

## Electrochemistry in Liquid Ammonia. 5. Electroreduction of Oxygen

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The reduction of O<sub>2</sub> in liquid NH<sub>3</sub> at a Pt electrode has been investigated. Chemical and electrochemical measurements show that the first reduction of O<sub>2</sub> is a one-electron process producing O<sub>2</sub><sup>-</sup>, which is a stable species in liquid NH<sub>3</sub> and precipitates as KO<sub>2</sub> in the presence of K<sup>+</sup>. The solubility of O<sub>2</sub> in liquid NH<sub>3</sub> at temperatures between -60 and -40 °C was determined, and from these results, the diffusion coefficient of O<sub>2</sub> in liquid NH<sub>3</sub> was evaluated as 4.4 × 10<sup>-5</sup> cm<sup>2</sup>/s at -55 °C.

## Introduction

The chemistry of the dioxygen species (e.g., O<sub>2</sub>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup>, HO<sub>2</sub><sup>-</sup>) and their roles in various processes such as corrosion, biological oxidation, and energy conversion has been the subject of many studies. Many electrochemical investigations of the reduction of oxygen in aqueous and nonaqueous solutions have also appeared. The electrochemical reduction of O<sub>2</sub> in a number of aprotic solvents such as *N,N*-dimethylformamide (DMF), MeCN, dimethyl sulfoxide (Me<sub>2</sub>SO), and pyridine usually occurs with the formation of the stable superoxide ion, O<sub>2</sub><sup>-</sup>; further reduction leads to production of O<sub>2</sub><sup>2-</sup>, which reacts so rapidly with the solvent, electrolyte, or residual impurities (e.g., H<sub>2</sub>O) that a reverse (anodic) voltammetric wave for O<sub>2</sub><sup>2-</sup> oxidation is not observed.<sup>1-4</sup> However, the electrochemical behavior of O<sub>2</sub> in liquid ammonia has not been the subject of many studies. Until a very recent gas chromatographic determination,<sup>5</sup> even the solubility of O<sub>2</sub> in the liquid NH<sub>3</sub> had not been reported. In an early dc polarographic study of O<sub>2</sub> in NH<sub>3</sub> at a dropping-mercury electrode, rather distorted waves were obtained and no evidence of stepwise reduction of O<sub>2</sub> via superoxide was found.<sup>6</sup>

We describe here the electrochemical behavior of O<sub>2</sub> in liquid NH<sub>3</sub> and discuss the electrochemical synthesis of superoxide salts.<sup>7</sup> Moreover, because of the low impurity levels and acidity of NH<sub>3</sub>, evidence for the intermediacy of the O<sub>2</sub><sup>2-</sup> species could be obtained. Finally, we have determined solubility and diffusion coefficient data for O<sub>2</sub> in this medium.

## Experimental Section

**Chemicals.** The ammonia used was Matheson (Anhydrous Grade, 99.99%); its handling and purification have been described previously.<sup>8,9</sup> Oxygen, obtained from Big Three Industries, Inc., was purified and dried by passing it through a 60-cm column containing (successively) soda lime and magnesium perchlorate to remove carbon dioxide and water, respectively. A mass spectrum of this purified oxygen showed only significant impurity peaks corresponding to nitrogen. Cyclic voltammograms found with this oxygen in liquid ammonia were identical with those obtained when pure oxygen from the thermal decomposition of potassium permanganate was used.<sup>10</sup> KI (Aldrich

Table I. Cyclic Voltammetric Results for the Reduction of O<sub>2</sub>, O<sub>2</sub><sup>-</sup> at a Pt Electrode in Liquid Ammonia at -50 °C<sup>a</sup>

scan rate, V/s	$i_{pc}/v^{1/2}$ , $\mu\text{A s}^{1/2} \text{V}^{-1/2}$	$i_{pa}/i_{pc}^d$	$\Delta E_{pa}^b$ , mV	$10^3 k^c$ , cm/s
0.020	57	1.21	123	2.2
0.050	49	1.30	158	2.1
0.100	42	1.32	197	1.8
0.200	42	1.35	213	2.0
0.500	39	1.33	308	0.9
1.00	37	1.35	360	0.6

<sup>a</sup> Saturated (<0.025 M) MeBu<sub>3</sub>NI. <sup>b</sup>  $E_{pa} - E_{pc}$ . <sup>c</sup> Standard heterogeneous rate constant with the assumption of a quasi-reversible electron-transfer reaction.<sup>16</sup> <sup>d</sup> The base line for determining  $i_{pa}$  was estimated by assuming diffusional decay of the cathodic current beyond the peak potential.

Chemical Co., 99.999%), KBr (MCB, reagent grade), and methyltri-*n*-butylammonium iodide (MeBu<sub>3</sub>NI; Southwestern Analytical Chemical, Inc., polarographic grade) were used as supporting electrolytes and were dried at 110 °C for at least 24 h before each experiment.

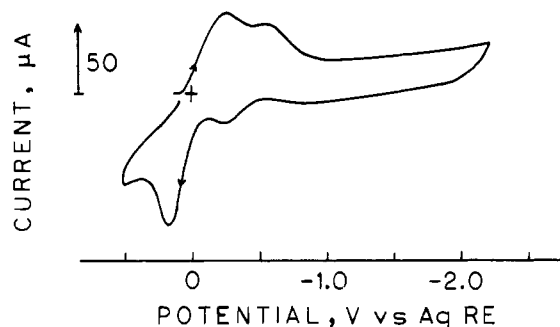
**Cell and Electrodes.** The three-compartment electrochemical cell was similar to the one described previously.<sup>9</sup> The working electrode for cyclic voltammetry and potential step experiments was a platinum disk sealed in soft glass. The Pt was polished with an alumina slurry (0.3- $\mu\text{m}$  particle size) on a felt cloth, rinsed with deionized water and then with ethanol, and finally wiped with an absorbent tissue. In one experiment, a glassy carbon disk sealed in Teflon and pretreated in the same manner as the Pt disk was used. For coulometry, a Pt gauze ~6 cm × 2 cm was used as a working electrode. This was soaked in warm 6 M HNO<sub>3</sub> for ~10 min and then rinsed in the same manner as the disk electrodes. The reference electrode was a silver wire inserted into a glass tube containing supporting electrolyte and was separated from the test solution by a fine-porosity sintered-glass disk (AgRE). This electrode was pretreated by polishing it with an alumina slurry and then soaking it in concentrated HNO<sub>3</sub> for ~10 s until the surface appeared white. Finally, it was rinsed successively with deionized water and ethanol and then wiped with an absorbent tissue. This pretreatment resulted in a stable potential of the reference electrode for at least 6 h. A cylindrical piece of reticulated vitreous carbon (0.6-cm diameter × 2.5 cm) was used as a counterelectrode for bulk electrolysis. Before insertion into the cell, it was allowed to stand in ethanol for 24 h and then dried at 110 °C for 2 h.

All electrochemical experiments were performed with a Princeton Applied Research (PAR) Model 173 potentiostat-galvanostat and a Model 179 digital coulometer-current to voltage converter equipped with positive feedback IR compensation. A PAR Model 175 universal programmer provided the desired potential or current programs. For scan rates up to 200 mV/s, a Houston Instrument Model 2000 X-Y recorder was used. For higher scan rates and other data acquisition, a Norland Model 3001 digital oscilloscope was employed.

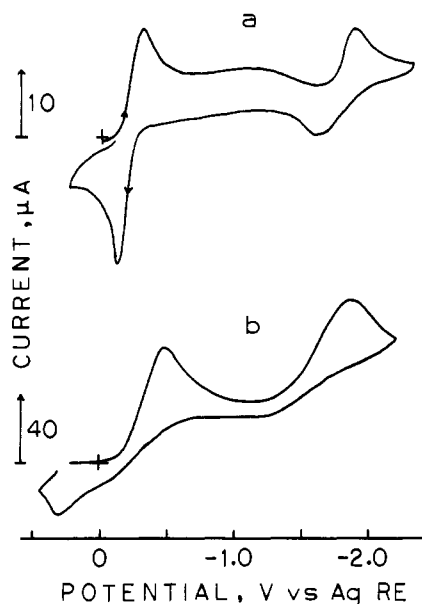
**Preparation of KO<sub>2</sub> and Controlled-Potential Coulometry (CPC).** Potassium superoxide, which is insoluble in liquid NH<sub>3</sub>, was prepared by controlled-potential coulometry at -0.35 V vs. AgRE of a 0.2 M

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**Figure 1.** Cyclic voltammogram of  $O_2$  (1 atm total pressure) in liquid  $NH_3/0.1$  M KI ( $-55$  °C) (scan rate 200 mV/s; Pt disk working electrode ( $0.039$  cm $^2$ )).



**Figure 2.** Cyclic voltammograms of  $O_2$  (1 atm total pressure) in liquid  $NH_3$  saturated with  $MeBu_3NI$  ( $-55$  °C): (a) at Pt disk electrode ( $0.039$  cm $^2$ ), 50 mV/s; (b) at glassy carbon electrode ( $0.071$  cm $^2$ ), 200 mV/s.

KBr/liquid  $NH_3$  solution, with constant bubbling of gaseous  $O_2$  into the solution. After 80 C ( $0.83$  mmol  $KO_2$ ) had passed, the electrolysis was stopped and the solvent was allowed to evaporate. The remaining mixture of KBr and  $KO_2$  was dried in the cell at room temperature under vacuum for 24 h. The potassium superoxide was determined by the decomposition of  $KO_2$  to gaseous  $O_2$  by the action of acetic acid in diethyl phthalate.<sup>11</sup> A 20.0-mL sample of a mixture of these compounds was injected into the cell through the rubber septum via a syringe. After the reaction,  $10.2 \pm 0.2$  mL of gaseous  $O_2$  was recovered ( $25.0$  °C, 751.8 mmHg,  $\sim 0.41$  mmol of  $O_2$ ).

## Results and Discussion

**Cyclic Voltammetry. Tetraalkylammonium Electrolyte.** Cyclic voltammetry (CV) of  $O_2$  in  $NH_3$  yields different voltammograms, which depend on the nature of the supporting electrolyte cation ( $K^+$  or  $MeBu_3N^+$ ; Figures 1 and 2). With  $MeBu_3NI$ , two well-separated reduction waves were observed. The first wave is quite similar to the one obtained in other aprotic solvents<sup>1-4,12,13</sup> and represents a quasi-reversible one-electron reduction to superoxide ion, eq 1. Typical CV data



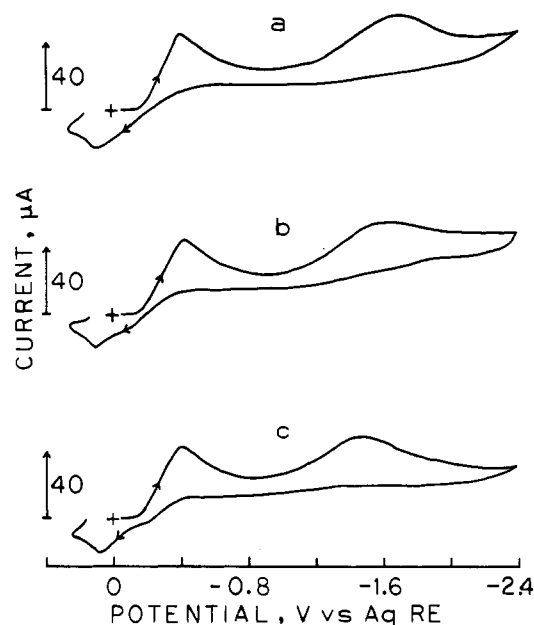
are given in Table I. Controlled-potential coulometric (CPC) reduction of a solution (saturated  $MeBu_3NI$ ) and subsequent reoxidation (reversal coulometry) show that the  $O_2^{\cdot-}$  is stable

**Table II.** Controlled-Potential Coulometric Results of Reduction of  $O_2$  and Reoxidation of  $O_2^{\cdot-}$  in Liquid  $NH_3$  at  $-55$  °C

$Q_f^a$ , C	$Q_b^b$ , C	$ Q_b/Q_f $	$t,^c$ min
0.2 M KBr <sup>d</sup>			
-2.21	2.21	1.00	1
-5.00	4.93	0.986	1
-5.01	4.94	0.986	10
-7.00	6.92	0.989	15
-10.00	9.69	0.969	30
Saturated $MeBu_3NI$			
-1.23	1.23	1.00	2
-2.50	2.41	0.964	15
-5.00	4.69	0.938	60

<sup>a</sup> Number of coulombs for reducing  $O_2$  at  $E = -0.35$  V.

<sup>b</sup> Number of coulombs for oxidizing  $O_2^{\cdot-}$  at  $E = +0.25$  V. <sup>c</sup> Time elapsed between the end of the reduction and the beginning of the oxidation. <sup>d</sup>  $Q_b$  was obtained by reoxidation of a suspended  $KO_2$  precipitate, under constant stirring.



**Figure 3.** Cyclic voltammograms of  $O_2$  (1 atm total pressure) in liquid  $NH_3$  saturated with  $MeBu_3NI$  ( $-52$  °C). The solutions contained  $H_2O$ : (a) 0.28 M; (b) 0.56 M; (c) 1.12 M (glassy carbon electrode; scan rate 100 mV/s).

for at least 1 h (Table II). In  $MeBu_3NI$  a second CV wave at  $\sim -1.8$  V vs. AgRE appears. This second reduction step for  $O_2$  has been attributed to formation of peroxide anion, eq 2, and is irreversible in other aprotic solvents because of the



reaction of  $O_2^{2-}$  with the solvent, electrolyte, or impurities. However, in  $NH_3$  at a Pt electrode this reduction shows some degree of reversibility, probably because  $NH_3$  can be more highly purified than other aprotic solvents, the temperature is low, and  $NH_3$  is a very weak acid. When crystals of  $NH_4Cl$  are dissolved in the solution, the second wave becomes totally irreversible. The nature of the electrode, however, also plays some role in the reversibility of this wave, because at a glassy carbon electrode this wave shows no reversibility (Figure 2b). This can probably be attributed to reaction of the  $O_2^{2-}$  with carbon. There are also differences between Pt and C in the nature of the current decay following the first wave. At a Pt electrode the current at potentials 300 mV beyond  $E_{pc}$  of the first wave does not show diffusion-controlled decay but rather a plateau suggestive of several small waves. These might be caused by some reaction of  $O_2^{\cdot-}$  with the Pt surface or by a

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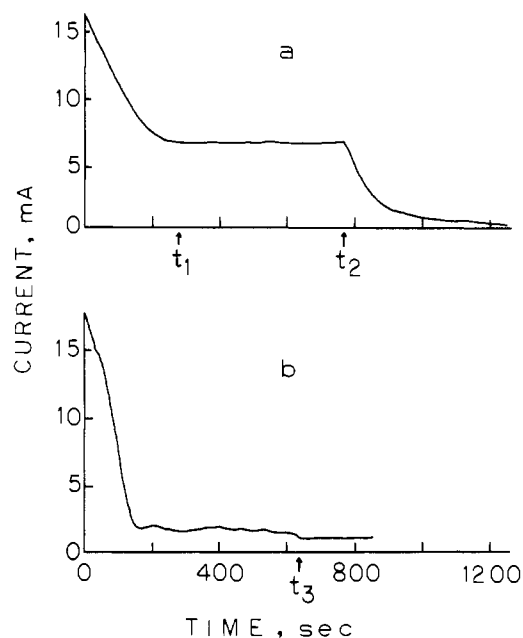
reaction of  $O_2^-$  catalyzed by Pt. Reactions of  $O_2^-$  with Pt also occur in other aprotic solvents.<sup>14</sup> At a glassy carbon electrode the current shows diffusion-controlled decay beyond the first peak potential. Even significant amounts of water do not appreciably affect the nature of the wave for electro-generation of  $O_2^-$ .  $E_{pc}$  and  $i_{pc}$  for the first wave are almost the same, either in water-free solutions or in those containing various concentrations of water up to 1.12 M (Figure 3). However, the second reduction step is strongly affected; the wave becomes irreversible and shifts to more positive potentials with an increase in the water concentration. This suggests rapid reaction of  $O_2^{2-}$  (probably protonation and disproportionation). An attempt to fit the CV results for the first reduction to a simple quasi-reversible one-electron-transfer reaction (Table I)<sup>15</sup> also suggests some reaction of  $O_2^-$  with the Pt surface. Although  $\Delta E_p$ , the separation of anodic and cathodic peak potentials, is a function of the scan rate,  $v$ , and the standard rate constant for the electron transfer,  $k^o$ , evaluated from the variation of  $\Delta E_p$  with  $v$ ,<sup>15</sup> yields a constant value of  $k^o$  for  $v$  between 0.020 and 0.200 V/s of  $2.0 \times 10^{-3}$  cm/s, at larger  $v$  the apparent value of  $k^o$  decreases. Some of this might be attributed to increased, uncompensated  $iR$  drop for the larger currents at higher  $v$ ; the resistance of  $NH_3$  solutions with the more soluble tetraalkylammonium salt supporting electrolyte,  $MeBu_3NI$ , is still rather high, since a saturated solution has a concentration of less than 0.025 M. The ratio  $i_{pa}/i_{pc}$  is constant but slightly larger than 1. This may be caused by the difficulty in correcting for the decaying cathodic current base line in determining  $i_{pa}$  because of the current leveling shown in Figure 2a but might also involve some adsorption or precipitation of the reduced species, as happens to a larger extent with KI or KBr supporting electrolyte (see below). Moreover,  $i_p/v^{1/2}$  shows some decrease with  $v$ , as is characteristic of a quasi-reversible reaction.

**Cyclic Voltammetry. KBr or KI Electrolyte.** When the supporting electrolyte contains  $K^+$ , the CV behavior is very different (Figure 1). The value of  $i_{pa}/i_{pc}$  for the first wave is large, a small peak follows the first wave, and the reduction peak at  $-1.8$  V is absent. This can be attributed to the precipitation of potassium superoxide,  $KO_2$ , which is highly insoluble in  $NH_3$ . This is clearly demonstrated in coulometry experiments, where precipitation during the first reduction step is observed. That this is indeed  $KO_2$  was demonstrated by collection of the precipitate and treatment of it with acetic acid to cause liberation of  $O_2$  via the reaction



as described in the Experimental Section. The experimental number of faradays used in the reduction step and the number of moles of  $O_2$  recovered by reaction 3 satisfied the predicted stoichiometric ratio of 2:1. If part of the current involved in the electrolysis had been used to generate a more highly reduced species, the amount of  $O_2(g)$  recovered would have been smaller because the decomposition with acetic acid occurs only with superoxides.<sup>11</sup>

**Solubility of  $O_2$  in Liquid  $NH_3$ .** The determination of the diffusion coefficient for  $O_2$  in  $NH_3$  and evaluation of the CPC  $n_{app}$  values depend upon a knowledge of the concentration of  $O_2$  in  $NH_3$  at a given temperature and partial pressure of  $O_2$ . The solubility of  $O_2$  in a number of aprotic solvents is available,<sup>16,17</sup> but data for  $NH_3$  under the conditions of these experiments are not available. Therefore, we determined the



**Figure 4.** Current-time curves for controlled-potential coulometry of  $O_2$  in liquid  $NH_3/0.2$  M KBr at  $-40$  °C. The potential was set at  $-0.35$  V vs. AgRE: (a) saturated oxygen solution (1 atm total pressure); (b)  $O_2$  from gaseous phase swept out of the cell with  $N_2$ , before starting the coulometry.

solubility of  $O_2$  at three temperatures by means of CPC of a stirred solution of  $O_2$  in liquid ammonia (0.1 M KBr) initially at equilibrium with  $O_2(g)$  (total pressure 1 atm). The current decreases to a stationary value, as shown by curve a of Figure 4. As soon as the electrochemical reduction started, dissolved  $O_2$  was rapidly consumed by the reaction at the large surface area electrode. Oxygen in the gas phase then dissolved into the liquid. When the steady-state current, at time  $t_1$ , was reached, the current depended upon the rate at which gaseous  $O_2$  dissolved into the liquid  $NH_3$ . The current dropped to near zero very quickly when the oxygen in the gaseous phase in the electrochemical cell was swept out with  $N_2(g)$  (time  $t_2$ ). Since the reduction of  $O_2$  is a one-electron process, the number of coulombs recorded until time  $t_1$  is slightly greater than the number of moles of  $O_2$  in liquid  $NH_3$  at equilibrium. The coulometry was repeated under the same conditions, except that, after the equilibration between the gaseous and liquid phases was attained, the  $O_2$  in the gaseous phase was rapidly swept out of the cell with  $N_2(g)$  and then the electrolysis was immediately started (curve b, Figure 4). At the beginning, the current-time curves are similar for both experiments, indicating that the rate of loss of  $O_2$  from solution into the gas phase does not change significantly the initial concentration of  $O_2$  in solution. In this experiment, however, the current dropped almost to zero (indicated by  $t_3$  in curve b, Figure 4). The  $O_2$  that was being reduced was no longer replaced by dissolution from the gas phase. The number of coulombs recorded up to  $t_3$  should be slightly smaller than the actual number of moles of dissolved  $O_2$  at equilibrium. Therefore the amount of  $O_2$  dissolved in liquid ammonia must correspond to an extent of electrolysis represented by a number between the number of coulombs recorded to  $t_1$  and those registered to  $t_3$ . These two values differ by about 10% as shown in Table III. Recently the determination of the  $O_2$  in the liquid  $NH_3$  at various pressures by gas chromatography has been reported.<sup>5</sup> Although values at temperatures lower than 253 K were not given, the enthalpy of solution estimated from these results allowed us to estimate the solubility between 213 and 233 K, corresponding to the range of our own data. The experimental values determined electrochemically are 25–40% smaller than

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Table III. Controlled-Potential Coulometric Determination of Solubility of O<sub>2</sub> in Liquid NH<sub>3</sub> (0.1 M KBr)

temp, °C	Q <sub>a</sub> , <sup>a</sup> C	Q <sub>b</sub> , <sup>b</sup> C	concn, <sup>c</sup> mol/L	solubility, <sup>d</sup> mol/L
-60	-7.20	-6.20	0.0034	0.0045
-50	-5.20	-4.75	0.0022	0.0038
-40	-2.88	-2.54	0.0012	0.0039

<sup>a</sup> Number of coulombs recorded until current dropped to a constant value, with O<sub>2</sub> in the gas phase. <sup>b</sup> Q without O<sub>2</sub> in the gas phase. <sup>c</sup> 1 atm total pressure (O<sub>2</sub> + NH<sub>3</sub>). <sup>d</sup> 1 atm O<sub>2</sub> partial pressure.

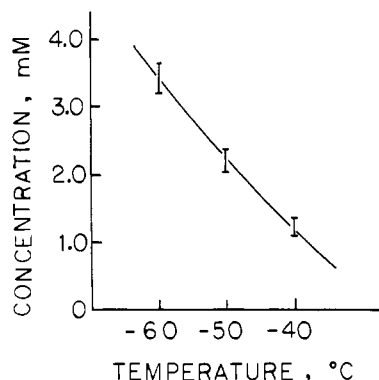


Figure 5. Concentration of O<sub>2</sub> in liquid NH<sub>3</sub> (M) vs. temperature (1 atm total pressure).

those calculated from data given by Ahrens and Heusler.<sup>5</sup> These differences are not too large in light of the uncertainty of the enthalpy of solution and the uncertainties of our experimental determination.

**Diffusion Coefficient of O<sub>2</sub>.** Potential step chronoamperometry was employed to determine the diffusion coefficient, *D*,

for O<sub>2</sub> in NH<sub>3</sub> at -55 °C.<sup>18</sup> A potential step from +0.10 to -0.35 V vs. AgRE for 5 s was employed and the slope of the plot of *i* vs. *t*<sup>-1/2</sup> was determined to be 14.1 ± 0.7 μA s<sup>-1/2</sup>. From the known area of the electrode (0.0145 cm<sup>2</sup>) and the solution concentration determined from the coulometric measurements (2.7 mM) a value of *D* in saturated MeBu<sub>3</sub>NI of 4.4 × 10<sup>-5</sup> cm<sup>2</sup>/s was obtained. This value is generally of the order of that expected on the basis of diffusion coefficients found in other nonaqueous solvents<sup>2,4a,16</sup> when account is taken of the low viscosity of NH<sub>3</sub> (0.317 cP at -50 °C).<sup>19</sup> The diffusion coefficient estimated from the Stokes-Einstein equation<sup>20</sup> with a radius for O<sub>2</sub> of 1.4 Å and *T* = 223 K is 3.6 × 10<sup>-5</sup> cm<sup>2</sup>/s.

### Conclusions

The results presented here suggest that the electroreduction of O<sub>2</sub> in liquid ammonia provides a convenient procedure for preparing stable solutions or precipitates of O<sub>2</sub><sup>•-</sup>. Liquid ammonia may also be a useful solvent for carrying out and studying reactions of O<sub>2</sub><sup>•-</sup>, since NH<sub>3</sub> is a good solvent for both organic and inorganic compounds, provides a very low proton availability, and has a wide low-temperature liquid range. Studies of reactions of O<sub>2</sub><sup>2-</sup> may also be possible since this species shows some stability in this medium.

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**Registry No.** O<sub>2</sub>, 7782-44-7; NH<sub>3</sub>, 7664-41-7; KO<sub>2</sub>, 12030-88-5.

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## Effect of Two Ligands on Ternary Complex Stability

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The formation constants for the complexes of the type [CuAL], where A = 2,2'-bipyridyl, 1,10-phenanthroline, 2-(2-pyridyl)benzimidazole, or 2-(2-pyridyl)imidazoline and L = ethylenediamine, 1,2-diaminopropane, *N*-methylethylenediamine, *N*-ethylethylenediamine, glycine,  $\alpha$ -alanine, or malonate, have been determined in dioxane-water (1:1 v/v) solutions and 0.2 mol dm<sup>-3</sup> NaClO<sub>4</sub> at 30 °C. The formation constant values have been determined by a graphical method and further refined by using a computer program. The value of  $\Delta \log K = \log K_{MAL}^{MA} - \log K_{ML}^M$  is small negative or positive showing astatisticality, and an increase in the value of mixed-ligand complexes is due to a lowering in repulsion between metal *d* electrons and the ligand electrons in the mixed-ligand complex.

### Introduction

In the study of mixed-ligand complexes of the type [MAL], where A is a heteroaromatic N base, it has been observed that the stability constant of the ternary complex is higher than expected from statistical consideration.<sup>1,2</sup> This has been explained to be due to a M → bpy  $\pi$  interaction.<sup>3-6</sup> Sigel has

shown that the complex [MA] shows discrimination toward secondary ligands L with coordinating atoms N-N, N-O<sup>-</sup>, and O<sup>-</sup>-O<sup>-</sup>.<sup>7,8</sup> In cases of ternary complexes in which L coordinates through two nitrogen atoms or one nitrogen and one oxygen atom,  $\Delta \log K = \log K_{MAL}^{MA} - \log K_{ML}^M$  is a small negative quantity. However, when L coordinates through two oxygen atoms,  $\Delta \log K$  in [CuAL] complexes is positive. Sigel extended this observation to explain the greater stability of mixed-ligand complexes in biological systems involving the imidazole ring.<sup>9,10</sup> However, in a recent publication Abbott

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