

## Metal Ammonia Solutions: Solutions Containing Argentide Ions

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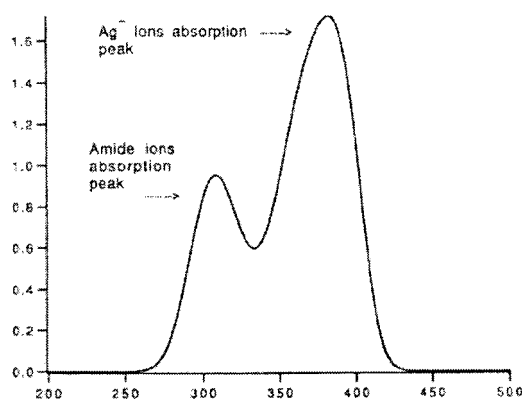
Received March 28, 2000

### Introduction

The chemistry of metals historically has been associated with their ability to form cations, especially in aqueous solutions. However, the ability of some metals to form monatomic anions is an unusual area of interest for inorganic chemistry. Stable negative metal ions are known in the gas phase,<sup>1</sup> and the stabilities of monatomic metal anions in water and in liquid ammonia have been discussed.<sup>2</sup> Monatomic metal ions are good reducing agents, and they would not be expected to exist in solvents with relatively high proton activities. However, monatomic metal anions ( $M^-$ ) are known in nonaqueous solvents<sup>3,4</sup> and as solid crystalline compounds<sup>5</sup> that include  $Na^-$ ,  $K^-$ ,  $Rb^-$ ,  $Cs^-$ , and  $Au^-$ . We report here spectroscopic and electrochemical data on the existence of  $Ag^-$  in liquid ammonia, a species that had been anticipated earlier.<sup>3c,6</sup>

### Experimental Section

The experimental details for obtaining electrochemical<sup>4–7</sup> and spectroscopic<sup>4a,b</sup> information from liquid ammonia solutions have been reported previously.<sup>6</sup> Rather than attempting to use chemically produced solvated electrons (via the dissolution of alkali metals), we chose to use electrochemically generated solvated electrons in the presence of nonreducible supporting electrolytes; earlier work showed little difference between solvated electrons from these sources.<sup>8</sup> By this strategy we could control the concentration (number) of solvated electrons brought into contact with various silver-containing substrates from which we might expect to produce liquid ammonia solutions containing  $Ag^-$ . The solutions so formed were investigated electrochemically, in situ, as well as spectrophotometrically. The latter measurement involved a three-compartment electrochemical cell that incorporates a detachable optical cuvette with a 1.00 cm path length.<sup>6</sup> The coulometric strategy for depositing solvated electrons permits us to produce a reasonably precise known number of solvated electrons in contact with the substrate for a known time and to remove excess electrons electrolytically; the



**Figure 1.** Absorption spectrum of amide ions and  $Ag^-$  ions in (0.1 M)  $KCF_3SO_3-NH_3$  solution ( $l = 1.00$  cm and  $T = -65$  °C).

**Table 1.** Redox Potentials of Argentide Anion in Various Liquid Ammonia Solutions<sup>a</sup>

$Ag^-$ production method	electrolyte (0.1 M)	$E_{ap}$ (V) ( $\pm 0.02$ ) <sup>b</sup>	$E_{cp}$ (V) ( $\pm 0.02$ ) <sup>b</sup>	$E^\circ$ (V) ( $\pm 0.02$ ) <sup>c</sup>
reducing metallic Ag by $e^-$		-2.25	-2.37	-1.47
		-2.20	-2.35	-1.44
CV scan of $AgCF_3SO_3$ (8.5 mM)	$KSO_3CF_3$	-2.25	-2.35	-1.46
		-2.26	-2.35	-1.46
CV scan of AgI (8.0 mM)		-2.20	-2.30	-1.41
		-2.20	-2.30	-1.41

<sup>a</sup> Scan rate = 100 mV/s, temp =  $-65 \pm 2$  °C. <sup>b</sup>  $E_{cp}$  = cathodic peak and  $E_{ap}$  = anodic peak vs  $Ag/AgNO_3$ . <sup>c</sup> vs SHE at 25 °C.

last-named process could be followed (spectroscopically) by the loss of the blue color of the solvated electrons. A typical spectrum appears in Figure 1.

A three-compartment electrochemical cell<sup>4,7</sup> containing an auxiliary electrode (silver mesh working electrode), a microdisk working electrode (a platinum electrode at which anions could be deposited anodically), and a reference electrode ( $Ag/AgNO_3$ ) was used to produce  $Ag^-$ -containing solutions and to collect conventional current–voltage data on these solutions. All experiments and measurements were conducted at  $-65 \pm 2$  °C. Solutions of argentide ion in 0.1 M potassium triflate show an anodic wave (platinum disk microelectrode) at  $-2.25$  V ( $Ag^- \rightarrow Ag^0$ ) and a cathodic wave at  $-2.35$  V ( $Ag^0 \rightarrow Ag^-$ ). Typical electrochemical data appear in Table 1. The  $E^\circ$  values listed in Table 1 are corrected to the standard hydrogen electrode (SHE) at 25 °C (in liquid ammonia), and the potential of the reference electrode was calibrated against the potential of the solvated electron ( $e^-$ ).<sup>9</sup>

### Results and Discussion

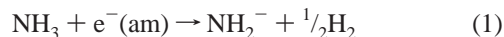
**Spectroscopy.** The spectra of ammonia solutions containing coulometrically generated solvated electrons (at a silver sheet cathode) were determined at  $-65 \pm 2$  °C. The solutions containing solvated electrons were originally dark-blue, turning sky-blue and, finally, yellow after about 15 min. The blue solution contains excess solvated electrons, and the yellow solution contains the decomposition product of solvated electrons ( $NH_2^-$ ) and  $Ag^-$ . The spectra of these solutions as a function of time reinforce the assignment that the lower energy band in the spectrum ( $\sim 30$  nm) is assigned to the  $NH_2^-$  species; this band grows as the blue color disappears. The intensity of the band at 382 nm remains virtually unchanged with time. The

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spectrum of a typical yellow solution appears in the figure. The band at 306 nm is attributed to  $\text{NH}_2^-$ ;<sup>10</sup> the band at 380 nm is attributed to  $\text{Ag}^-$ , which agrees with Peer's prediction<sup>4b</sup> (382 nm) using a charge-transfer model based on the extant  $\text{Au}^-$  data.<sup>4a</sup> The production of  $\text{NH}_2^-$  from solvated electrons,

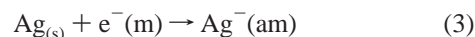


is consistent with the observation<sup>8</sup> that this reaction is catalyzed by metal surfaces. The amide ion detected spectroscopically (Figure 1) could have resulted from the reaction of  $\text{Ag}^-$  with the solvent,

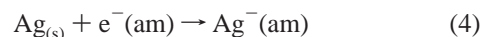


but we feel this is an unlikely source because the spectrum (Figure 1) did not change with time. If eq 2 were the source of the  $\text{NH}_2^-$ , we would expect that the intensity of the band attributed to  $\text{Ag}^-$  would also change with time.

**Electrochemistry.** Argentide ions are produced coulometrically in ammonia solutions of 0.1 M potassium triflate ( $\text{KSO}_3\text{-CF}_3$ ) at a silver wire mesh cathode using potentials (vs  $\text{Ag}/\text{AgNO}_3$ ) of  $-2.8$  V or higher. We assume that the anionic silver species is monatomic, which is consistent with the corresponding chemistry of the gold species, which was shown to be monatomic.<sup>4d</sup> It is unclear at this time whether argentide ions form directly, electrochemically as shown by



or by reaction of solvated electrons with the silver electrode as shown by



The one observation that seems to favor the former process (eq 3) is that clean silver surfaces in contact with metal ammonia solutions rapidly produce  $\text{NH}_2^-$  presumably from the reaction of solvated electrons with the solvent, which is catalyzed by metals.<sup>11</sup> Typical electrochemical data appear in Table 1. The electrochemical events of interest occur very close to the cathodic limit of the system, which corresponds to the dissolution of electrons from the cathode. The formal potential ( $E^\circ$ , Table 1) as established by cyclic voltammetry ( $2.49 \pm 0.02$  vs  $\text{Ag}(\text{AgNO}_3)$ ) is essentially the same value ( $2.40 \pm 0.02$  V) as that established by independent differential pulse voltammetric methods.<sup>6</sup> Solutions of argentide ions deposit elemental silver anodically (at a platinum electrode), the identity of the anodic product being confirmed by X-ray diffraction and chemical methods.

**Acknowledgment.** The generous support of the Robert A. Welch Foundation is gratefully acknowledged.

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