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## Electrochemical Studies on the Reduction of Dioxygen by Hexaammineruthenium(II) at High pH

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Recently Anson *et al.*, introduced a new amperometric mode with disk electrode rotated at constant rate and held at constant potential to investigate the reduction of dioxygen by hexaammineruthenium(II) while they were studying the first example of a preactivation catalytic mechanism at a polymer-coated electrode of three components.<sup>1</sup> The method has been since then advantageously applied for the kinetic studies of redox catalysis.<sup>2,3</sup> We thought that this new electrochemical mode would be useful as one method compensating for or excelling other, *e.g.*, spectrophotometric or magnetic resonance, methods to investigate the kinetics of redox reactions in homogeneous solutions and employed it here to investigate the redox reaction between dioxygen and hexaammineruthenium(II) from pH 1 to pH 12 where spectrophotometric studies were not perfected.

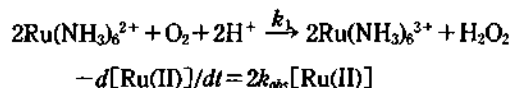
The original spectrophotometric studies of the redox reaction between dioxygen and hexaammineruthenium(II) were initiated by Taube *et al.*,<sup>4</sup> who recognized the fact that Ru(II) among metal ions in the 2+ oxidation state was unique in being the only one forming a series of substitution-inert octahedral complexes,<sup>6</sup> and were extremely carefully and beautifully performed by following the decrease in absorbance at 250 nm where Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> ( $\epsilon_{250}$  540 M<sup>-1</sup>cm<sup>-1</sup>) is oxidized to Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ( $\epsilon_{250}$  300 M<sup>-1</sup>cm<sup>-1</sup>). The results have been believed reliable<sup>1-3</sup> but their studies were limited to the reaction in acidic medium up to pH 6.05. In addition, Taube *et al.*, first investigated the reaction in the acidic medium mainly at low temperatures and reported the bimolecular rate constant 126 M<sup>-1</sup>s<sup>-1</sup> at pH 5.44 and 25.5°C,<sup>4</sup> and later presented a corrected value 63 M<sup>-1</sup>s<sup>-1</sup> at the latter conditions.<sup>5</sup> Thus it was required to have the redox reaction examined at high pH over a decade. In this Note we wish to report the results on kinetic studies of the redox reaction at room temperature up to pH 12 from pH 1 using the amperometric method at rotating disk electrode.

Hexaammineruthenium(III) chloride was prepared by a slight modification of literature procedure.<sup>7-9</sup> Hexaammineruthenium(II) chloride prepared by following the literature method<sup>8</sup> in this laboratory was found to be usually impure

partly because of the oxidation by dioxygen in aqueous solution which is the reaction medium for synthesis and was completely oxidized to be separated as the oxidized form Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> by repeated recrystallization procedure in the air. Electronic absorption spectra were in agreement with the literature and the elemental analysis (Korea Basic Science Center) gave N=26.92% (27.14% calc). Diffusion coefficient of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> measured from the Levich slope of rotating disk voltammograms at several different rotation rates (Pine AFMSRX with RDE4) was 5.4×10<sup>-6</sup> cm<sup>2</sup>/s, which is in good agreement with the value 5.48×10<sup>-6</sup> cm<sup>2</sup>/s reported by Wightman *et al.*<sup>10</sup> Solution was buffered with hydrochloric acid (pH 1-2), phthalate (pH 3-4), acetate (pH 4-5), phosphate (pH 6-8), carbonate (pH 9-11) and sodium hydroxide (pH 12) and contained 0.1 M NaCl. Laboratory distilled water was further purified by passage through Millipore system. All experiments were performed in the electrochemical cell thermostated at 22±1°C.

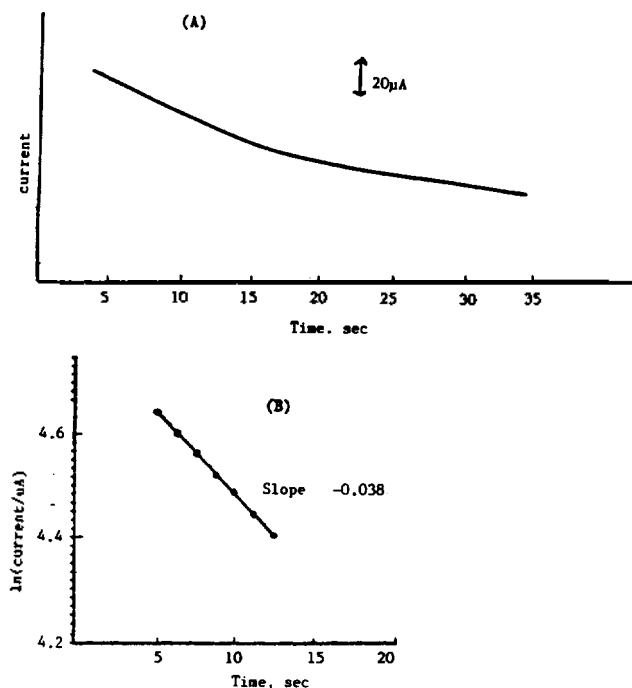
The method introduced by Anson *et al.*,<sup>1</sup> was employed to investigate the reaction. Solution of hexaammineruthenium(II) was prepared by reduction of hexaammineruthenium(III) with zinc amalgam under nitrogen atmosphere. This procedure typically took an hour.<sup>9</sup> The kinetics of the reaction between Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and O<sub>2</sub> was followed under pseudo-first-order conditions by means of a glassy carbon rotating disk electrode after aliquot of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> was syringed into an air-saturated solution, where the electrode was rotated at 3600 rpm. Air from a gas dispersion tube was passed through the solution throughout each run to ensure that the concentration of O<sub>2</sub> remained constant. The electrode potential was maintained at +0.5 V where the oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> to Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> produced a limiting current proportional to the time-dependent concentration of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>. No significant contributions to the current at this potential observed from the solution containing O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> only.

Figure 1 shows a trace of the current for the oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> at a rotating disk electrode in a solution saturated with air and the corresponding plot of ln(current/μA) vs. time. The magnitude of the current produces a continuous measure of the concentration of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and the linear semi-logarithmic plot confirms that the reduction of O<sub>2</sub> by Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> is first-order with respect of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>.<sup>1-6</sup>

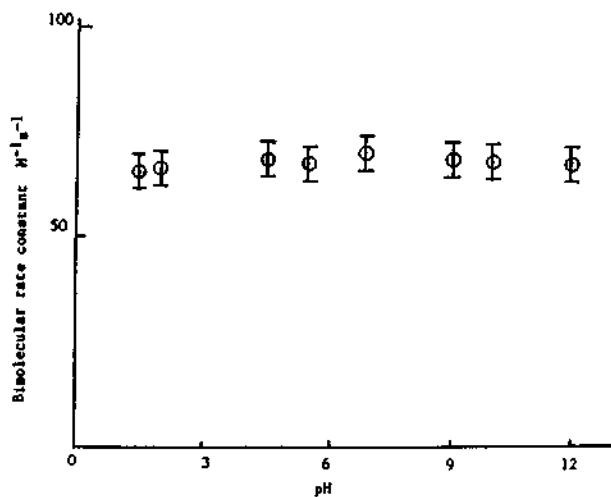


Since the redox reaction is also known to be first-order with respect to O<sub>2</sub>,<sup>4,5</sup> the linear slope 3.8×10<sup>-2</sup> s<sup>-1</sup> gives rise to a second-order rate constant of 68 M<sup>-1</sup>s<sup>-1</sup> under the present experimental conditions ([O<sub>2</sub>]=0.28 mM and pH 5.5). The measured value of the rate constant is in good agreement with the 63 M<sup>-1</sup>s<sup>-1</sup> value by Taube *et al.*,<sup>4,5</sup> indicating that the present amperometric method with disk electrode rotated at the constant rate 3600 rpm and held at the constant potential +0.5 V is a reliable technique to investigate the kinetics of the reaction as was first demonstrated at pH 4.5 by Anson *et al.*<sup>1-3</sup>

The procedure is applied to the reaction in the medium from pH 1 up to pH 12 and the results are shown in Figure 2. It is interesting to observe that the bimolecular rate con-



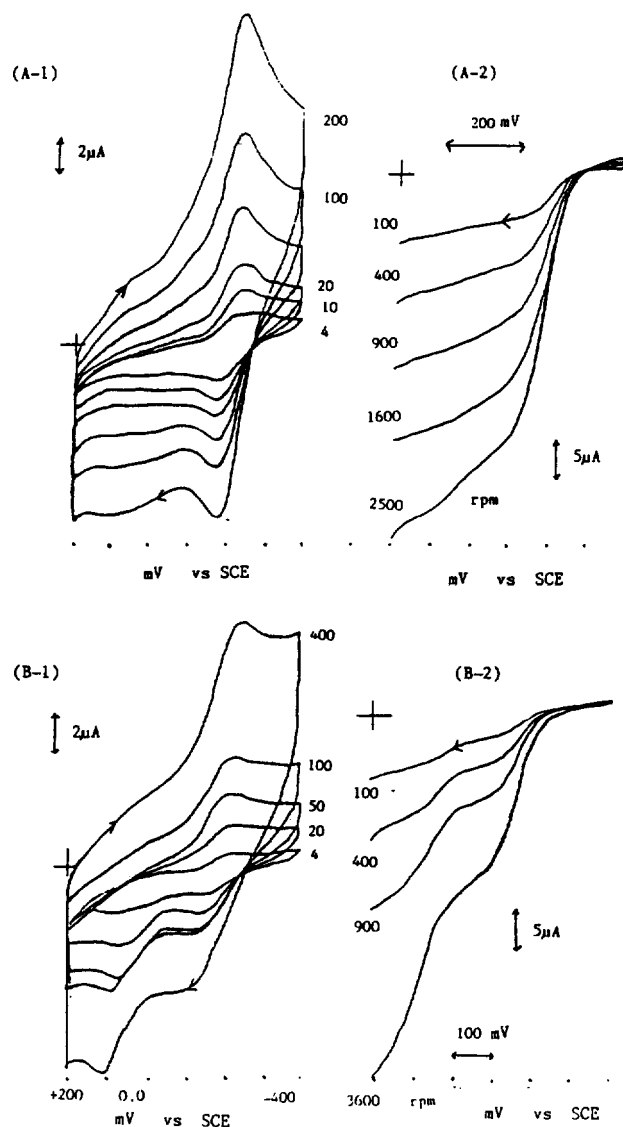
**Figure 1.** (A) Current vs. time plot for the oxidation of  $\text{Ru}(\text{NH}_3)_6^{2+}$  by  $\text{O}_2$  at disk electrode rotated at 3600 rpm and held at +0.5 V (vs. SCE) in air-saturated aqueous solution of pH 5.5. Initial concentration of  $\text{Ru}(\text{NH}_3)_6^{2+}$ : 500  $\mu\text{M}$ . (B) Corresponding plot of  $\ln(\text{current}/\mu\text{A})$  vs. time.



**Figure 2.** Plot of the bimolecular rate constant for reduction of  $\text{O}_2$  by  $\text{Ru}(\text{NH}_3)_6^{2+}$  at different pH values.

stant  $70 \text{ M}^{-1}\text{s}^{-1}$  remains unchanged up to pH 12 as was found at low temperatures from pH 0 to 6.05 by Taube *et al.*<sup>4</sup> Since it is firmly established that reduction of dioxygen by  $\text{Ru}(\text{NH}_3)_6^{2+}$  occurs with the primary coordination sphere intact,<sup>4</sup> the first electron transfer step from one Ru(II) to one  $\text{O}_2$  is believed to be rate determining.

Since attempted kinetic studies of the reaction were often frustrated by irreproducible rate data,<sup>4</sup> in addition to cautious rigorous purification of the complex  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  stability of hexammineruthenium(II) was checked in this study. Figure 3 shows cyclic and rotating disk voltammograms for hexam-



**Figure 3.** Cyclic voltammograms (-1) and rotating disk voltammograms (-2) for aqueous solution of  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3 + \text{Zn}(\text{Hg})$  at pH 10(A) and 12(B) under argon atmosphere. Scan rates and rotation rates are labeled in mV/s and rpm, respectively.

mineruthenium(II) solution prepared by the present experimental procedure (see above). Although solution of  $\text{Ru}(\text{NH}_3)_6^{2+}$  is completely stable below pH 10 and recent electrochemical studies did not reveal any sign of the problem to be caused by lability of  $\text{Ru}(\text{NH}_3)_6^{2+}$  up to pH 10,<sup>11</sup> a significant amount of a new species to be oxidized at +0.1 V is generated at pH 12.0. Also solution of  $\text{Ru}(\text{NH}_3)_6^{2+}$  at pH 12.0 was deep colored and apparently the new species strongly absorbed in the ultraviolet-visible region. The new species is oxidized at rotating disk electrode held at +0.5 V and should contribute to the measured oxidation current but the reaction between the new species and dioxygen apparently did not occur to the extent to cause the current studies to be thwarted at pH 10 and 12. The measured currents as a function of time gave the semi-logarithmic plots of slope  $0.04 \text{ s}^{-1}$ , similar to those obtained at lower pHs, at the present experimental condition. The observed limiting current was assumed to

be proportional to the overall concentration of Ru(II) ( $=[\text{Ru}(\text{NH}_3)_6^{2+}] + [\text{new species}]$ ) in the solution. It is possible, however, that the new species reacts with  $\text{O}_2$  at the same rate as  $\text{Ru}(\text{NH}_3)_6^{2+}$  does. This could give the same results as the one obtained in the present investigation. We did not attempt to rule out this possibility and the characterization of the new species was not pursued either.

In summary, the electrochemical method introduced by Anson *et al.*<sup>1,3</sup> was employed to investigate the reduction of dioxygen by hexaammineruthenium(II) at room temperature up to pH 12 from pH 1. The bimolecular rate constant measured was  $70 \text{ M}^{-1}\text{s}^{-1}$  independent of the solution pH. The amperometric method at rotating disk electrode appears to have potential usefulness for kinetic studies of redox reactions in homogeneous solution.

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### Conversion of Aromatic Nitriles into Aldehydes by Lithium Tris(dialkylamino)aluminum Hydrides

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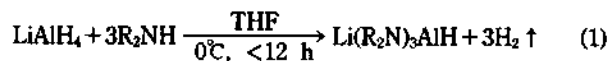
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Easy conversion of nitrile function into aldehyde is impor-

tant in organic synthesis. Several reagents have been applied successfully for such conversion.<sup>1</sup> Especially noteworthy is that potassium 9-*sec*-amyl-9-boratabicyclo[3.3.1]nonane (K 9-*sec*-Am-9-BBNH) nicely achieved the chemoselective reduction of aromatic nitriles to the corresponding aldehydes in the presence of aliphatic nitriles.<sup>2</sup>

Recently, we synthesized various dialkylamino-substituted derivatives of lithium aluminum hydride and have been investigating the reducing properties of the derivatives.<sup>3</sup> In this course we found that lithium tris(dihexamino)aluminum hydride (LTDHA) converts aromatic nitriles into aldehydes in excellent yields. Accordingly, we examined other analogous, lithium tris(diethylamino)aluminum hydride (LTDEA) and lithium tris(dibutylamino)aluminum hydride (LTDBA), in order to probe the structural features of dialkylamino-substituents in the conversion of nitrile function into aldehyde.

The dialkylamino-substituted derivatives are readily prepared by treating  $\text{LiAlH}_4$  with 3 equiv of the corresponding dialkylamines in THF at  $0^\circ\text{C}$  (Eq 1).<sup>4</sup>



LTDEA (R=Et)

LTDBA (R=Bu)

LTDHA (R=Hex)

In general, as shown in Table 1, the yields of aldehydes in the reduction of aromatic nitriles are in order of LTDEA < LTDBA < LTDHA. The alkyl group evidently plays a role in obtaining high yields of aldehydes. Thus, as the length of alkyl-chain increases the yields become higher. LTDEA seems to be too reactive to stop at the aldehyde stage. LTDBA is also good enough to convert aromatic nitriles into aldehydes. However, LTDHA reduces various nitriles, except for nitrobenzotrile, to aldehydes in essentially quantitative yields. The yield from nitrobenzotrile is significantly low (62%), due to the reduction of nitro group itself by this reagent. Dinitriles, such as phthalonitrile and terephthalonitrile, are reduced to aldehydes in yields of 76-97%. LTDHA also converts cyanopyridines into the corresponding aldehydes in essentially quantitative yields. As a result, this reagent appears to be superior to K 9-*sec*-Am-9-BBNH in the conversion of aromatic nitrile function into aldehyde stage.

The reduction of aliphatic nitriles with these reagents appears to be unsuccessful. In addition, sequence for yielding aldehydes is in the reverse order. Examination of the reaction mixture of LTDHA reveals that almost all the starting nitriles is unreacted. This remarkable feature in the rate of reaction suggests the possibility of achieving the chemoselective reduction of aromatic nitriles to aldehydes in the presence of aliphatic nitriles. In fact, LTDHA in a limiting amount reacted only with benzotrile in the equimolar mixture of benzotrile and hexanenitrile at  $0^\circ\text{C}$  to provide benzaldehyde in a yield of 93%, whereas hexanenitrile being intact.

The following procedure for the reduction of benzotrile is described as a representative. An oven-dried 50-ml flask, equipped with side arm and an adaptor connected to a mercury bubbler, was flushed with anhydrous nitrogen and charged with 0.41 g (4 mmol) of benzotrile and 2 ml of THF.