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The Reduction Kinetics and Mechanism of Bis(2,2′-bipyridine)silver(II) Ion by Hydrogen Peroxide

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A kinetic study on the reduction of bis(2,2′-bipyridine)silver(II) ion by hydrogen peroxide in aqueous solution was conducted using the stopped-flow technique. The reaction is sensitive to the pH of the solution and a pH kinetic titration curve was obtained. The rate increases sharply when the pH is lowered from 3.5 to 1.75. In the pH range above 3.5 and below 1.75, the reaction is independent of pH. The second-order rate constant for the pH dependence is found to be $[a(1+b[H^+]^2)/(1+c[H^+]^2)]$. *Possible mechanisms for the pH dependency are considered and discussed.*

Introduction

Silver(II) complexes containing heterocyclic amines such as pyridines, bipyridine and *o*-phenanthroline have been prepared and are found to be powerful oxidizing agents.[1] Magnetic subsceptibility measurements and EPR studies have shown that the d^9 silver(II)–heterocyclic amines have an effective magnetic moment, μ, of 1.7–2.0 Bohr magnetons indicating a spin-only paramagnetism.[2]

That bis(2,2′-bipyridine)silver(II) ion exists in aqueous solution coordinated to four nitrogens was reported by Thorpe and Kochi from their EPR evidence.[2d] Recently, the x-ray crystal structure of bis(2,2′-bipyridine)silver(II) nitrate monohydrate[3] has confirmed that the silver nucleus is coordinated to the four nitrogens of bipyridines. Both lines of evidence point to the square planar preference of the silver(II) complex.

Some silver(II) containing compounds such as silver(II) oxide, silver(II) picolinate and bis(2,2'-bipyridine)silver(II) nitrate have been used directly in the oxidative decarboxylation of organic acids.[4a] Silver(II) picolinate has also been used to oxidize alcohols to ketones and aldehydes.[4b] Relatively few kinetic studies involving the silver(II)–heterocyclic amines as oxidants have been conducted except for the aquo complexes of silver(II) in the oxidation of some hydroxylamines[4c] and some *3d* transition metal ions such as V(IV), Cr(III), Mn(III), Fe(II), Co(II) and Ce(III).[4d] We are reporting herein the study of the reduction of the square planar d^9 complex of bis(2,2′-bipyridine) silver(II) ion by hydrogen peroxide.

Experimental

Preparation of $[Ag^{II}(bipy)_2][NO_3]_2 \cdot H_2O$

Anodic oxidation of a solution containing silver(I) nitrate and 2,2′-bipyridine was carried out according to the procedure described elsewhere.[2d] The dark reddish brown crystals obtained were dried and stored in the dark. *Analysis.* Calc'd: C 43.4, H 3.07, N 15.18. Found: C 41.73, H 3.07, N 15.26.

The visible absorption spectrum and the ε of the bis(2,2′-bipyridine)silver(II) at $\lambda_{max} = 455$ nm and $\lambda_{min} = 400$ nm were measured. The concentration of the bis(2,2′-bipyridine)silver(II) was analyzed using the iodometric method immediately after the spectrum of the cold aqueous solution was recorded. Triplicate measurements gave the $\varepsilon = 2.60 \pm 40$ (455 nm) and $1750 \pm 90 M^{-1} cm^{-1}$ (400 nm). Some values which have been reported previously are 1600[1b] and 1980[1c] $M^{-1} cm^{-1}$ at 455 nm. These values were obtained from the ε or logε *vs.* λ plots in these papers. It was observed that $Ag^{II}(bipy)_2{}^{2+}$ undergoes slow reaction with the solvent and this can account for the small discrepancy between our result and the others.

Materials and Methods of Analysis

The reagents used in the kinetic runs were of high purity grade from Mallinckrodt and J. T. Baker. One of the reagents, H_2O_2 was from Mallinckrodt. Bipyridine was obtained from Aldrich Chemical Co. These chemicals were used with no further purification. The distilled water used to prepare the solutions was passed through two columns of mixed bed of ion exchangers from Illinois Water Treatment Co. and a first distillation was carried out. To determine the hydrogen peroxide concentration, the standard cerium(IV) spectrophotometric titration technique[5] was employed. The bis(2,2′-bipyridine)silver(II) concentration was determined by the iodometry method.[6]

Instrumentation

Visible absorption spectra of solutions were obtained using a Cary Model 14 recording spectrophotometer. The cell compartment was thermally equilibrated to ±0.5° C with water circulated from a Forma constant temperature bath. Measurements of pH were made using a Beckman Research Model pH meter with a glass electrode and a calomel reference electrode at 25° C. The stopped flow apparatus was assembled by replacing the cell compartment of a Beckman DU spectrophotometer with an Aminco–Morrow pneumatic mixer.

Kinetic Measurements

The rate of disappearance of bis(2,2′-bipyridine) silver(II) in reaction with hydrogen peroxide was followed at 455 nm using the modified stopped-flow apparatus described above. The reaction solutions and the stopped-flow mixing chamber were kept at constant temperature with water from Forma constant temperature water bath circulated through the thermostat jackets in the cell compartment. Pseudo-first-order conditions were maintained in all cases of the kinetic studies by using a very large excess of $[H_2O_2]$ over the bis(2,2′-bipyridine)silver(II) ion. The rate data recorded on the Tektronik R 564 B storage scope screen was photographed on a Polaroid 146L negative and enlarged on graph paper. The data were converted to absorbance units and plotted as $\mathrm{Log}(A_\infty - A_t)$ *vs.* time, where A_∞ and A_t are the absorbances at infinity and time t. The observed rate constants were calculated from the slopes of the linear plots.

Results

Reaction Stoichiometry

A solution containing 0.44 mmol of bis(2,2′-bipyridine)silver(II) nitrate was allowed to react completely with excess hydrogen peroxide. The amount of hydrogen peroxide used was 0.215 mmol. This gives a ratio of $\Delta[Ag^{II}(bipy)_2^{2+}]/\Delta[H_2O_2] = 2.05$, which is close to the theoretical consumption ratio of 2.00. Therefore, the stoichiometry equation can be written as

$$2Ag^{II}(bipy)_2^{2+} + H_2O_2 \rightarrow 2Ag^{I}(bipy)_2^{+} + 2H^{+} + O_2 \quad (1)$$

Kinetics of the Reduction

The reaction was studied under the following conditions: $[Ag^{II}(bipy)_2^{2+}] = (4.5\text{–}16) \times 10^{-4} M$, $[H_2O_2] = (2.8\text{–}16.9) \times 10^{-3} M$, pH from 5.4 to 1.68, t = 15.0°–35.0° C, and at constant ionic strength of 0.17*M*. Sodium nitrate solution was used to maintain the ionic strength constant. Under these pseudo-first-order conditions, $35 \le [H_2O_2]_0/[Ag^{II}(bipy)_2^{2+}]_0 \le 125$, the reaction plots were linear over three half-lives. Replicate runs were performed for each kinetic measurement and all the reaction solutions were freshly prepared to achieve reproducibility.

At constant $[H_2O_2]$ and with about a four fold variation in $[Ag^{II}(bipy)_2^{2+}]$ the values of k_{obsd} remain essentially constant indicating a first-order dependence in $[Ag^{II}(bipy)_2^{2+}]$. To test the effect of changing $[H_2O_2]$ at constant $[Ag^{II}(bipy)_2^{2+}]$, the data in Table I (last four entries) are plotted as k_{obsd} *vs.* $[H_2O_2]$ and shown in Figure 1. A good linear plot with zero intercept is obtained giving a slope of 2600 M^{-1} sec^{-1}. This linearity suggests a first-order dependence in $[H_2O_2]$. Therefore the observed reaction follows the rate law expressed below.

$$-d\ln[Ag^{II}(bipy)_2^{2+}]/dt = k_{obs'd} = 2k[H_2O_2] \quad (2)$$

The second order rate constant is k and the coefficient 2 before it is included to correct for the stoichiometry of the reaction. The value of k at 25° C calculated from the slope of the plot in Figure 1 is 1300M^{-1} sec^{-1}.

TABLE I. Effects of $[Ag^{II}(bipy)_2^{2+}]$ and $[H_2O_2]$ on the Reaction at 25.0° C.[a]

$10^5[Ag^{II}(bipy)_2^{2+}]$, *M*	$10^3[H_2O_2]$, *M*	$k_{obs'd}$ sec^{-1}
4.5	5.64	14.1
13.5	5.64	14.0
16.1	5.64	13.6
7.0	2.81	9.2
7.0	5.62	14.9
7.0	11.2	28.9
7.0	16.9	44.0

[a] $\mu = 0.17$ *M* ($NaNO_3$ added to adjust μ), pH ~ 5.4 (natural pH of redistilled–deionized–distilled water), followed at 455 nm.

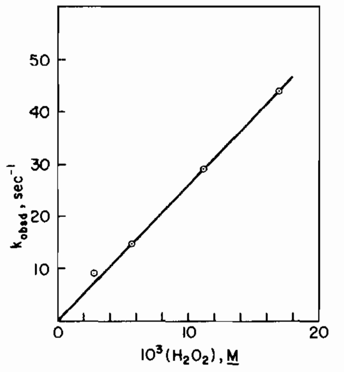

Figure 1. $k_{obs'd}$*vs.*$[H_2O_2]$. $[Ag^{II}(bipy)_2^{2+}] = 7.0 \times 10^{-5} M$, $[H_2O_2] = (2.81\text{–}16.9) \times 10^{-3} M$. $\mu = 0.17M$, pH ~ 5.4 and t = 25.0° C.

Hydrogen Ion Dependence

The effect of hydrogen ion concentration on the rate of reaction was studied under the following conditions: $[H_2O_2] = 9.55 \times 10^{-3} M$, $[Ag^{II}(bipy)_2{}^{2+}] = 1.58 \times 10^{-4} M$, $\mu = 0.17 M$ and the pH varied from 5.40 to 1.68. The second order rate constants, k, at each pH were determined and listed in Table II. A sigmoid dependence of rate on pH can be observed as shown by the plot in Figure 2. The sigmoid dependence requires an elaborate expression for k with a hydrogen ion dependence in the denominator. An expression of the form

$$k = \frac{a(1+b[H^+]^2)}{(1+c[H^+]^2)} \qquad (3)$$

converges rapidly at lower pH values and it fits the data in Table II reasonably well when we use a = 1300, $b = 4.022 \times 10^5$ and $c = 1.216 \times 10^5$ (see $k_{calc'd}$ column in Table II). The calculated plot is shown in Figure 2 along with the experimental points. Other expressions used to fit to the pH kinetic data do not give such a good agreement as equation (3) does.

Temperature Dependence

The effect of temperature on $k_{obs'd}$ was measured carefully with the reaction solutions and cell all thermally equilibrated for at least thirty minutes. The following experimental conditions were used: $[H_2O_2] = 5.73 \times 10^{-3} M$, $[Ag^{II}(bipy)_2{}^{2+}] = 4.5 \times 10^{-5} M$ and pH ~ 5.4. With the temperature covering the range 15° to 35° C. The data are tabulated in Table III. From the log(k/T) *vs.* 1/T plot, the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, are evaluated to be 11.8 kcal/mol and −3.1 cal mol^{-1} deg^{-1}, respectively.

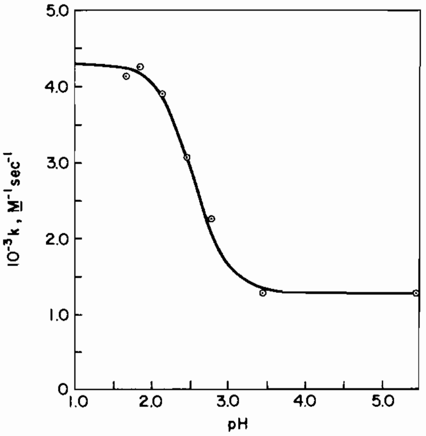

Figure 2. Rate constant/pH profile. Experimental points obtained under the following conditions: $[Ag^{II}(bipy)_2{}^{2+}] = 15.8 \times 10^{-5} M$, $[H_2O_2] = 9.55 \times 10^{-3} M$, $\mu = 0{,}17 M$, pH = 1.68–5.4, t = 25.0° C. The solid curve is calculated by using equation (3). The respective values of the constants a, b, and c are 1300, 4.022×10^5 and 1.216×10^5.

TABLE II. pH Dependence at 25.0° C.[a]

pH	$10^{-3}k_{calc'd}$, M^{-1} sec^{-1} [b]	$10^{-3}k$, M^{-1} sec^{-1}
1.68	4.24	4.13
1.86	4.17	4.27
2.16	3.86	3.90
2.46	3.08	3.08
2.76	2.10	2.27
3.46	1.34	1.29
5.4	1.30	1.30

[a] $[Ag^{II}(bipy)_2{}^{2+}] = 1.58 \times 10^{-4} M$, $[H_2O_2] = 9.55 \times 10^{-3} M$, $\mu = 0.17 M$ and $k = {}^1/_2\,(k_{obs'd})$. [b] The $k_{calc'd}$ values are calculated from equation (3) with the values of a = 1300, $b = 4.022 \times 10^5$ and $c = 1.216 \times 10^5$.

TABLE III. Temperature Dependence.[a]

t, ° C	$10^{-3}k$, M^{-1} sec^{-1}
15.	0.80
20.0	0.98
25.0	1.30
30.0	2.01
35.	2.58

[a] $[Ag^{II}(bipy)_2{}^{2+}] = 4.5 \times 10^{-5} M$, $[H_2O_2] = 5.73 \times 10^{-3} M$, $\mu = 0.17 M$, pH ~ 5.4. The value of k at 25.0° C is calculated from the slope of plot in Figure 1.

Discussion

Mechanism

A reasonable mechanism is proposed for the reduction of bis(2,2'-bipyridine)silver(II) ion by hydrogen peroxide. The reaction mechanism which is consistent with the constant pH rate law and stoichiometry is

$$Ag^{II}(bipy)_2{}^{2+} + H_2O_2 \xrightarrow{k_4} Ag^{I}(bipy)_2{}^{+} + H^+ + O_2H\cdot \qquad (4)$$

$$Ag^{II}(bipy)_2{}^{2+} + O_2H\cdot \xrightarrow{k_5} Ag^{I}(bipy)_2{}^{+} + H^+ + O_2 \qquad (5)$$

The production of $O_2H\cdot$ in the first step is obviously the rate determining step follows by the rapid reaction step (5). We know that equation (4) cannot have a reverse path, k_{-4}, since the inclusion of such a reaction would yield a rate law second-order in $[Ag^{II}(bipy)_2{}^{2+}]$, first-order in $[H_2O_2]$ and a term $(k_{-4}[Ag^{I}(bipy)_2{}^{+}][H^+] + k_5[Ag^{II}(bipy)_2{}^{2+}])^{-1}$. The inverse term suggests an inhibition in rate as $[H^+]$ is increased which is contradictory to the experimental observation that $[H^+]$ enhances the reaction. This strongly argues against the reverse reaction in equation (4). In addition the reaction is independent of the $[Ag^{I}(bipy)_2^{2+}]$ which is attested by the linearities of the semi-log plots.

Hydrogen Ion Effect on the Mechanism

From the sigmoid plot in Figure 2 a midpoint value of 2.6 is obtained. This type of plot is very similar to the familiar kinetic titration plot and suggested perhaps that the rate is influenced by the equilibrium involving protonation of the reacting species. The possibilities of the following equilibria are ruled out based on the kinetic evidence and the reported pK values of these systems. These are the acid dissociation of $Hbipy^+$ ($pK_{HL} = 4.49$) [7], ligand dissociation of $Ag^{I}(bipy)^+$ and $Ag(bipy)_2^+$.[8]

Previously, Taube[9] had studied the reactions of O_3, H_2O_2, H^+ and Br^- in solution and reported a variation in rate constants with increasing $[H^+]$. The assumption of $HO_2 \cdot H^+$ complex was invoked to explain the results and the estimated K_{diss} set at about 10^{-2}. Bielski and Allen[10] applied ESR technique to investigate the kinetics of recombination of $HO_2\cdot$ radicals generated by ceric sulfate and H_2O_2 as a function of pH. They reported a pK value of 1.0 ± 0.4 for the dissociation of the protonated radical $HO_2\cdot$:

$$H_2O_2\cdot^+ \rightleftharpoons HO_2\cdot + H^+$$

Although $HO_2\cdot$ is postulated as the radical undergoing rapid termination reaction with bis(2,2′-bipyridine) silver(II), we again rule out the possibility of its conjugated acid $H_2O_2^+\cdot$ reacting with the oxidant. When this rapid equilibrium is incorporated into the steady-state derivation, we can obtain a derived rate equation similar to equation (2) this is because the rate determining step is equation (4) and not (5). Once the radical $HO_2\cdot$ is generated it could undergo the rapid equilibrium "proton-transfer" process and would not alter the rate law.

A probable mechanistic scheme that conforms to expression (3) the sigmoid kinetic pH dependence equation, is the incorporation of steps (6) and (7) into reaction steps (4) and (5).

$$Ag^{II}(bipy)_2^{2+} + 2H^+ \overset{K_6}{\rightleftharpoons} Ag^{II}(H_2bipy)_2^{4+} \quad (6)$$

$$Ag^{II}(H_2bipy)_2^{4+} + H_2O_2 \xrightarrow{k_7} Ag^{I}(bipy)_2^+ + 3H^+ + O_2H \quad (7)$$

Steady-state approximation yielded the following derived rate law.

$$-d\ln[Ag(bipy)_2^{2+}]/dt = \frac{2k_4\left(1+\frac{K_6k_7}{k_4}[H^+]^2\right)}{(1+K_6[H^+]^2)}[H_2O_2] \quad (8)$$

A correction term, $(1+K_6[H^+]^2)$, appears in the denominator so that the derived rate law can conform to the observed rate law. This is because the apparent rate monitored by following the rate of disappearance of the total $[Ag^{II}(bipy)_2^{2+}]$ is $[Ag(bipy)_2^{2+}](1+K_6[H^+]^2)$ when the equilibrium reaction (6) is involved. Relating the rate constant in equation (8) to (3), we find $a = k_4 = 1300M^{-1}\ sec^{-1}$, $c = K_6 = 1.216 \times 10^5 M^{-2}$, $b = K_6k_7/k_4 = 4.022 \times 10^5 M^{-2}$ and the value for k_7 calculated to be $4300M^{-1}\ sec^{-1}$.

The postulation of the reactive intermediate in equation (6) could imply that the "unwrapping" process occurs by protonation of the terminal nitrogen atom of the two coordinated bidentate ligands leaving only one end of each ligand remaining intact and attached to the central atom. We can visualize that it is impossible to confirm this point. However, equation (6) certainly can be refined to show that one of the bis ligand is probably removed as H_2bipy^{2+}. This is quite possible but equation (8) must then be modified to include $[H_2bipy^{2+}]$ in the rate expression.

Mechanism such as the single protonation of the $Ag(bipy)_2^{2+}$ either by unwrapping process or loss of ligand was also considered. This would lead to a derived rate law with the second order rate constant expression

$$k = \frac{a'(1+b'[H^+])}{(1+c'[H^+])} \quad (9)$$

However, equation (9) does not yield a reasonable fit to the experimental data. This expression simply can not converge rapidly in $[H^+]$ above 10^{-2}. The best values of a′, b′ and c′ used to test the fit of equation (9) are 1300, 800 and 200, respectively. We have attempted to perform the experiment at higher acidity (pH < 1.7) to further test equation (8) and (9) but have encountered experimental difficulty. The nature of the $Ag^{II}(bipy)_2^{2+}$ is not very well characterized in solution and at the moment it can only be suggested that hydrogen ions promote the reaction via some form of unwrapping process or the loss of a ligand.[2d]

Activation Energy Comparison

There are two additional studies on Ag^{II} complexes reduction by H_2O_2. They are the $Ag^{II}NO_3^+$ in $3M$ HNO_3[13] and Ag^{II} aquo complex[14] in 1.5–$3.7M$ $HClO_4$ reactions with H_2O_2. However, in the Ag^{II}–aquo complex reduction by H_2O_2, the authors proposed a first-order inner-sphere electron transfer mechanism and their rate constants and E_a are not suitable for comparison with the present data.[14] It can be seen from Table IV that the "unwrapped" complex reacts approximately three-times faster than $Ag(bipy)_2^{2+}$. The ΔH^+ values for $Ag^{II}(bipy)_2^{2+}$ and $Ag^{II}(NO_3)^+$ are fairly close with the latter having a lower values. This is due to $Ag^{II}(NO_3)^+$ being a more powerful oxidizing agent than the $Ag^{II}(bipy)_2^{2+}$ in accordance with their ε^0 values. Tentatively, the ε^0 for the postulated reactive Ag(II) species can be given a limit $1.46 < \varepsilon^0 < 1.93$ v.

TABLE IV. Activation Parameters Comparison.

Oxidant	ε^0, volt	k,M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, Kcal/mol	$\Delta S^{\ddagger}$, e.u.	Ref.
$Ag^{II}(bipy)_2^{2+}$	1.453[11]	1300 (25° C)	11.9	−3.1	this work
$Ag^{II}(NO_3)^+$	1.927[12]	~5 x 10^6 (23° C)	~10± .8	–	ref. 13
$Ag^{II}(H_2bipy)_2^{4+}$	–	4300 (25° C)	–	–	this work

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