# ELECTROCHEMISTRY IN LIQUID AMMONIA

# PART VI. REDUCTION OF CARBON MONOXIDE

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ABSTRACT

Cyclic voltammograms of CO solutions in liquid $NH_3$ (0.1 $M$ KI, $-50°C$) at various working electrodes (Pt, Ni, C, Hg) show a irreversible wave just before the onset of the generation of solvated electrons ($e_s^-$). The reaction of CO with electrogenerated $e_s^-$ produces the dimeric species $C_2O_2^{2-}$, which precipitates as $K_2C_2O_2$. Current-reversal chronopotentiometry for solvated electrons generated in the presence of CO at various pressures (up to 14 atm) and analyzed by digital simulation techniques indicates that the second-order rate constant for the reaction of $e_s^-$ with CO is $> 10^3 \ M^{-1} \ s^{-1}$ at $-50°C$.

INTRODUCTION

Carbon monoxide promises to be a future chemical feedstock [1], and this fact has stimulated research into the reduction of CO. However, most studies have been aimed at the elucidation of the mechanism of the Fischer–Tropsch reduction of CO with $H_2$. Few studies on the reduction of CO with species other than $H_2$ or hydride sources have appeared, although Joannis [2] reduced CO with K in liquid $NH_3$ almost a century ago. The main product was identified as potassium acetylenediolate (I).
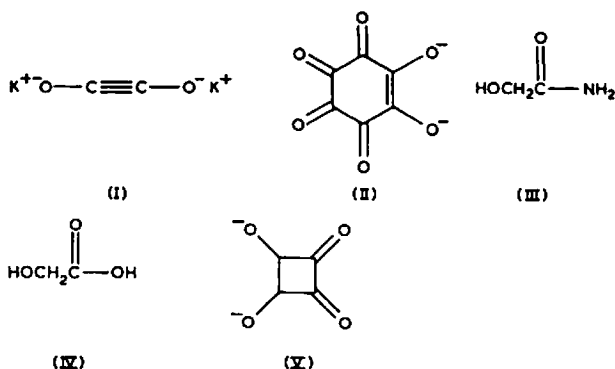
Reaction of Na and CO in liquid $NH_3$ followed by the addition of $NH_4Cl$ or $H_2S$ produces $NH_4^+$ or $Na^+$ rhodizonate (II), glycolic acid amide (III) and glycolic acid (IV) [3]. The synthesis of squarate anion, $C_4O_4^{2-}$ (V) was claimed by Silvestri et al. [4] by an electrolytic reductive cyclotetramerization of CO dissolved under high pressure in various nonaqueous solvents (HMPA, THF and DMF). This study was later extended [5] to consider the influence of the supporting electrolyte, the electrode material, the solvent and the pressure on the yield of squaric acid. The only other work with electrochemical reduction of CO was by Bockmair and Fritz [6], who proposed a mechanism for the reduction of adsorbed CO to $C_4O_4^{2-}$ on Ti, Co and Ni cathodes from DME solutions. We report here a study of the electroreduction of CO in liquid $NH_3$ at pressures of 1 to 14 atm (1 atm $\equiv$ 101325 N m$^{-2}$), and discuss the electrosynthesis of reduced CO products in this medium. The application of liquid $NH_3$ to electrochemical studies and the methodology involved have been discussed in previous papers from this laboratory [7–9].

EXPERIMENTAL

*Chemicals*

The $NH_3$ (Matheson, anhydrous) was purified under vacuum by condensation in a trap containing several small pieces of clean sodium metal. The metal–ammonia
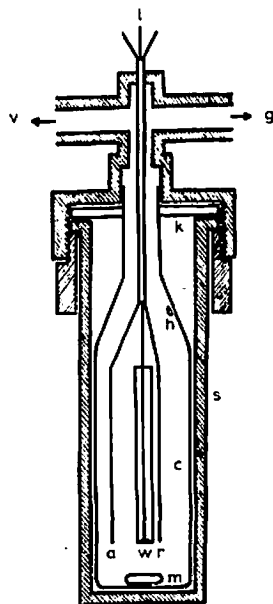


Fig. 1. High pressure cell: (l) electrical connections to electrodes, (v) CO gas inlet and vacuum, (g) to pressure gauge, (k) rubber O-ring, (h) hole to equalize pressure, (s) stainless steel cylinder, (c) glass cell, (a) auxiliary electrode (Pt wire), (w) working electrode (Pt disk), (r) reference electrode (Ag wire), (m) glass coated magnetic stirring bar.

solution was allowed to stand overnight, and then redistilled into an adjacent trap also containing pieces of sodium [7,9,10]. Finally the solvent was distilled directly into the electrochemical cell. The supporting electrolyte KI (Aldrich, 99.999%) was dried in an oven at 110°C for at least 24 h before use. The carbon monoxide (Big Three Industries, CP grade 99.5%) was used as received.

*Cell and electrodes*

The three-compartment cell, the electrodes and their pretreatment have been previously described [7,9]. The one-compartment glass cell used for chronopoten-tiometry experiments was similar to that described in ref. 8 but was without the side ports. The glass cell was contained inside a stainless-steel body for working at pressures higher than 1 atm. The apparatus is diagrammed in Fig. 1. Leads to the electrodes passed through a vacuum feedthrough and the cell was attached to the vacuum line via a section of vacuum tubing. A glass-covered magnetic stirring bar was employed, since Teflon reacts with solvated electrons in liquid $NH_3$.

*Electrochemical measurements*

All electrochemical experiments were performed with a Princeton Applied Research (PAR) Model 173 potentiostat-galvanostat equipped with a PAR Model 179 digital coulometer current-to-voltage converter. A PAR Model 175 universal programmer provided the desired potential or current program. For slow scan rates (up to 500 mV/s) a Model 2000 x–y recorder (Houston Instruments, Austin, TX) was used to record the current–potential ($i–E$) curves. Higher-scan-rate voltammograms and chronopotentiograms were recorded with a Norland Model 3001 digital oscilloscope (Norland Corp.). The cell assembly was thermostatted using a model LC-100 cryostat equipped with a Model TCH-1 temperature controller (FTS Systems, Inc.). The current-reversal chronopotentiometric experiments to study the reaction between solvated electrons and CO consisted of a series of constant-current pulses (0.200 s) with currents ranging from 0.200 to 1.50 mA. Each series was repeated at various pressures of CO (1.4–13.6 atm). Spectrometric data for product analysis were obtained with the following instruments: (1) IR: Beckman, Model IR54 spectrometer (Nujol mull)); (b) NMR: Perkin–Elmer, Model R12A NMR spectrometer ($D_2O$ solvent).

RESULTS

*Cyclic voltammetry (CV)*

The cyclic voltammogram of CO (1 atm, total pressure) at a Pt electrode (0.0107 $cm^2$) in liquid $NH_3$ ($-50°C$, 0.1 $M$ KI or sat. $MeBu_3NI$) shows an irreversible reduction wave just prior to the onset of the generation of solvated electrons (Fig. 2b). The background CV in the absence of CO is shown in Fig. 2a. Similar behavior was observed at a Ni wire and at a frozen hanging Hg drop electrode but not at an
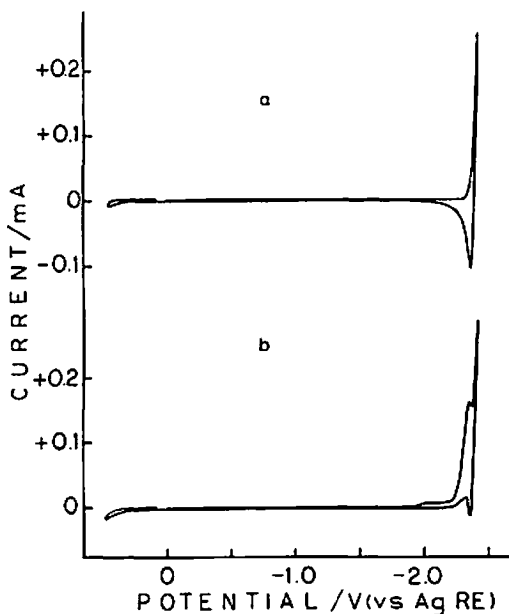
Fig. 2. Cyclic voltammograms at Pt disk electrode (0.011 cm$^2$) in liquid NH$_3$ ($-54°$C, scan rate 100 mV/s, 0.1 $M$ KI) (a) background; (b) with CO at 4 atm.

Au disk electrode *. The peak current ($i_{pc}$) of the wave generally increased with increasing CO pressure (1.4 to 8.2 atm) but also depended upon the time and the rest potential between scans. For example, at $-55°$C after the CO pressure was held at 140 psi (1 psi = 6984 N m$^{-2}$) for 15 min, $i_{pc}$ was ~ 60 $\mu$A. A second scan 10 min later gave $i_{pc}$ = 250 $\mu$A. On repeated scans (without pauses between scans up to a total of ten), $i_{pc}$ decreased nearly to zero. However, if the electrode was held at $-1.8$ V, $i_{pc}$ returned to ~ 60 $\mu$A. These results suggest the formation of a surface film (or another surface phenomenon) involving reduced product which blocks the electrode. Scan reversal immediately following the CO reduction peak and before appreciable generation of solvated electrons produced no anodic current peak for scan rates up to 50 V/s. Attempted bulk reduction at the potential of the CO wave with a Pt gauze electrode did not give any significant currents.

*Preparation of $K_2C_2O_2$ by controlled-potential electrolysis*

When a working electrode of large surface area was employed and the potential was held at values more negative than $-2.3$ V vs. AgRE, cathodic current of up to 6 mA were produced which yielded blue solutions ($-50°$C, 0.1 $M$ KI) of solvated

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* The formation of Au$^-$ at Au electrode [11] could interfere with the observation of the adsorbed CO reduction wave. Alternatively, its absence could be a result of a low adsorption of CO on Au [12].

electrons. The color of these solutions faded with stirring when CO was injected into the cell under 1 atm total pressure and a yellow-white precipitate formed. After passage of 120 C, this precipitate was removed by filtration and washed several times with liquid $NH_3$. An IR spectrum * of a Nujol mull prepared under He indicated the presence of potassium acetylenediolate ($K_2C_2O_2$, I) and potassium glycolate ($HOCH_2CO_2K$) by comparison with an authentic sample prepared by the procedure set out in ref. 2. The latter compound is a known hydrolysis product of pyrophoric $K_2C_2O_2$ [13], apparently resulting from inadvertent partial hydrolysis of the primary product $K_2C_2O_2$ during sample preparation. The formation of $HOCH_2CO_2K$ from complete hydrolysis of the electrosynthesized product by reaction with $H_2O$ was confirmed by $^1H$ NMR.

*Chronopotentiometry (CP)*

To obtain kinetic information about the reaction of solvated electrons with CO, current-reversal chronopotentiometry was employed. The constant-current technique was more convenient than a controlled-potential one, since the initial reductive step was into the background current region where solvated electrons are produced. A current-reversal pulse and its corresponding chronopotentiogram are shown in Fig. 3. During time, $t_f$, solvated electrons are generated at constant current at the surface of the electrode, while the potential stays almost constant ($\sim -2.4$ V). When the reverse pulse is applied, the potential drops a few mV (10 mV) as the solvated electrons which have not diffused too far from the electrode are reoxidized during



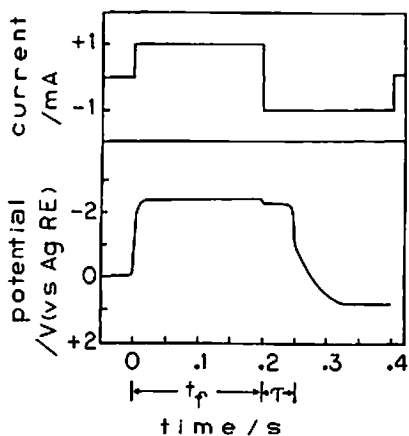Fig. 3. (a) Current-reversal steps at Pt electrode (0.011 cm$^2$) in liquid $NH_3$ (0.1 *M* KI, $-55°C$). (b) The corresponding current-reversal chronopotentiogram for solvated electrons.

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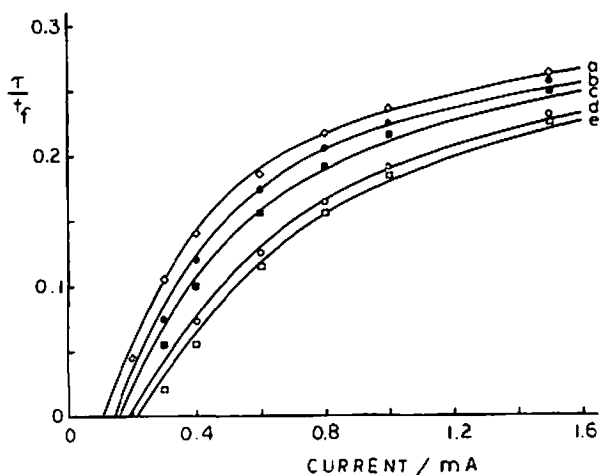* IR data for $K_2C_2O_2$: 1580 s, 1280 m cm$^{-1}$, Nujol mull.

Fig. 4. Experimental (points) and simulated (————) plots of the ratio $\tau/t_f$ vs. current from current-reversal chronopotentiometry of $e_s^-$ (0.10 $M$ KI, $-50°$C) with following reaction with CO at various pressures; ($\Diamond$) no CO; ($\bullet$) 2.7 atm; ($\blacksquare$) 5.6 atm; ($\bigcirc$) 10.9 atm; ($\square$) 13.6 atm. The simulated curves were calculated with $k_5 = 1.0 \times 10^3$ $M^{-1}$ $s^{-1}$ and with the following concentrations of CO: (a) 3.0 m$M$; (b) 6.0 m$M$; (c) 12.0 m$M$ and (d) 15.0 m$M$.

reversal time, $\tau$. The parameter $\tau/t_f$ is $1/3$ when there are no chemical reactions coupled with the generation of solvated electrons which consume a portion of the $e_s^-$ [14]. Experimental plots of $\tau/t_f$ vs. $i$ are shown in Fig. 4 as a function of CO pressure. As expected the ratio $\tau/t_f$ decreased with increasing pressure of CO. However, even in the absence of CO this ratio is smaller than $1/3$ (top curve), showing that there was a substantial background reaction of solvated electrons at these current densities with $t_f = 0.2$ s. The ratio $(\tau/t_f)$ in the absence of CO approached $1/3$, only at currents considerably larger than 1.5 mA ($\sim 4$ mA, $t_f = 0.20$ s). At such high currents the presence of CO did not significantly affect the concentration of solvated electrons, as $\tau/t_f$ did not decrease appreciably even at 200 psi CO pressure. One possible cause of the $\tau/t_f$ values of less than $1/3$ in the blank solutions at low current densities is the irreversible reaction of $e_s^-$ with some adventitious impurity. However, this is unlikely because a digital simulation of this reaction scheme shows that an unreasonably high concentration of impurity ($\sim 10$ m$M$) would be required. This appears unlikely with the highly purified [8,10] NH$_3$ solutions employed. Moreover pregeneration of excess solvated electrons did not affect the blank solution $\tau/t_f$ ratios. For example, in one experiment before starting the chronopotentiometric measurements, a light blue solution of excess electrogenerated $e_s^-$ was allowed to stand for about 10 min (a three-compartment cell was used). Then the excess of solvated electron was eliminated from the solution by controlled potential oxidation. The current-reversal chronopotentiometric measurements ($\tau/t_f$) with this solution, showed no significant differences from those given in the top curve of Fig. 4. Moreover, reversal controlled-potential coulometric experiments [15]

have required equal numbers of coulombs for the cathodic and anodic processes, demonstrating the stability of $e_s^-$ in liquid $NH_3$ for long periods of time (up to 3 h). Therefore, we attribute the background reaction to a reversible reaction between $e_s^-$ and $K^+$ (from the supporting electrolyte) to form ion pairs.

$$K^+ + e_s^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} K^+ e^- \tag{1}$$

Thus, in the time window of coulometric measurements (minutes or hours), most of the electrogenerated $e_s^-$ ($> 95\%$) are reoxidized. On the other hand, each of these current-reversal chronopotentiometric measurements lasted only 0.4 s. If the dissociation rate of $K^+ e^-$ ion pairs is not sufficiently fast to replenish $e_s^-$ during the reverse current pulse, $\tau/t_f$ would be decreased. This effect would be more pronounced at low current densities (low concentration of $e_s^-$; see Fig. 4) and at high concentration of supporting electrolyte. The last effect is apparent in Fig. 5, which shows plots of $\tau/t_f$ vs. current at three concentrations of KI. The full lines of these plots were calculated by digital simulation techniques (see next section). We assume that reaction (2) is initially at equilibrium and that the ratio $k_3/k_4 = K_{eq} = 4.2 \times 10^{-3}$ (as found in investigations of the $e_s^-$ potential as a function of KI concentration [16]).

$$K^+ I^- \underset{K_4}{\overset{k_3}{\rightleftharpoons}} K^+ + I^- \tag{2}$$

The choice of $k_3$, which governs the instantaneous concentration of $K^+$, thus determines $k_4$. Similarly the ratio $k_1/k_2 = 10^3$ was taken from the potentiometric
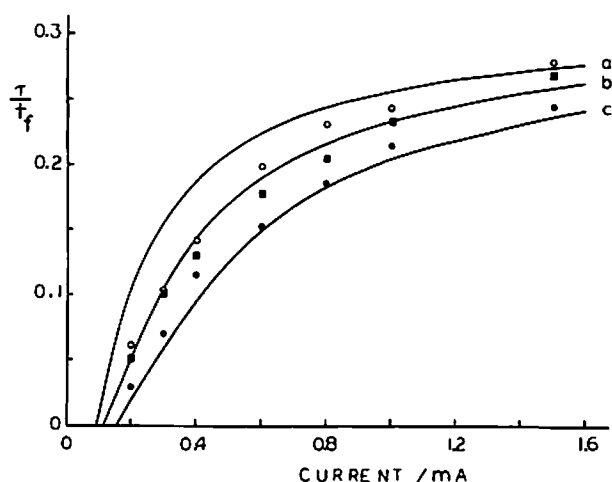


Fig. 5. Experimental (points) and simulated (———) plots of the ratio $\tau/t_f$ vs. current from current-reversal chronopotentiometry of $e_s^-$ with various concentrations of supporting electrolyte, KI. (a) 0.05 $M$; (b) 0.10 $M$ and (c) 0.20 $M$. The simulated curves were calculated with $k_1/k_2 = 10^3$ and $k_3/k_4 = 4.2 \times 10^{-3}$ and with rate constants: $k_2 = 1.0$ s$^{-1}$; $k_3 = 2.1 \times 10^{-3}$ s$^{-1}$.

studies [16], and choice of $k_1$ immediately fixes $k_2$. Thus simulation of this system requires two adjustable parameters. By trial-and-error with variation of these two adjustable rate constants, we found that the best fit we could obtain, shown in Fig. 5, was with the following: $k_1 = 1.0 \times 10^3\ M^{-1}\ s^{-1}$, $k_2 = 1.0\ s^{-1}$; $k_3 = 2.1 \times 10^{-3}\ s^1$, $k_4 = 0.50\ M^{-1}\ s^{-1}$. Although the calculated results fit the general trend fairly well, the simulated points deviate significantly from the experimental values. This is probably because the actual process is more complex, e.g., involving the formation of species like $e^- K^+ e^-$ [15-17] and there is some uncertainty in the actual values of the equilibrium constants. However, since we are interested here in only estimating the rate of the $e_s^-$–CO reaction, we feel that the fit to the background process is probably adequate. Because the concentrations of CO are low, the reaction between CO and $e_s^-$ must be considered as a second-order one so that the pseudo first-order theoretical treatment for chronopotentiometry could not be applied [18,19]. We, therefore, treated this system by digital simulation techniques assuming that $e_s^-$ and CO react irreversibly in a second-order reaction.

*Digital simulation*

Simulation of the current-reversal chronopotentiometric experiment followed published procedures [18b]. However, for the case of the solvated electrons, where there is no initial form in solution (i.e., oxidized $e_s^-$), a slight modification was required. The fractional concentrations, used for the dimensionless calculations, are usually defined as the concentrations divided by the initial bulk concentration ($c_{O*}$) of the electroactive species (O). For solvated electrons generated by a current pulse, $c_{O*}$ is conveniently replaced by the concentration of $e_s^-$ at the electrode surface at the end of the forward pulse. Note that this is essentially the same as using $c_{O*}$ provided that the forward pulse time, $t_f$, is equal to the forward transition time in standard current-reversal chronopotentiometry. With no kinetic complications (i.e., no following reaction), the simulation gave $\tau/t_f$ of 0.32 after 1000 iterations (compared to the theoretical value of 0.33).

Then the effects of first- and second-order reactions involving $e_s^-$, $K^+$ and $I^-$ were added by taking into account reactions (1) and (2). This was accomplished by allowing each reaction to occur independently in each simulation box for the time of the iteration step. The new fractional concentrations at the end of each reaction were calculated from the integrated first-order and second-order laws. The simulation, up to this stage, gave rise to the results shown in Fig. 5 (discussed in the previous section) and those of the top curve in Fig. 4.

Finally, second-order kinetics for reaction (4) was added. The simulated calculations yielded the theoretical curves shown in Fig. 4, along with the experimental results, for various pressures of CO.

$$e_s^- + CO \xrightarrow{k_5} CO^{\cdot -} \tag{4}$$

The Henry's Law constant of CO in liquid $NH_3$ is not available in the literature

for calculating the concentrations of CO at various pressures. CO and $O_2$, however, exhibit very similar solubilities in several solvents (i.e., water, $CCl_4$, ether) [20]. On the other hand, solubility of $O_2$ in $NH_3$ has been determined to be of the order of $10^{-3}$ $M$ at 1 atm $O_2$ pressure between $-40°C$ and $-60°C$ [9,21]. On this basis we assume that the concentration of CO in $NH_3$ is about the same order of magnitude (1 atm CO). Thus, the simulated results shown in Fig. 4 were obtained with the following estimated initial concentrations of CO: 3.0 m$M$, 6.0 m$M$, 12.0 m$M$ and 15 m$M$. The rate constant, $k_5$, which produces the best fit was $1.0 \times 10^3$ $M^{-1}$ $s^{-1}$. The values of these initial concentrations are in the same proportion as the experimental pressures of CO (1:2:4:5). Clearly a change in CO concentration would be reflected by a proportional change in $k_5$. The results of the simulation are consistent with a second-order reaction betweeen $e_s^-$ and CO, at least as a first approximation. The simulated ratios $\tau/t_f$ are much more sensitive to changes in concentration than to changes in the value of the kinetic constants. Large variations in $k_5$ (over one order of magnitude) have little effect on $\tau/t_f$, and the values of $k_5$ needed to model the reaction are at the limit of the modeling range. Therefore, only at lower limit the rate constant can be assigned (i.e., $k_5 > 10^3$ $M^{-1}$ $s^{-1}$).

DISCUSSION

Although CO can be reduced directly at a Pt electrode in liquid $NH_3$ at pressures of up to 14 atm, coating of the electrode does not allow bulk electrolysis. However, electrolysis of CO via reaction with electrogenerated solvated electrons is possible and yields $C_2O_2^{2-}$, the same product obtained in the reaction of CO with alkali metals in liquid $NH_3$.

The formation of $C_2O_2^{2-}$ can occur either by dimerization of $CO^{\cdot-}$ (eqn. 5) or by addition of a second electron to the product formed by reaction of $CO^-$ and CO (eqns. 6 and 7).

$$CO^{\cdot-} + CO^{\cdot-} \rightarrow C_2O_2^{2-} \tag{5}$$

$$CO^{\cdot-} + CO \rightarrow C_2O_2^{\cdot-} \tag{6}$$

$$C_2O_2^{\cdot-} + e_s^- \rightarrow C_2O_2^{2-} \tag{7}$$

The dimerization of $CO^{\cdot-}$ (eqn. 5) is analogous to the dimerization of $CO_2^{\cdot-}$ to give oxalate [22], and probably occurs via an ion pair (e.g., $K^+CO^{\cdot-}$). Because of the short lifetime of the $CO^{\cdot-}$ species, which cannot be detected in reversal experiments, the mechanism of the following reaction cannot be probed. Because no reversal wave for $CO^{\cdot-}$ oxidation can be observed in cyclic voltammetric experiments for scan rates of 50 V/s, the lifetime of this species is below $4 \times 10^{-4}$ s.

We can contrast our results to those of Silvestri and co-workers [4,5] (under substantially different experimental conditions, e.g., a CO pressure of 188 atm) who isolated $C_4O_4^{2-}$ (formally the cyclized product of 2CO and 2$CO^-$) from a variety of solvents including liquid $NH_3$. This difference could be the result of the generally higher CO pressure used, which would favor the reaction of CO with anionic CO

species (e.g., eqn. 6) ultimately yielding $C_4O_4^{2-}$. However, they have also reported [5] that the reaction of CO with Na in THF or with K in DMF at high pressure does not yield $C_4O_4^{2-}$. An alternative explanation is that $C_4O_4^{2-}$ is the product of the surface reduction as proposed by Bockmair and Fritz [6] and that the higher pressure increases the rate of adsorption of CO enough to allow the direct surface reduction to predominate. However, the results here demonstrating relatively ineffective direct reduction of CO in liquid $NH_3$ and blockage of the electrode make this latter route less attractive.

## NOTE ADDED IN PROOF

After acceptance of this paper we became aware of work by Dr. Dirna Cipris reported at the 1980 Meeting of the Electrochemical Society which was also concerned with CO reduction in liquid ammonia.

## ACKNOWLEDGEMENT

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