

## Electrochemical behavior and standard potential of gold(1-) ion in liquid ammonia

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*J. Am. Chem. Soc.*, **1978**, 100 (24), 7768-7770 • DOI: 10.1021/ja00492a077 • Publication Date (Web): 01 May 2002

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**Table I.** Summary of Cyclic Voltammetric Data Obtained for the Oxidation of  $\text{Au}^-$  and Reduction of Gold(I) in Liquid  $\text{NH}_3$  Containing 0.1 M KI at  $-40^\circ\text{C}^a$

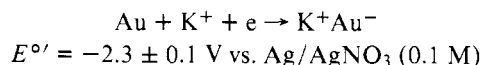
scan rate, $v$ , V/s	$\text{Au}^-$ , $c$ 2.54 mM		$\text{Au(I)}$ , $c$ 6.3 mM	
	$i_{\text{pa}}$ ( $\mu\text{A}$ )	$-E_{\text{pa}}$ (V vs. Ag)	$i_{\text{pc}}$ ( $\mu\text{A}$ )	$-E_{\text{pc}}$ (V vs. Ag)
0.02	13	2.17	29	0.30
0.05	20	2.15	45	0.31
0.10	26	2.14	62	0.32
0.20	36	2.13	85	0.33
0.50 <sup>b</sup>	50	2.11	125	0.35
	$i_{\text{pa}}/v^{1/2}c = 32(\mu\text{A s}^{1/2})$ $L/V^{1/2}$ mmol)		$i_{\text{pc}}/v^{1/2}c = 31(\mu\text{A s}^{1/2})$ $L/V^{1/2}$ mmol)	

<sup>a</sup>  $i_{\text{pa}}$  = anodic peak current,  $i_{\text{pc}}$  = cathodic peak current,  $E_{\text{pa}}$  = anodic peak potential,  $E_{\text{pc}}$  = cathodic peak potential. <sup>b</sup> There is a slight decrease in the current function at the higher scan rates which is primarily due to the difficulty in base-line estimation as well as response time of the recorder.

chemical generation and oxidation of  $\text{Au}^-$  in liquid  $\text{NH}_3$  containing 0.1 M KI as the supporting electrolyte and an estimate of the standard potential of the  $\text{Au}/\text{Au}^-$  couple.

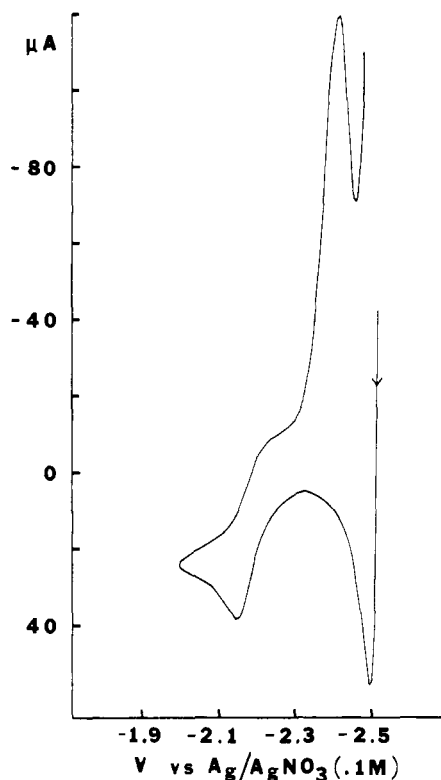
The electrochemical cell and apparatus used in these experiments has been previously described.<sup>2-4</sup> The working electrode consisted of a platinum disk (0.039  $\text{cm}^2$ ) sealed in soft glass. The quasi-reference electrode was a Ag wire isolated from the test solution by a fine-porosity glass frit. This reference electrode has been found to be stable in liquid  $\text{NH}_3$  within  $\pm 15$  mV for a series of experiments in a given solution. We purposely avoided using a standard reference electrode such as  $\text{Ag}/\text{AgNO}_3$  redox couple to minimize any contamination of the test solution by silver(I). The potential of the reference electrode was calibrated against the potential of solvated electron ( $e_s^-$ ),  $-2.69$  V vs.  $\text{Ag}/\text{AgNO}_3$  (0.1 M).<sup>3</sup>

A typical experiment consisted of the coulometric generation of excess solvated electrons followed by the introduction into the solution of a known amount of Au foil. The solution was kept at  $-40^\circ\text{C}$  using dry ice-2-propanol bath and stirred for at least 2 hours or until all of the gold dissolved. A cyclic voltammogram of this solution initiated at a potential where  $e_s^-$  is generated is shown in Figure 1. The first oxidation wave corresponds to the collection of  $e_s^-$  ( $\sim -2.5$  V). The second oxidation wave, at  $-2.15$  V vs. Ag, shows an anodic peak current ( $i_{\text{pa}}$ ) proportional to  $v^{1/2}$  (where  $v$  is the scan rate) and is attributed to oxidation of  $\text{Au}^-$ . On scan reversal a cathodic wave at  $-2.42$  V, caused by reduction of the anodically deposited Au, occurs. This wave is not observed if the anodic scan does not encompass the wave at  $-2.15$  V. The large potential difference between the peak potentials ( $E_{\text{pa}} - E_{\text{pc}}$ ) of the two waves ( $\sim 0.27$  V) suggests some kinetic limitations in the electrode process. The dissolution of gold in liquid  $\text{NH}_3$  caused by the presence of  $e_s^-$  probably leads to the formation of ion pairs (e.g.,  $\text{K}^+\text{Au}^-$ ) (and/or dimers). A recent paper suggested extensive dimerization and ion-pair formation of solvated electrons in liquid  $\text{NH}_3$ .<sup>3</sup> The peak potential,  $E_{\text{pa}}$ , of the anodic wave shifted in the positive direction by  $\sim 40$  mV for each tenfold increase in scan rate. A summary of the cyclic voltammogram results is given in Table I. These results allow an estimation of the formal potential of the  $\text{Au}/\text{Au}^-$  redox couple, estimated as the mean of  $E_{\text{pa}}$  and  $E_{\text{pc}}$ :



i.e.,  $E^\circ = +0.4 \pm 0.1$  V vs. the solvated electron couple. Thus the  $\Delta G^\circ$  for the reaction of solid gold with  $e_s^-$  to produce  $\text{Au}^-$  is estimated to be  $-9$  kcal/mol.

To investigate the role of  $e_s^-$  in stabilizing the Au species



**Figure 1.** Cyclic voltammometric behavior of a 3.63 mM  $\text{Au}^-$  solution in liquid  $\text{NH}_3$  containing 0.1 M KI at  $-40^\circ\text{C}$ . Scan rate 0.1 V/s.

and to confirm the number of electrons consumed per Au atom, controlled potential oxidation following Au dissolution was carried out to remove excess  $e_s^-$ . The remaining solution was clear and exhibited cyclic voltammometric results identical with those obtained in the presence of excess  $e_s^-$ . A controlled potential electrolysis of this solution at a large Pt electrode at  $-2.0$  V resulted in the passage of 0.92 faradays/mol of Au. A bright metallic coating was found on the platinum foil anode. Surface examination of the electrode by ESCA spectroscopy clearly indicated a strong signal for  $\text{Au}(0)$  with accompanying peaks observed at exactly the same binding energies found for gold foil.

Auride ion was also generated from solutions of  $\text{Au(I)}$  (added as gold(I) iodide). A cyclic voltammogram of a  $\text{Au(I)}$  solution in liquid  $\text{NH}_3$  showed an irreversible wave ( $E_{\text{pc}} = -0.33$  V vs. Ag) with an  $i_{\text{pc}}$  varying with  $v^{1/2}$ , corresponding to the reduction of  $\text{Au(I)}$  to  $\text{Au}(0)$  (Table I). When the scan was continued to more negative potentials, the reduction wave for production of  $\text{Au}^-$  and, on reversal, the anodic wave for  $\text{Au}^-$  oxidation, as shown in Figure 1, were observed. Controlled potential electrolysis at  $-0.5$  V resulted in the formation of a layer of finely divided gold on the large Pt foil electrode. When the electrode potential was then stepped to the region for generation of  $e_s^-$ , the cathodic dissolution of Au occurred. A cyclic voltammogram of this solution showed the wave corresponding to the oxidation of  $\text{Au}^-$ .

These experiments show the electrochemical behavior of the first reported transition metal monoanion in liquid  $\text{NH}_3$  and are consistent with the previously reported spectroscopic studies.<sup>1</sup> Moreover they demonstrate that  $\text{Au}^-$  is stable even in the absence of excess  $e_s^-$ . Further investigations of the properties of this anion as well as an extension of these studies to different metals in liquid ammonia and other solvents are in progress.<sup>5</sup>

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## Chemistry of Singlet Oxygen. 29. A Specific Three-Phase "Kautsky Test" for Singlet Oxygen<sup>1</sup>

Sir:

In 1933, Kautsky reported experimental evidence for a "metastable, reactive state of the oxygen molecule" by observing photochemical oxidation of leucomalachite green supported on dry silica gel which was intimately mixed with a separate batch of silica gel on which was adsorbed a sensitizer (tryptaflavin).<sup>2</sup> Reaction was observed only over a rather limited range of pressures, with the maximal effect being found at 0.02 mmHg. This experiment provides strong evidence for a volatile reactive intermediate, but provides little information about its nature. Although this intermediate was probably singlet oxygen,<sup>3</sup> neither the sensitizer nor the acceptor<sup>4</sup> used have been much studied and the chemistry involved is obscure. Similar problems attend an analogous experiment carried out by Rosenberg and Shombert;<sup>5</sup> indeed, this experiment was used to suggest that a *vibrationally* excited oxygen molecule was the reactive intermediate.

Bourdon and Schnuriger carried out a related experiment in which oxidation of methoxynaphthalene, rubrene, or diphenylanthracene was photosensitized by methylene blue or eosin (separated from the acceptor by stearate layers).<sup>6</sup> This experiment is easier to interpret as singlet oxygen chemistry, but no product identification was reported.

Experiments in which a supported sensitizer is irradiated in a stream of O<sub>2</sub> and a downstream acceptor is oxidized have also been carried out, but give miniscule yields of product which often cannot readily be distinguished from that of auto-oxidation.<sup>7</sup>

Because of the central nature of this type of experiment to the singlet oxygen field, we wished to use a system in which both sensitizer and acceptor were well-characterized singlet oxygen reagents. We report the generation and trapping of <sup>1</sup>O<sub>2</sub> in a "three-phase" system<sup>8</sup> using polymer-bound rose bengal<sup>9</sup> as acceptor and a polymer-bound olefin (6-methyl-5-heptenoate, **1a**) as acceptor.<sup>10</sup>

Photooxidation of polymer-bound ester **1a** or the methyl ester **1b** in methanol containing soluble rose bengal produced a mixture of the two allylic products (**2** and **3**, analyzed after reduction to alcohols) in 1:4 ratio.<sup>11</sup> The ratio of products was the same from **1a** and **1b** (but subject to analytical difficul-

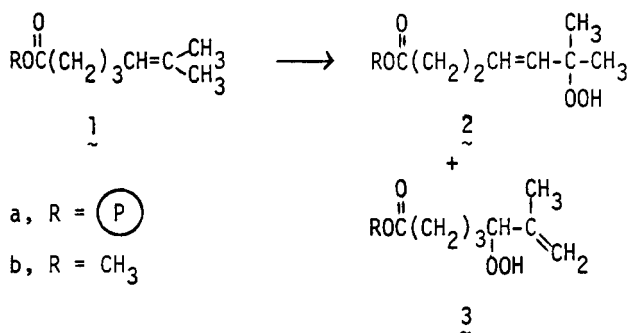


Table I. Photooxidation of  $\text{P}$ -6-Methyl-5-heptenoate (**1a**) Sensitized by  $\text{P}$ -Rose Bengal<sup>a</sup>

conditions	irradiation time, h	yield of <b>2</b> + <b>3</b> , %	$\tau(^1\text{O}_2)$ , s
CCl <sub>4</sub>	9	~0 <sup>b</sup>	$7 \times 10^{-4}$ <sup>c</sup>
air, 760 mmHg	8	~0 <sup>b</sup>	$8.8 \times 10^{-2}$ <sup>d</sup>
O <sub>2</sub> , 25 mmHg	14	1-2	$5.6 \times 10^{-1}$ <sup>d</sup>
O <sub>2</sub> , 10 mmHg	14	5-6	1.4 <sup>d</sup>

<sup>a</sup> References 11 and 12. <sup>b</sup> <<1 % could have been easily detected. <sup>c</sup> Reference 13. <sup>d</sup> Calculated from rate constant in ref 14.

ties<sup>11</sup>). No oxidation of **1a** occurred in the absence of sensitizer.

Mixtures of bound sensitizer and bound acceptor were mixed and irradiated under various conditions. The results are summarized in Table I.<sup>12</sup> Substantial product formation occurred when photolysis was carried out at 25 mm of O<sub>2</sub>, and more at 10 mm; in contrast, no product formation was observed in air or in CCl<sub>4</sub>, a solvent in which <sup>1</sup>O<sub>2</sub> has a comparatively long lifetime. The product ratio was the same as with the soluble photosensitized reaction with **1a** and **1b**.<sup>11</sup>

Although the exact efficiency of the <sup>1</sup>O<sub>2</sub> trapping in this system cannot be calculated from the data, and, although the amount of <sup>1</sup>O<sub>2</sub> formed would not be easy to make reproducible because of the variability of light adsorption associated with the inhomogeneous system, it is clear that singlet oxygen does not have sufficient lifetime to diffuse efficiently from one solid phase to the other through carbon tetrachloride ( $\tau(^1\text{O}_2) = 700 \mu\text{s}$ ) or air ( $8.8 \times 10^{-2}$  s), but that at 25 mm of O<sub>2</sub> (0.56 s) or 10 mm (1.4 s) measurable trapping occurs. Since the mean radius of diffusion of singlet O<sub>2</sub> during its lifetime varies from  $\sim 3 \times 10^{-4}$  cm in CCl<sub>4</sub> to  $\sim 3$  cm at 10 mm of O<sub>2</sub>, and is  $\sim 0.1$  cm in air, this experiment also sets some limits for the use of the "three-phase test" for trapping short-lived species.<sup>8</sup>

We believe the polymer-bound system used here may be of general utility for trapping <sup>1</sup>O<sub>2</sub>, both in gas-phase systems and in liquid media where <sup>1</sup>O<sub>2</sub> is homogeneously generated. It does not appear to be useful in heterogeneous liquid <sup>1</sup>O<sub>2</sub>-generating systems such as the three-phase system because of the short diffusion radii for <sup>1</sup>O<sub>2</sub> in solution.

**Acknowledgment.** We thank Professors H. Reiss and K. D. Bayes for helpful discussions.

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- Resin-bound products were reduced (NaBH<sub>4</sub>) and subjected to ester interchange using NaOMe-dry CH<sub>3</sub>OH. Products were gas chromatographed, and isolated samples characterized by IR, NMR, and mass spectral analysis.