KINETICS OF THE OXIDATION OF CHROMIUM(III) BY BIS(BIPYRIDINE)SILVER(II)

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ABSTRACT

The hydrated silver(II) ion is known to be a particularly strong oxidizing agent, and its four-coordinate complex with 2,2'-bipyridine is moderately strong (standard reduction potentials +1.98 v and about +1.45 v respectively). Oxidation of hydrated chromium(III) by hydrated silver(II) is too rapid to follow by hand mixing, and it has been studied indirectly by others in a catalytic system.

In this study it is found, however, that bis(bipyridine)silver(II) ion oxidizes hydrated chromium(III) with rates in a convenient range. The reactant bis(bipyridine)silver(II) is generated electrolytically, and oxidation of solvent by the silver(II) complex is much slower than the redox reaction of interest. The reaction with chromium(III) is followed spectrophotometrically in nitric acid solution. The rate law and activation parameters for the reaction are reported.

INTRODUCTION

Silver(II) is a strong oxidizing agent. The chemistry of silver(II) was the subject of a classic review by McMillan (1). Standard reduction potentials pertinent to the present investigation are as follows (1-5).

$Ag^{+3} + e^- = Ag^+$	$E^\circ = +1.98$ V
$Ag(bpy_2)^{+2} + e^- = Ag(bpy_2)^+$	$E^\circ = +1.45$ V
$O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$	$E^\circ = +1.23$ V
$Cr_2O_7^{-2} + 14\ H^+ + 6\ e^- = 2\ Cr^{+3} + 7\ H_2O$	$E^\circ = +1.33$ V

Protonation of bpy (2,2'-bipyridine) in acid solution is likely to destroy the $Ag(bpy_2)^+$ species, thereby enhancing somewhat the strength of $Ag(bpy_2)^{+2}$ as an oxidizing agent. Both hydrated Ag^{+2} and the $Ag(bpy_2)^{+2}$ complex are sufficiently strong oxidizing agents to oxidize a range of substrates, including Cr^{+3} and the water solvent itself. However $Ag(bpy_2)^{+2}$ is much milder than Ag^{+2}. $Ag(bpy_2)^{+2}$ has

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been used as an oxidizing agent for nitrous acid, oxalic acid, and vanadium(IV) in titrations (6).

Kinetic studies of reduction of Ag^{+2} and $Ag(bpy_2)^{+2}$ by the water in acidic media have been reported (7-13). The former proceeds by a mechanism involving Ag(III) as a reactive intermediate. This is also the case with one of the reaction paths in the reaction of Ag^{+2} with phosphorous acid, while for the other path the transition state entails the rate-determining breaking of the P-H bond and does not involve silver (14). In a number of other cases, oxidation by the silver(II) aquo ion involves simple bimolecular electron transfer as the rate-determining step. Reducing agents representative of this latter pattern include several transition metal ions (15) and the sulfur oxoanion dithionate (16). Oxidative decarboxylation of aliphatic carboxylic acids (17, 18), oxidation of amino acids (19), and oxidative cleavage of glycols (20) by silver(II) aquo ion also resemble the latter type of mechanistic pattern.

A number of redox reactions of peroxodisulfate are catalyzed by Ag^{+} ion, through a mechanism involving Ag(II) or Ag(III) species as reaction intermediates (21). Cr(III) (22, 23) and glycols (24, 25) are illustrative of numerous substrates oxidized by this catalytic system (21, 26, 27). Such catalytic oxidation, or direct oxidation by AgO, can be used for the analytical determination of Cr(III) as dichromate (28). A kinetic study of silver(I) catalysis in the oxidation of Cr(III) by Co(III) has also been reported, together with a proposed reaction mechanism in which Ag(II) is formed as a reaction intermediate and rapidly oxidizes the Cr(III) substrate to dichromate (29).

The present study explores further the interactions of silver(II) with Cr(III). The kinetics of the oxidation-reduction reaction of $Ag(bpy_2)^{+2}$ with Cr(III) are investigated in acidic aqueous solution.

EXPERIMENTAL SECTION

Reagent grade chemicals were used without further purification. Ion exchange water was further purified by distillation using a glass still. Stock solutions contained 0.9 M HNO_3 and 0.1 M $AgNO_3$, together with a low concentration of either $Cr(NO_3)_3$ or 2,2′-bipyridine. Ionic strength was 1.0 M. The 0.01 M Cr(III) solution in this medium was equilibrated at ambient temperature for a month or longer prior to the kinetic runs from which rate constants are reported here. The $Ag(bpy_3)^{+2}$ ion was generated in the solution by anodic oxidation using platinum electrodes, in a manner similar to the generation of Ag^{+2} in previous work (14, 16). It was observed that the $Ag(bpy_2)^{+2}$ oxidized solvent much more slowly than does Ag^{+2}. Solutions of $Ag(bpy_2)^{+2}$ could be stored and used over a period

of weeks. Slow oxidation of the solvent is observed in the kinetic results reported below.

UV-visible spectrophotometry was carried out using a Beckman DB spectrophotometer and a Varian DMS 100 spectrophotometer. The latter is a microprocessor controlled instrument. After a series of preliminary observations at ambient temperature, a Polyscience circulating thermostat was used with the Varian spectrophotometer for temperature controlled runs leading to rate constants reported here.

UV-visible spectra of $Ag(bpy_2)^{+2}$ (30), $Cr(H_2O)_6^{+3}$ (31), $Cr(NO_3)^{+3}$ (32), Cr(VI) species (3, 33), and a variety of other Cr(III) complexes (34, 35, 36) are well known. Equilibrium and kinetic studies are available for a number of Cr(III) and Cr(VI) systems (32, 37, 38, 39). In particular, the visible band of $Ag(bpy_2)^{+2}$ is reported at 455 nm, with an extinction coefficient of about 1370 M^{-1} cm^{-1} (30).

It was observed in the course of the present work that Cr(III) stock solutions initially seemed to undergo a little slow spectral change. This led to the decision to equilibrate the stock solution for a month or longer prior to the kinetic runs leading to rate constants reported below. Although hydrated chromium(III) nitrate contains predominantly the $Cr(H_2O)_6^{+3}$ ion, there may be small amounts of polynuclear materials present which presumably revert slowly to the hexaquo ion (37).

Initial concentrations in the reaction mixture were in the range of 0-0.0050 M Cr(III) and 0.0001-0.0004 M Ag(II). The reaction was followed at five wavelengths: 365, 405, 440, 450, and 570 nm, with a spectral band width of 1.0 nm and with absorbances printed out for each wavelength at 10 minute intervals on the Varian DMS 100 for an hour or more. $A\infty$ values for the absorbances were recorded after seven half lives or longer.

RESULTS AND DISCUSSION

The reaction studied here may be summarized as

$$3\ Ag(II) + Cr(III) = 3\ Ag(I) + Cr(VI)$$

In preliminary experiments we have confirmed that when the Ag^{+2} aquo ion is used, the reaction is too rapid for hand mixing observations, in agreement with the rate constant inferred by Kirwin et al. (29). Thus the kinetic results presented here are for the system in which Ag(II) is $Ag(bpy_2)^{+2}$, Cr(III) is $Cr(H_2O)_6^{+3}$, and the reaction is carried out in nitric acid media.

In a check of the spectrum of the $Ag(bpy_3)^{+2}$, this complex was prepared by electrolysis at constant current for a measured time. The visible band maximum was observed at 451 nm, with an ex-

tinction coefficient of 1.4 x 10^3 M^{-1} cm^{-1}, in good agreement with the literature (30).

For the concentrations used, Cr(III) was present in substantial excess over Ag(II). From initial conditions to "infinite time," the Ag(II) was used up completely, while the relative change in Cr(III) concentration was small. Thus the Cr(III) concentration was substantially constant during the kinetic run. The absorbance data was analyzed by finding the slope of a plot of $-\ln(A-A\infty)$ vs time through a linear least square analysis (40). The elapsed time from the beginning of a kinetic run to the "infinite time" absorbance values corresponded to seven half lives or longer.

For kinetics without Cr(III) the absorbances of the Ag(I) solution before electrolysis were used as the $A\infty$ values, but agreed with those at the end of the run within 0.004.

The pseudo-first order rate constant is the slope. The plots are quite linear, and have similar slopes for the different wavelengths, indicative of a first order dependence of the rate on the Ag(II) concentration. The wavelengths 440 and 450 nm, at or near the peak of the visible band of the Ag(II) complex, are emphasized in the calculations. The temperature dependence of the rate was evaluated over the range 20 - 32 °C.

The reaction with Ag(II) was monitored successively at three temperatures. The resulting pseudo first order rate constants, as averages over the wavelengths 440 and 450 nm, are given in Table 1 for several Cr(III) concentrations. Correlation coefficients for the individual runs reported are 0.99 or higher. (Parentheses indicate probable error or standard deviation of least squares values of k′ within a run.)

TABLE 1

Pseudo First Order Rate Constants

Cr(III), (10^{-3} M)	k′ (10^{-5} sec^{-1}) 20.0 °C	25.0 °C	32.0 °C
0.000	1.26 (0.03)	1.65 (0.09)	3.65 (0.13)
1.25	1.96 (0.02)	4.22 (0.04)	10.75 (0.10)
2.50	2.84 (0.03)	4.64 (0.02)	11.99 (0.05)
5.00	5.59 (0.04)	11.35 (0.04)	29.3 (0.1)

The pseudo-first order rate constants are analyzed as

$$k' = k_1 + k_2 (Cr(III))$$

The linear least squares results are shown in Table 2 (correlation coefficient 0.988).

TABLE 2

Rate Constants

Temp (°C)	k_1 (10^{-5} s^{-1})	k_2 (10^{-2} M^{-1} s^{-1})
20.0	0.99 (0.19)	0.88 (0.06)
25.0	1.34 (0.61)	1.89 (0.21)
32.0	3.03 (1.51)	4.98 (0.53)

From these data, the activation parameters are determined by plotting $-\ln(k_n/T)$ vs (1/T). Linear least squares results are given in Table 3 (correlation coefficients: 0.984 for k_1, 0.9998 for k_2).

TABLE 3

Activation Parameters

	k_1 path	k_2 path
ΔH^* (KJ mol^{-1})	68 (8)	104.8 (1.2)
ΔH^* (kcal mol^{-1})	16 (2)	25.0 (0.3)
ΔS^* (J mol^{-1} K^{-1})	−109 (28)	74 (4)
ΔS^* (cal mol^{-1} K^{-1})	−26 (7)	18 (1)

CONCLUSIONS

The rate of reaction between Cr(III) and $Ag(bpy_3)^{+2}$ has been found to fall in a convenient range, in contrast to the much more rapid reaction between Cr(III) and the Ag^{+2} aquo ion. The rate law for the former reaction involves two paths, each first order in the Ag(II) complex. One path is independent of Cr(III) and presumably involves oxidation of the solvent. The second and major pathway is first order in Cr(III). The rate constants and activation parameters are reported.

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