

Kinetics and Mechanism of the Reaction between Chromium(II) and 4,4'-Bipyridine in Acidic Aqueous Solution^{1a,b}

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The reaction between chromium(II) and the diprotonated 4,4'-bipyridine ion was studied at 25 °C and ionic strength 1.0 M (LiClO₄-HClO₄). A highly absorbing, blue intermediate is produced, reaches a maximum concentration, and then fades to yield a solution containing chromium(III) and *N,N'*-dihydro-4,4'-bipyridine. The intermediate was identified as the 4,4'-bipyridine radical. The kinetics of the formation and disappearance of the radical were studied as a function of the concentrations of 4,4'-bipyridine, chromium(II), and hydrogen ions. Analysis of the observed kinetics indicates a sequence of two pseudo-first-order steps, the radical intermediate being present in transient equilibrium. The first step is the outer-sphere reduction of diprotonated 4,4'-bipyridine (bpyH₂²⁺) by chromium(II) according to the rate law $k_d[\text{Cr}^{2+}][\text{bpyH}_2^{2+}]$, where $k_d = (2.0 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and $\mu = 1.0 \text{ M}$. The second step involves the disappearance of the radical according to the rate law $a + b[\text{Cr}^{2+}][\text{H}^+]$, with $a = (4.79 \pm 0.62) \times 10^{-2} \text{ s}^{-1}$ and $b = 6.46 \pm 0.39 \text{ M}^{-2} \text{ s}^{-1}$ at 25 °C and $\mu = 1.0 \text{ M}$.

It is well-known² that *N*-alkyl derivatives of 4,4'-bipyridine yield stable free radicals upon one-electron reduction. On this basis, it occurred to us that 4,4'-bipyridine could be a suitable ligand to probe the chemical mechanism³ of electron transfer. According to this mechanism, an electron originally in an orbital of the reducing agent is transferred to an orbital of a ligand in the coordination sphere of the oxidizing agent and, subsequently, from the reduced ligand to the metal center.³ To be sure, a good candidate for the direct demonstration of the chemical mechanism involves a ligand capable of forming a relatively stable radical bound to an oxidizing metal center. Therefore, we set out to synthesize (4,4'-bipyridine)penta-aminocobalt(III) perchlorate and to study its reduction by chromium(II).^{1b,4} However, preliminary studies^{1b} showed that an outer-sphere mechanism was operative and that the 4,4'-bipyridine liberated upon reduction of Co(III) to Co(II) increased the rate of reaction. Therefore, in an attempt to resolve this problem, we carried out a study of the reaction between free 4,4'-bipyridine and chromium(II) and report the results obtained herein.

Experimental Section

Materials. Lithium perchlorate was prepared by neutralization of solutions of lithium carbonate with perchloric acid. The material obtained was recrystallized three times from water. The stock solutions of lithium perchlorate were analyzed gravimetrically.⁵ The chromium(III) perchlorate solution was a gift from Dr. Dennis Gaswick. It had been purified by ion exchange⁶ and was shown to contain negligible amounts of polymeric species. Chromium(II) solutions were obtained by reduction of chromium(III) with zinc amalgam. BDH reagent grade 4,4'-bipyridine was recrystallized three times from water and then dried at 60–65 °C overnight. The argon used to maintain an inert atmosphere was purified by passing it through a column of BTS catalyst. The water used in all the experiments was house-distilled water passed through a Barnstead ion-exchange demineralizer and then distilled in a Corning AG-1b all-glass distilling apparatus. 4,4'-Bipyridine radical was prepared by the method of Dimroth and Frister.⁷ [Co(en)₃]Cl₃ was synthesized by standard methods.⁸

Analyses. Chromium was determined spectrophotometrically as CrO₄²⁻ (molar absorbance $4815 \pm 15 \text{ M}^{-1} \text{ cm}^{-1}$ at 373 nm) after oxidation in alkaline peroxide medium. The total perchlorate con-

centration of the chromium(III) stock solutions was determined by passing an aliquot of the solution through a column of Dowex 50W-X8, 50–100 mesh, and titrating the acid produced. 4,4'-Bipyridine concentrations were estimated spectrophotometrically by using a molar absorbance of $1.59 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 249 nm.

Kinetic Measurements. The increase in absorbance at 381 nm attending the chromium(II)–4,4'-bipyridine reaction was followed by stopped-flow techniques for half-lives shorter than 6 s and by conventional⁹ spectrophotometric techniques for slower reactions.

Stoichiometric Measurements. An excess of chromium(II) was added to 4,4'-bipyridine in 1.0 M perchloric acid. The formation and disappearance of the 4,4'-bipyridine radical was monitored at 381 nm. After the radical had disappeared, a solution of peroxydisulfate was added, whereby the Cr²⁺ was oxidized to a mixture of CrSO₄⁺ and Cr³⁺.¹⁰ The chromium(III) products were separated by ion-exchange techniques, and the yields were measured. From the known¹⁰ stoichiometry of the Cr²⁺–S₂O₈²⁻ reaction, the number of moles of chromium(II) consumed per mole of 4,4'-bipyridine was calculated.

Results

When solutions of chromium(II) and of 4,4'-bipyridine are mixed, a purple-blue species forms rapidly (few seconds), reaches a maximum, and then fades slowly (thousands of seconds) to yield a solution containing chromium(III). When an oxidant is initially present in the 4,4'-bipyridine solution (at a concentration smaller than that of Cr²⁺), the formation of the highly absorbing blue species is inhibited for a period of time which depends on the concentration of the oxidant. Once the oxidant is consumed, the blue species is formed and its behavior is identical with that observed in similar solutions prepared without the oxidant. Dimroth and Frister⁷ reported that when solutions of chromium(II) chloride and 4,4'-bipyridine are mixed at ~0.1 M concentrations, a deep violet solution is formed, from which a green-black solid separates. The substance produced in this manner was found to be at the oxidation level of a quinhydrone, intermediate between 4,4'-bipyridine and *N,N'*-dihydro-4,4'-bipyridine. It was also found that the purple species was readily oxidized to 4,4'-bipyridine.⁷ Volke and Volkova¹¹ studied the electrochemical reduction of 4,4'-bipyridine and interpreted their results as a reversible one-electron reduction of 4,4'-bipyridine at low pH followed by an irreversible two-electron reduction with formation of *N,N'*-dihydro-4,4'-bipyridine. The one-electron-reduction process was found to yield an intensely colored radical cation. We have measured the spectrum of the blue-violet intermediate formed in the chromium(II)–4,4'-bipyridine reaction and found that the spectrum is almost identical with that of *N,N'*-dimethyl-4,4'-bipyridine radical.² Moreover, our stoichiometric

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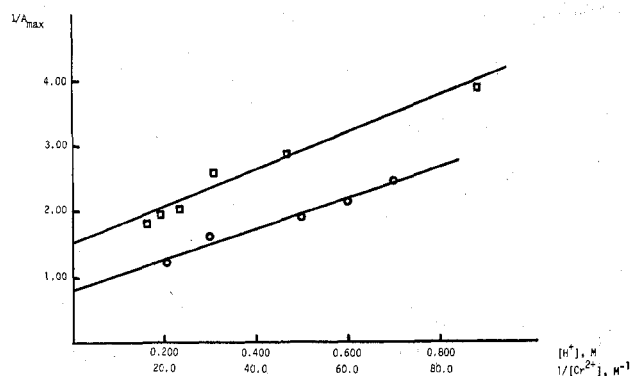
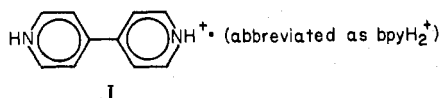
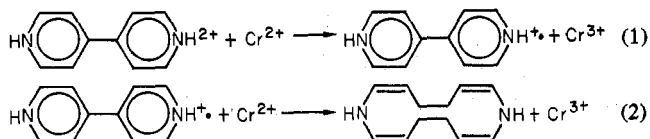


Figure 1. Dependence of maximum absorbance upon hydrogen ion and chromium(II) concentrations ($[\text{bpyH}_2^{2+}] = 9.57 \times 10^{-4} \text{ M}$, 25°C , ionic strength 1.00 M): \square , $[\text{H}^+] = 0.400 \text{ M}$; \circ , $[\text{Cr}^{2+}] = 0.0313 \text{ M}$. Each point is the average of four measurements.

measurements indicate that when the intermediate has disappeared, 2–2.5 mol of Cr^{2+} have been consumed/1 mol of 4,4'-bipyridine. On the basis of all this information, it is apparent that the blue-violet intermediate is the radical cation



I and that the chromium(II)–4,4'-bipyridine reaction proceeds according to the two stages represented by eq 1 and 2.¹²



The appearance and disappearance of the radical $\text{bpyH}_2^{\bullet+}$ were studied as a function of the concentrations of chromium(II), 4,4'-bipyridine and hydrogen ion concentrations. Three pieces of information were obtained: the maximum absorbance at 381 nm, the rate of increase in absorbance, and the rate of decrease in absorbance. At constant hydrogen ion and 4,4'-bipyridine concentrations, the values of the maximum absorbance were found to increase with increasing chromium(II) concentration. A plot of $1/A_{\text{max}}$ vs. $1/[\text{Cr}^{2+}]$, where A_{max} is the maximum absorbance, is linear with a nonzero intercept (see Figure 1). At constant chromium(II) and 4,4'-bipyridine concentrations, the values of the maximum absorbance were found to increase with decreasing acid concentration, a plot of $1/A_{\text{max}}$ vs. $[\text{H}^+]$ being linear with a nonzero intercept (see Figure 1).

Since the two stages of the reaction proceed at markedly different rates, pseudo-first-order rate constants for the increase and decrease in absorbance were obtained from plots of $\ln(A_{\text{max}} - A_t)$ vs. time and of $\ln(A'_t - A_\infty)$ vs. time, respectively. A_t and A'_t represent the absorbances at times shorter and longer, respectively, than the time for maximum absorbance, and A_∞ is the absorbance after the two stages are complete. Both plots exhibited some curvature, and therefore, the rate constants k_{inc} and k_{dec} were obtained from initial slopes. It was found that k_{inc} is independent of 4,4'-bipyridine concentration (0.0100–0.0400 M) at constant hydrogen ion (0.400 M) and chromium(II) (1.00×10^{-3} M) concentrations. k_{inc} is linear in $[\text{H}^+]$ (0.207–0.699 M) at constant 4,4'-bipyridine (1.00×10^{-3} M) and chromium(II) (0.0313 M) concentrations.

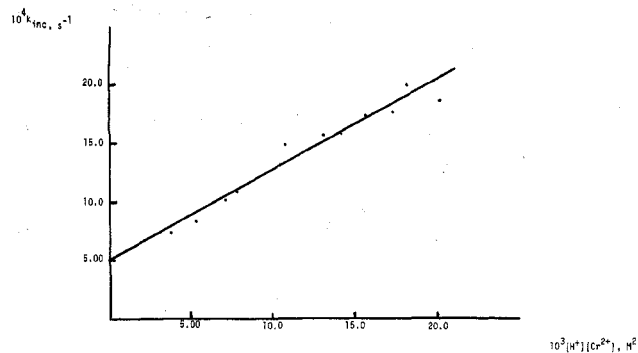


Figure 2. Dependence of k_{inc} upon hydrogen ion and chromium(II) concentrations ($[\text{bpyH}_2^{2+}] = 1.00 \times 10^{-3} \text{ M}$, 25°C , ionic strength 1.00 M). Each point is the average of three to five measurements.

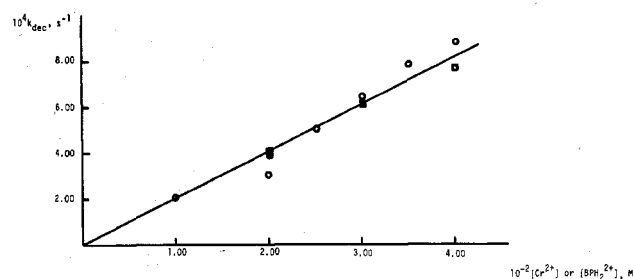


Figure 3. Dependence of k_{dec} upon 4,4'-bipyridinium and chromium(II) concentrations ($[\text{H}^+] = 0.400 \text{ M}$, 25°C , ionic strength 1.00 M): \circ , $[\text{Cr}^{2+}] = 1.00 \times 10^{-3} \text{ M}$; \square , $[\text{bpyH}_2^{2+}] = 1.00 \times 10^{-3} \text{ M}$. Each point is the average of two to three measurements.

At constant 4,4'-bipyridine ($1.00 \times 10^{-3} \text{ M}$) and hydrogen ion (0.400 M) concentrations, k_{inc} increases linearly with chromium(II) (0.0113–0.0605 M). The functional dependence of k_{inc} upon $[\text{H}^+]$ and $[\text{Cr}^{2+}]$ is given by eq 3 (see Figure 2).

$$k_{\text{inc}} = a + b[\text{Cr}^{2+}][\text{H}^+] \quad (3)$$

Least-squares values of a and b are $(4.79 \pm 0.62) \times 10^{-2} \text{ s}^{-1}$ and $6.46 \pm 0.39 \text{ M}^{-2} \text{ s}^{-1}$, respectively, at 25°C and ionic strength 0.10 M.

It was found that at constant chromium(II) (2.00×10^{-3} M) and 4,4'-bipyridine (1.00×10^{-3} M) concentrations, k_{dec} is independent of $[\text{H}^+]$ (0.400–0.600 M). At $[\text{H}^+] = 0.400 \text{ M}$ and with $[\text{4,4'-bipyridine}] = 1.00 \times 10^{-3} \text{ M}$, k_{dec} increases linearly with Cr^{2+} (see Figure 3). At $[\text{H}^+] = 0.400 \text{ M}$ and with $[\text{Cr}^{2+}] = 1.00 \times 10^{-3} \text{ M}$, k_{dec} increases linearly with $[\text{4,4'-bipyridine}]$ (see Figure 3). The plots of k_{dec} vs. $[\text{Cr}^{2+}]$ or $[\text{4,4'-bipyridine}]$ have least-squares slopes of $(2.1 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and $(1.9 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, respectively. Therefore, the rate law for the absorbance decrease is given by eq 4 where $k_d = (2.0 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$.

$$\text{rate} = k_d[\text{Cr}^{2+}][\text{bpyH}_2^{2+}] \quad (4)$$

In order to test one possible mechanistic interpretation of the chromium(II)–4,4'-bipyridine reaction, we carried out a cursory study of the chromium(II) reduction of tris(ethylenediamine)cobalt(III) in the presence of catalytic amounts of 4,4'-bipyridine. The absorbance of $\text{Co}(\text{en})_3^{3+}$ at 460 nm was monitored and was found to decrease according to a zeroth-order rate law. At 25°C , ionic strength 1.00 M, $[\text{H}^+] = 0.400 \text{ M}$, and $[\text{Cr}^{2+}] = 2.00 \times 10^{-3} \text{ M}$, values of the zeroth-order rate constant were 5.3×10^{-7} , 4.9×10^{-8} , and $4.6 \times 10^{-9} \text{ M s}^{-1}$ at $[\text{4,4'-bipyridine}] = 1.00 \times 10^{-3}$, 1.00×10^{-4} , and $1.00 \times 10^{-5} \text{ M}$, respectively. These measurements yield a value of $k_c = (2.5 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ defined by the rate law given by eq 5. After this work was completed,^{1b} the same

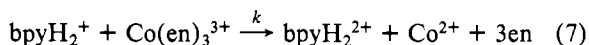
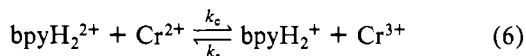
$$\text{rate} = k_c[\text{Cr}^{2+}][\text{bpyH}_2^{2+}] \quad (5)$$

(12) At the acidities used in the present work ($>0.20 \text{ M}$), 4,4'-bipyridine is present as the diprotonated form. The diprotonated radical ion is expected to be a weaker acid than the parent compound.

catalytic reaction was investigated¹³ and the reported value of $k_c = 2.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and 1.0 M HClO_4 is in excellent agreement with our value.

Discussion

The chromium(II) reduction of cobalt(III) complexes catalyzed by various nitrogen heterocycles has been studied extensively by Gould and co-workers.¹³ The proposed mechanism involves the rate-determining formation of a radical followed by the rapid reaction of the radical with the cobalt(III) complex. An entirely analogous mechanism is adopted here as shown in eq 6 and 7 (bpy = 4,4'-bipyridine).



Since as long as there is $\text{Co}(\text{en})_3^{3+}$, the radical bpyH_2^+ does not reach detectable concentrations, the steady-state approximation is applicable and the rate of disappearance of $\text{Co}(\text{en})_3^{3+}$ is given by eq 8. For zeroth-order kinetics to be

$$-\frac{d[\text{Co}(\text{en})_3^{3+}]}{dt} = \frac{k_c k [\text{bpyH}_2^{2+}] [\text{Cr}^{2+}] [\text{Co}(\text{en})_3^{3+}]}{k_r [\text{Cr}^{3+}] + k [\text{Co}(\text{en})_3^{3+}]} \quad (8)$$

obeyed, the condition $k[\text{Co}(\text{en})_3^{3+}] \gg k_r[\text{Cr}^{3+}]$ must be met, and eq 8 reduces to eq 9. The measured catalytic constant

$$-\frac{d[\text{Co}(\text{en})_3^{3+}]}{dt} = k_c [\text{bpyH}_2^{2+}] [\text{Cr}^{2+}] \quad (9)$$

k_c (eq 5) is ascribed to the forward reaction in eq 6, and therefore $k_c = (2.5 \pm 0.2) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$.

With the value of k_c in hand, it is possible to interpret the kinetic observations on the formation and disappearance of bpyH_2^+ . First, it must be noted that the value of k_d in eq 4, $(2.0 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, is equal, within a rather large uncertainty, with the value of k_c . Therefore, we identify k_d with k_c and infer that the observed decrease in absorbance is associated with the reaction that *generates* the radical. Since the radical is formed and then disappears, a reaction sequence involving two steps is indicated, namely, the reaction of Cr^{2+} with 4,4'-bipyridine to produce the radical followed by the consumption of the radical. Regardless of whether the formation is faster than the disappearance or the reverse situation obtains, the intermediate B produced in a series first-order sequence $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ disappears, at sufficiently long times, at a rate characteristic of the slower of the two exponentials.¹⁴ Since the radical bpyH_2^+ disappears at a rate characteristic of its formation, we conclude that the intermediate is formed slowly and disappears rapidly, e.g., we are dealing with the situation known as transient equilibrium in radioactive decay.¹⁴ Additional evidence bearing on this point comes from calcu-

lations of the molar absorbance of the radical when the absorbance reaches a maximum. It can be shown that the maximum concentration of the intermediate in the series first-order sequence $\text{bpyH}_2^{2+} \xrightarrow{k_d} \text{bpyH}_2^+ \xrightarrow{k_{inc}} \text{bpyH}_2$ is given by eq 10. With use of $k_d = 2.0 \times 10^{-2} [\text{Cr}^{2+}]$ and $k_{inc} = 4.8 \times$

$$[\text{bpyH}_2^+]_{\text{max}} = [\text{bpyH}_2^{2+}]_0 k_d / (k_{inc} - k_d) \times [(k_d/k_{inc})^{-k_d/(k_d-k_{inc})} - (k_d/k_{inc})^{-k_{inc}/(k_d-k_{inc})}] \quad (10)$$

$10^{-2} + 6.5 [\text{Cr}^{2+}] [\text{H}^+]$, values of $[\text{bpyH}_2^+]_{\text{max}}$ for the data reported in Figure 1 were calculated. Since bpyH_2^+ is the only absorbing species at 381 nm, the molar absorbance of the intermediate can be calculated from $\epsilon = A_{\text{max}} / [\text{bpyH}_2^+]_{\text{max}} l$, where l is the cell path length. The experiments in Figure 1 yield an average value of $\epsilon = (5.5 \pm 0.9) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The agreement between this value and the value $5.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ reported² for the *N,N'*-dimethyl-4,4'-bipyridine radical provides strong support for the proposed, somewhat unconventional interpretation involving an intermediate in transient equilibrium.^{14,15} Moreover, the dependence of A_{max} upon the concentrations of Cr^{2+} and H^+ (Figure 1) can be predicted on the basis of the proposed mechanism. Since k_{inc} is at least 144 times larger than k_d for all experiments in Figure 1, the ratio $[\text{bpyH}_2^+]_{\text{max}} / [\text{bpyH}_2^{2+}]_0$ is closely approximated by the ratio k_d/k_{inc} . Therefore, $[\text{bpyH}_2^{2+}]_0 / [\text{bpyH}_2^+]_{\text{max}} = 325 [\text{H}^+] + 2.4 / [\text{Cr}^{2+}]$ and $1/A_{\text{max}}$ should be linear in $[\text{H}^+]$ at constant $[\text{Cr}^{2+}]$ and linear in $1/[\text{Cr}^{2+}]$ at constant $[\text{H}^+]$. Both of these dependences are borne out by the experimental findings.

The first step in the proposed sequence, namely, the reaction of Cr^{2+} with bpyH_2^{2+} has a straightforward mechanistic interpretation. Since there are no donor atoms in the diprotonated 4,4'-bipyridine and no inverse H^+ dependence obtains, the reaction must proceed by an outer-sphere mechanism. The observed rate constant of $2.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ compares favorably with the value $4 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ calculated from Marcus' equation $(k_{11} k_{22} K_{12})^{1/2}$ by using $k_{11} = 5.5 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{22} = 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and $K_{12} = 3.2$. k_{11} and k_{22} are the self-exchange rate constants for the $\text{Cr}^{3+/2+}$ and $\text{bpyH}_2^{2+/+}$ couples, respectively,^{16,17} and K_{12} is the equilibrium constant for eq 1.¹⁸

The mechanistic implications of the rate law (eq 3) for the second step of the proposed reaction sequence remain somewhat obscure. The concentration independent term suggests reaction with the solvent, with perchlorate, or, possibly, with oxidizing impurities which may be present despite precautions taken to purify all the reagents and solvents used. The second term in the rate law implies a second one-electron reduction by Cr^{2+} to produce *N,N'*-dihydro-4,4'-bipyridine, but we cannot offer an explanation for the H^+ dependence.

Registry No. Cr^{2+} , 22541-79-3; bpyH_2^{2+} , 46040-54-4; bpyH_2^+ , 35862-62-5; *N,N'*-dihydro-4,4'-bipyridine, 64429-05-6; $\text{Co}(\text{en})_3^{3+}$, 14878-41-2.

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(15) Although the radical concentration never reaches more than 0.7% of the initial 4,4'-bipyridine concentration, the radical is detected readily because of its enormous molar absorbance.

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