge would then lie at higher energies. Indeed our experimental results (Figure 2) show that for the Ar ion laser at more negative potentials ( $< -2.0$  V) the experimental points deviate from the line drawn at lower photocurrents and perhaps defines a new line of  $i^{0.4}$  vs.  $V$ . This line (shown as a dashed one in Figure 2) yields a higher threshold value ( $\sim -1.1$  V) corresponding to  $-3.64$  V vs.  $\text{Ag}/\text{AgNO}_3$  or an energy level of about  $-0.4$  eV (Figure 3), which is closer to the level usually assumed for the conduction band edge in liquid ammonia.<sup>15</sup> Clearly, electron photoinjection measurements from metals into liquid ammonia appear to be a very useful tool in studying electron energy levels. Further experiments with other irradiation energies, at other metallic electrodes (the threshold should be independent of character of metal), with other scavengers, and other electrolytes should be undertaken. Irradiation at shorter wavelengths and establishment of the reality of the "two-slope"  $i^{0.4}$ - $V$  plots would be of special interest.

Photoinjection of electrons into ammonia is also possible at a p-type semiconductor electrode, e.g., GaAs or Si.<sup>27,28,35</sup> In this case the nature of the injection process depends primarily on the characteristics of the semiconductor and the nature of the electrode surface and is probably less informative about the characteristics of the excess electrons themselves.

### Reactions of Excess Electrons Producing Excited States

Numerous studies of excited state formation upon homogeneous electron transfer reactions of electrogenerated species have been reported.<sup>29</sup> In general, when the energy

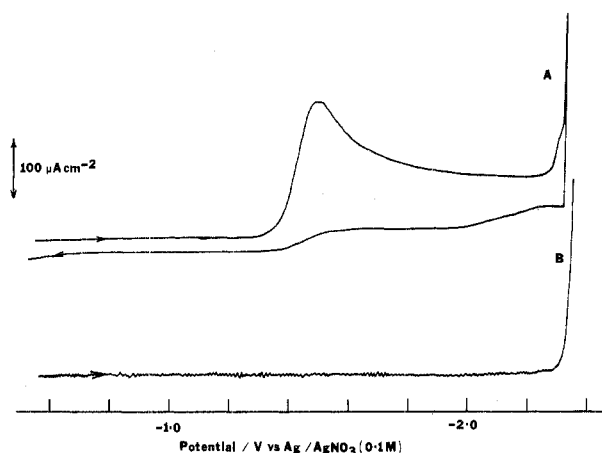
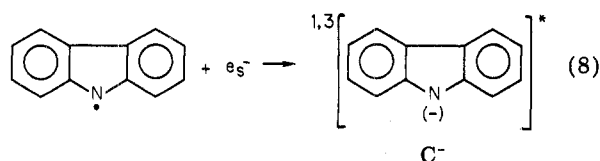
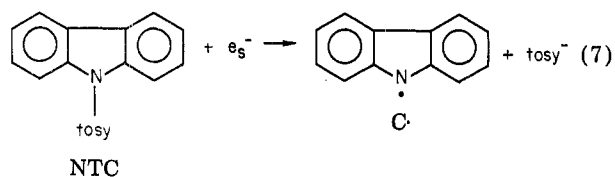


Figure 4. (A) Cyclic voltammogram of *N*-tosylcarbazole in  $\text{NH}_3$  (10 mL)-THF (5 mL) mixture. Supporting electrolyte: 0.1 M KI. Scan rate: 200 mV/s. Temperature,  $-55^\circ\text{C}$ . (B) ECL emission (in arbitrary units).

of the electron transfer reaction is larger than the excited state (singlet, triplet, exciplex) energy of one of the products, the redox reaction will lead to some production of excited states and frequently the emission of light. These studies are of interest because they probe the details of the course of electron transfer reactions and are relevant to theories of such reactions.<sup>17</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>30</sup> and by Chandross.<sup>31</sup> We thought it of interest to extend such studies to liquid  $\text{NH}_3$  where solvated electrons have greater stability and their thermodynamic properties are known. We report here investigations of such reactions utilizing  $\text{NH}_3$ -THF mixtures (2:1 by volume). THF was added in these experiments to increase the solubility of the organic compounds.

The electrochemical reduction of *N*-tosylcarbazole (NTC) at a Pt electrode in  $\text{NH}_3$ -THF is shown in Figure 4A. The NTC is reduced at about  $-1.5$  V vs. Ag followed by generation of excess electrons commencing at about  $-2.3$  V. Note that the stability and electrochemical behavior of the excess electrons in  $\text{NH}_3$ -THF are essentially the same as in liquid  $\text{NH}_3$  alone. In the presence of NTC a strong blue light emission is seen during the generation of  $e_s^-$  (Figure 4B). The ECL spectrum of this emitted light (Figure 5) is virtually identical with the fluorescence spectrum of carbazole anion in liquid  $\text{NH}_3$  produced by reaction of NTC with butyllithium in THF.

The proposed mechanism for the reaction is as follows:



The energy of the excited state of carbazole anions was estimated to be 3.00 eV ( $\pm 0.01$ ) from the position of the 0-0 bands of the absorption and fluorescence spectra. An oxidation wave was observed at about  $+0.1$  V which we ascribe to the oxidation of carbazole anion ( $\text{C}^-$ ) to the neutral radical ( $\text{C}^\cdot$ ). Although there is considerable un-

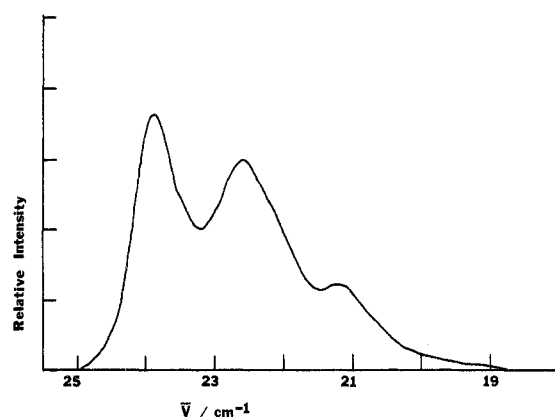
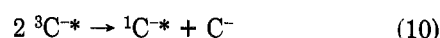
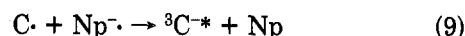


Figure 5. ECL spectrum of *N*-tosylcarbazole in a  $\text{NH}_3$  (10 mL)-THF (5 mL) mixture with 0.1 M KI. Temperature,  $-55^\circ\text{C}$ .

certainty in the determination of the redox potential for the  $\text{C}^\cdot/\text{C}^-$  couple, we can estimate that the free energy change for the reaction in eq 8 is about  $-2.8$  to  $-2.9$  eV, assuming that the standard redox potential of solvated electrons in pure liquid  $\text{NH}_3$  ( $-2.7$  V vs. Ag/0.1 M  $\text{AgNO}_3$ ) can be used. The observed ECL efficiency (photons emitted/redox event) was about 0.7% at  $-40^\circ\text{C}$ , as measured with an integrating sphere apparatus. We also found that the fluorescence quantum yield for  $\text{C}^-$  was approximately unity (i.e.,  $\Phi_f \approx 1$ ) at  $-40^\circ\text{C}$ . Interestingly, the fluorescence quantum yield of carbazole anions in liquid  $\text{NH}_3$  showed a very strong temperature dependence and decreased dramatically with increasing temperature. For example,  $\Phi_f$  was only about 0.01 at  $20^\circ\text{C}$ .

Although the estimated value ( $-2.8$  to  $-2.9$  eV) for the free-energy change of the redox reaction, eq 8, is not greater than the energy of the singlet state, the direct population of the excited singlet state by electron transfer reaction (S route) is probably the main route. Several side reactions (e.g., dimerization, hydrogen transfer) involving the neutral radical of carbazole and the temperature dependence of the fluorescence quantum yield might be taken into account to explain the relatively low excited state yield ( $\sim 0.7\%$ ).

Experiments involving the simultaneous reduction of NTC and naphthalene ( $\text{Np}^\cdot$ ) show a much weaker emission (less than 2% that of the  $e_s^-$  reaction). In this case the energy of the redox reaction,  $\sim -2.0$  eV, is insufficient to produce excited singlet  $\text{C}^-$  and the reaction producing excited singlet carbazole anion probably proceeds via triplets (the T route):



Similar studies of the reactions of excess electrons with other materials producing excited states (e.g.,  $\alpha$ - and  $\beta$ -naphthyl tosylates,  $\beta,\beta'$ -dinaphthyl disulfide, diphenyl disulfide, benzylic chlorides, tetrakis(*N,N*-dimethylamino)ethylene) have been carried out and will be described elsewhere.<sup>32</sup> Such chemiluminescence experiments with  $e_s^-$  in liquid  $\text{NH}_3$  may provide further details about the energy levels of excess electrons and the redox potentials of free radicals in this solvent. Photoproduced chemiluminescence, employing electrons photoejected from metals or semiconductors into  $\text{NH}_3$ , should also be possible; such processes have been observed in other solvents.<sup>33</sup>

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## References and Notes

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## Electrochemical Investigations of Solvated Electrons in Ammonia and Methylamine

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The electrochemical behavior of excess electrons is studied in ammonia and ammonia-methylamine mixtures with sodium iodide as a carrier electrolyte. By cyclic voltammetry, aided by spectral photometry, we found that the electrons are injected into ammonia at a potential more positive by  $0.22 \pm 0.02$  V than in methylamine (extrapolated from mixtures to pure methylamine). This implies that the chemical potential of dissolved sodium is about  $5.0 \pm 0.5$  kcal/mol more negative in ammonia than in methylamine under identical experimental conditions. In ammonia solvated electrons are formed, whereas in the amine-rich solutions the observed spectra prove the formation of Na<sup>-</sup> anions. From galvanostatic pulse experiments in ammonia containing solvated electrons we obtain the exchange current density  $j_0 = 0.01-0.1$  A/cm<sup>2</sup> in the  $e_{sol}^-$  concentration and temperature range from  $2 \times 10^{-4}$  to  $1.2 \times 10^{-3}$  M and from -75 to -35 °C; its concentration dependence is given by the transfer coefficient  $\alpha = 0.5 \pm 0.05$ , and its temperature dependence by the activation energy  $E_a = 3.8 \pm 1$  kcal/mol. The concentration of the electron acceptor in the solution, i.e., the traps into which the electrons jump and which are formed by random orientation of the solvent molecules, is found to be  $(1.6 \pm 0.7) \times 10^{-3}$  mol/L. From this information finally the rate constant for the electron exchange between solution and electrode is calculated as  $k = 0.2-1.0$  cm/s at temperatures between -75 and -35 °C.

## Introduction

In a preceding paper<sup>1</sup> we have evaluated by electrochemical means the thermodynamic properties of metal-ammonia solutions which contain metal cations and dissolved electrons in a paramagnetic, diamagnetic, or metallic state, depending on concentration. Now we are concerned with electrode kinetics of the electrons, which supplement the thermodynamic data, but which are also of interest with respect to the kinetic properties of the electrons. So far only very little information is available on the kinetics of the solvated electron-electrode reactions,<sup>2-4</sup> which can be described by



An electron in the metal electrode  $e_m^-$  is transferred to the solvent, where it is trapped in a shallow potential well to

form a solvated electron  $e_s^-$ . The potential well is formed by favorable random orientation of the solvent molecules and might be described as a hole "O" in the solvent structure.

The results of two sets of experiments are reported here as follows: (1) formation potential of solvated electrons in ammonia-methylamine solutions, measured by cyclic voltammetry, aided by spectral photometry; (2) kinetics of the electron transfer from the electrode to liquid ammonia, obtained by galvanostatic single pulse experiments.

## Experimental Section

All experiments were performed with the three-electrode technique: the reference electrode for obtaining the relative potential of the working electrode, through which a current is passing to the counterelectrode. The PAR