The Cr(II) Reduction of $[Co(bpy)_3]^{3+}$. Observation of a Dimeric Cr(III) Reduction Product*

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Abstract

The Cr(II) reduction of $[Co(bpy)_3]^{3+}$ proceeds by a series of steps which are accounted for by a complex and highly unusual mechanism. The chromium(III) product of the reaction is a dimer formulated as $[Cr_2(bpy)(OH)_2(OH_2)_6]^{4+}$. The cobalt products include $[Co(OH_2)_6]^{2+}$ and $[Co(bpy)(OH_2)_4]^{3+}$. Intact free 2,2′-bipyridine and a reduced bipyridine species are also recovered. Four consecutive reactions are observed on the stopped-flow traces. The first one is independent of the [Cr(II)] concentration indicating that reduction has already occurred. The rate constant for this reaction is 46.3 ± 0.2 s^{-1}. The second reaction is auto-catalyzed and has a rate constant of approximately (1.38 ± 0.2) X 10^2 s^{-1} assuming first order behavior. The thrid reaction is dependent on [Cr(II)] and has a rate constant $k_{obs} = k'_3 + k''_3[H^+]$ where $k'_3 = 53 \pm 3$ M^{-1} s^{-1} and $k''_3 = (4.6 \pm 0.2) \times 10^2$ M^{-2} s^{-1}. The fourth reaction is independent of [Cr(II)] and has a rate constant $k_{obs} = k'_4 + k''_4[H^+]$ where $k'_4 = 0.39 \pm 0.02$ s^{-1} and $k''_4 = 2.16 \pm 0.06$ M^{-1} s^{-1}. A mechanism consistent with these observations is proposed.

Introduction

During the past decade, there has been an increasing interest in the chemistry, photochemistry and photophysics of d^6 coordination complexes containing the ligand 2,2′-bipyridine (bpy) and its derivatives [1–6]. The most thoroughly studied of these species is $[Ru(bpy)_3]^{2+}$ because of its ability to serve as a photosensitizer in the decomposition of water by visible light [1]. Indeed, the knowledge gained from studies on this class of compounds has enormously contributed to the theoretical understanding of excited-state behavior of transition metal species. In the present work, we undertook to investigate the thermal reactions of metal–bipyridine complexes, especially their redox reactions. Since we anticipated that the thermal redox chemistry of the known photochemically active complexes might be complicated by light-catalyzed processes, we began our studies by examining the Cr(II) reduction of $[Co(bpy)_3]^{3+}$, an expected fast classical outer-sphere reaction.

The vanadium(II) reduction of $[Co(bpy)_3]^{3+}$ had been reported by Davis *et al.* in 1972 [7]. They concluded that the one-ended dissociation of 2,2′-bipyridine from Co(III) was slow and the reaction was clearly of the outer-sphere type. The final product of the reduction by V(II) was described as high-spin $[Co(bpy)_3]^{2+}$ having the electronic configuration $t_{2g}{}^5e_g{}^2$ which dissociates readily into $[Co(bpy)_2(OH_2)_2]^{2+}$ and free 2,2′-bipyridine.

We have previously reported the complex behavior that arises during the Cr(II) reduction of pentane-2,4-dionatobis(2,2′-bipyridine)cobalt(III) [8, 9]. We now describe an even more complicated series of reactions that arise after the reduction of $[Co(bpy)_3]^{3+}$ by Cr(II). Since the oxidant apparently does not have any lone pairs of electrons available for coordination to the incoming reductant, one would naturally anticipate that an outer-sphere process would occur. Even if some free 2,2′-bipyridine became available after the reaction began and became coordinated to Cr(II) to give a new reductant, $[Cr(OH_2)_4(bpy)]^{2+}$, an outer-sphere process is still expected. This expectation was not realized [10] so we examined this series of intriguing and highly unusual reactions in considerable detail.

Experimental

Reagents

Solutions for kinetic studies were prepared in water which was deionized and distilled using a Barnstead Glass Still (Sybron/Barnstead Ltd.) and then re-distilled from alkaline permanganate in an all-glass apparatus.

Chromium(II) perchlorate solutions were prepared by reducting chromium(III) perchlorate (G. Frederick

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Smith Chemical Co.) with zinc–mercury amalgam in aqueous perchloric acid solution. The chromium(II) concentration of the solution was determined every two or three days as described earlier [11]. All solutions were stored and handled using standard syringe techniques under an argon atmosphere.

Purification of Tris(2,2′-bipyridine)cobalt(III) Perchlorate Hydrate, $[Co(bpy)_3](ClO_4)_3 \cdot 2.5H_2O$

The complex was prepared by the method of Burstall and Nyholm [12] and was purified on an ion-exchange column. The yellow crystals of $[Co(bpy)_3](ClO_4)_3$ were dissolved in water and the resulting solution was applied on a Bio-Rex 70 cation exchanger (mesh size 100–200) in the sodium ion form (Bio-Rad Laboratories). The yellow band was physically removed from the column and the complex was removed from the resin by the application of a saturated aqueous sodium chloride solution. A saturated aqueous solution of sodium perchlorate was then added to cause precipitation. The crystals were washed with cold water, then ether and were dried in the air. The compound was twice re-crystallized from hot water. Each time, it was precipitated by adding a small amount of sodium perchlorate, filtered and air-dried. The infrared spectrum showed evidence for water in the sample. *Anal.* Calc. for $[Co(C_{10}H_8N_2)_3]\ (ClO_4)_3 \cdot 2.5H_2O$: C, 41.3; H, 3.33; N, 9.65. Found: C, 41.2; H, 3.14; N, 9.88%.

Physical Measurements

The proton magnetic resonance spectra were obtained on a Varian T60 instrument. The ^{13}C spectra were run on a Varian CFT-20 spectrometer. All visible and ultraviolet spectra were measured on a Coleman Recording Spectrophotometer, Hitachi Model EPS-3T or a Perkin-Elmer Model 330 Spectrophotometer.

Kinetic Measurements

The kinetic runs were performed on the Hitachi Model EPS-3T or on a Dionex D-110 stopped-flow apparatus using the temperature controls described previously [13]. All reactions were carried out with greater than tenfold excess of reductant.

Product Analyses

The product analyses were performed at ambient temperature by reacting $[Co(bpy)_3]^{3+}$ with Cr(II) in approximately 1:1 and 1:2 ratios in 0.1 M $HClO_4$ for 5 min. Another series of analyses were performed under 1:1 conditions but in a low acid environment, 0.01 M. After the reaction was complete, the solution was diluted to 200–300 ml with distilled water and a stream of air was bubbled through it for 10–20 min to ensure the complete oxidation of any remaining excess Cr(II). The mixture was then ion-exchanged on Sephadex SP-C25-120 strongly acidic cation exchange resin. Increasingly concentrated solutions containing NaCl and $HClO_4$ from 0.05 M NaCl in 0.004 M $HClO_4$ up to a maximum of 0.40 M NaCl in 0.004 M $HClO_4$ were used to elute the products.

The complex $[Co(byp)_3]^{3+}$ is sensitive to light so all experiments involving this species were performed in a darkened room. The visible spectrum of the complex remained unchanged for two days under these conditions.

All chromium(III) and cobalt(III) complexes were characterized by UV–Vis spectroscopy. The extinction coefficients were calculated on the basis of cobalt and chromium concentrations which were determined spectrophotometrically. Chromium(III) was converted to chromate for these analyses [14] and cobalt was analyzed as $[Co(SCN)_4]^{2-}$ employing the standard procedure of Kitson [15].

Extraction of Reduced 2,2′-Bipyridine

The reaction between $[Co(bpy)_3]^{3+}$ and Cr(II) was carried out in a 0.1 M hydrogen ion solution in the absence of air. The reaction mixture was then applied on a column containing Sephadex SP-C25-120. The first band to be eluted was free 2,2′-bipyridine. The second band was slightly pink in color and it was determined by NMR spectroscopy to be reduced 2,2′-bipyridine. This species was extracted from the aqueous solution with ether, concentrated and dried to give a colorless liquid (reduced 2,2′-bipyridine, *vide infra*). It was characterized by ^1H and ^{13}C NMR spectrometry. Control experiments on $[Cr(bpy)(OH_2)_4]^{3+}$ produced the expected amount of unreacted 2,2′-bipyridine.

Analysis of the 2,2′-Bipyridine Content of the Chromium Dimeric Product

Chromatographic separation of the reaction mixture of Cr(II) and $[Co(bpy)_3]^{3+}$ under 1:1 conditions yielded the red $[Cr_2(bpy)(OH)_2(OH_2)_6]^{4+}$ complex as the only product. The chromatographic separation of the product was accomplished on Sephadex SP-C25-120. The desired red band was eluted from the column with an auqeous mixture of 0.4 M NaCl in 0.004 M $HClO_4$. The 2,2′-bipyridine ligand was then stripped from the chromium product by converting it to the labile Cr(II) species using amalgamated zinc.

For each analysis, 10 ml of the red solution containing $[Cr_2(bpy)(OH)_2(OH_2)_6]^{4+}$ was reduced with zinc–mercury amalgam in an atmosphere of high purity argon. This solution was allowed to stand overnight before adding 2–3 ml of saturated Na_2CO_3 solution. After being set aside for a further 2 or 3 h, the solution was exposed to air, kept overnight in a sealed container and the free 2,2′-bipyridine was measured after extracting it into 250 ml of spectral grade n-heptane (Fisher Scientific Company) in several portions with vigorous shaking. The concentration of free 2,2′-bipyridine in n-heptane was calculated from three separate determinations, employing a standard curve prepared by dissolving known amounts of pure 2,2′-bipyridine in spectral grade n-heptane and then running the UV spectra of these solutions.

Results

The product analyses studies show that instead of the expected blue $[Cr(OH_2)_6]^{3+}$ (the product that should form as a result of outer-sphere electron transfer), a purple material appears upon ion-exchange of the reaction mixture. This complex does not elute from a Dowex cation exchange column (50WX2) even upon application of concentrated HCl. All subsequent analyses were therefore performed on a Sephadex strongly acidic cation exchanger (SP-C25-120) under controlled pH conditions which prevented the apparent decomposition process that was occurring on the Dowex column. On Sephadex, a red band is the only chromium-containing one obtained, except for $[Cr(OH_2)_6]^{3+}$ and the green chromium dimer, if Cr(II) were used in excess. As reported earlier [10], the most startling observation to arise from the product analyses is that the stoichiometry of the reaction is not 1:1. If an excess of Cr(II) is used, more than the stoichiometric quantity is consumed in the reaction. The red Cr(III) product obtained has a 4+ charge as determined by its behavior on the ion-exchange column and upon analysis (Table 1), it was found to contain two chromium(III) atoms and one 2,2′-bipyridine ligand, presumably arranged as in compound I where the 2,2′-bipyridine ligand may be either *cis* or *trans* to the bridging ligands.

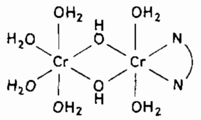

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TABLE 1. Analysis of Cr(III) and 2,2′-bipyridine in $[Cr_2(bpy)(OH)_2(H_2O)_6]^{4+}$

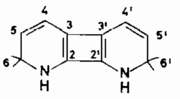
Amount of chromium (mol)	Amount of 2,2′-bipyridine (mol)	Ratio Cr:bpy
2.64×10^{-5}	1.28×10^{-5}	2.06:1.00
1.27×10^{-5}	6.90×10^{-5}	1.84:1.00
1.27×10^{-5}	6.76×10^{-5}	1.88:1.00

TABLE 2. Electronic spectra of Cr(III) and Co(III) complexes of 2,2′-bipyridine

Complex	λ_{max} (nm) (ϵ_{max} (M^{-1} cm^{-1}))
$[Cr_2(bpy)(OH)_2(OH_2)_6]^{4+}$	532 (26.7 ± 0.5) 442sh (31 ± 1) 412sh (84 ± 2) 390sh (126 ± 3) 307 (12700 ± 100) 247 (8600 ± 300)
$[Cr(OH_2)_4(bpy)]^{3+}$	538 (21 ± 1) 442sh (23 ± 1) 412sh (59 ± 4) 390sh (82 ± 7) 307 (8500 ± 700) 247 (5900 ± 400)
$[Co(bpy)_2(H_2O)_2]^{3+}$	492 (13.4 ± 0.3) 304 (200 ± 10) 296 (20300 ± 800) 245 (14000 ± 200)

This compound was found to be very stable and showed no decomposition upon storage at room temperature for several months. Details of the UV–Vis spectrum of the compound are given in Table 2.

In performing the product analyses, the first eluent obtained upon charging the column and washing it with water was analyzed spectrophotometrically and was found to be free 2,2′-bipyridine ligand. The next fraction to come off the column by adding 0.05 M NaCl in 0.004 M $HClO_4$ solution was also analyzed and was found to contain reduced 2,2′-bipyridine. The proton magnetic spectrum was run in deuterated chloroform. A set of unresolved peaks appears centered at 7.8 ppm due to the protons on the extensive conjugated double bond system. A doublet at 4.3 ppm (J = 6 Hz) indicates that some reduction has occurred. A possible structure which is also consistent with the ^{13}C NMR spectrum is given by II. In this spectrum there is a triplet at 68 Hz (J = 1.5 Hz) assigned to carbons 6 and 6′, two doublets centered at 130 (J = 2 Hz) and 132 (J = 2 Hz) Hz assigned to carbons 5 and 5′, 4 and 4′, and two singlets at 134 and 170 Hz assigned to carbons 3 and 3′ and 2 and 2′, respectively.



II

The next band to come off the column is the pink $[Co(OH_2)_6]^{2+}$ species. This is followed by an orange band which was identified as $[Co(bpy)_2(H_2O)_2]^{3+}$ (see Table 2 for UV–Vis spectral data). A yellow band of unreacted $[Co(bpy)_3]^{3+}$ complex,

TABLE 3. Product analysis data for recovery of $[Cr_2(bpy)(OH)_2(H_2O)_6]^{4+}$

$[H^+]$	Cr(II) used (μmol)	$[Co(bpy)_3]^{3+}$ used (μmol)	Dimer recovered (μmol)	Percentage Cr(III) recovered/ Co(III) used
0.10	335	334	161	96.4
0.10	335	334	162	97.0
0.10	337	334	166	99.4
				Average 98 ± 2
0.01	111	111	55.5	100
0.10	692	345	224	130

TABLE 4. Product analysis data for recovery of cobalt products[a]

Cr(II) used (μmol)	$[Co(bpy)_3]^{3+}$ used (μmol)	$[Co(H_2O)_6]^{2+}$ recovered (μmol)	$[Co(bpy)_2(H_2O)_2]^{2+}$ recovered (μmol)	% Co products recovered
335	334	27.0	220	74.0
335	334	28.9	230	77.5
337	334	25.0	200	67.4
				Average 73 ± 6
692	335	39.3	301	98.9

[a] All product analyses were performed at $[H^+] = 0.10$ M.

close to the highest red band, is eluted next. The final red band was found to contain the $[Cr_2(bpy)(OH)_2(OH_2)_6]^{4+}$ ion (compound I). This compound accounted for 98% of the reaction product based on initial cobalt complex used. However, only 73 ± 6% of the total cobalt is recovered as the orange complex, $[Co(bpy)_2(H_2O)_4]^{3+}$ and the pink complex $[Co(OH_2)_6]^{2+}$, the remainder being unreacted $[Co(bpy)_3]^{3+}$. The quantitative data for the product analyses are collected in Tables 3 and 4.

The actual reduction of $[Co(bpy)_3]^{3+}$ by Cr(II) occurs very rapidly and cannot be observed on the stopped-flow apparatus even at the lowest possible concentrations of the reactants. A lower limit for the reduction may be assigned to be $k = 1.3 \times 10^4$ M^{-1} s^{-1} (25.0 C, $\mu = 1.0$ M ($LiClO_4$), $[H^+] = 0.030$ M). On the stopped-flow instrument, four reactions are observed after the initial reduction. The first two were detected at 410 nm by observing a slow increase and then a rapid increase in absorbance on the oscilloscope. The second increase must be the result of an autocatalytic process. The order of this reaction could not be absolutely established since the rise was very sharp. However, the kinetics were more closely approximated by a first order treatment than by any other so the rate constants are listed in Table 6 as first order rate constants. Both of the first two reactions were independent of the hydrogen ion concentration. The kinetics of the first two observed reactions were studied at 540 and 420 nm, respectively, since there was very little interference by the other reactions at these wavelengths (Tables 5 and 6). The first observed reaction had a rate con-

TABLE 5. Kinetic data for the first reaction observed in the reaction of Cr(II) with $[Co(bpy)_3]^{3+}$

$[H^+]^a$	$[Co(bpy)_3]^{3+} \times 10^3$ [a]	$[Cr(II)] \times 10^2$ [a]	k_1 $(s^{-1})^b$
0.10	1.35	2.71	46.8
0.10	1.35	5.40	46.2
0.10	1.35	8.09	46.2
0.03	1.35	5.40	46.3
0.50	1.35	5.39	46.2
0.03	1.85	5.29	46.3
			$k_1 = 46.3$ s^{-1}

[a] Concentrations are initial values in molar units. [b] The ionic strength was controlled to 1.00 M ($LiClO_4$); the temperature was controlled to 25.0 ± 0.01 °C; wavelength employed to follow this reaction was 540 nm.

TABLE 6. Kinetic data for the second reaction observed in the Cr(II) reduction of $[Co(bpy)_3]^{3+}$

$[H^+]^a$	$[Co(bpy)_3]^{3+} \times 10^3$ [a]	$[Cr(II)] \times 10^2$ [a]	$k_2 \times 10^2$ $(s^{-1})^b$
0.10	1.35	2.71	1.37
0.10	1.35	5.40	1.38
0.10	1.35	8.01	1.37
0.10	1.35	5.40	1.38
0.03	1.35	5.39	1.37
0.03	1.35	5.39	1.37

[a] Concentrations are initial values in molar units. [b] The ionic strength was controlled to 1.00 M ($LiClO_4$); the temperature was controlled to 25.0 ± 0.1 °C; wavelength employed to follow this reaction was 420 nm.

TABLE 7. Kinetic data for the third reaction observed in the Cr(II) reduction of $[Co(bpy)_3]^{3+}$

$[H^+]^a$	$[Co(bpy)_3]^{3+} \times 10^{3\,a}$	$[Cr(II)] \times 10^2\,^a$	k_{obs} $(M^{-1}\,s^{-1})^b$
0.10	1.35	2.71	9.49×10^1
0.10	1.35	5.40	9.50×10^1
0.10	1.35	8.01	9.41×10^1
0.03	1.35	5.39	7.35×10^1
0.10	1.35	5.40	9.50×10^1
0.30	1.85	5.39	1.84×10^2
0.50	1.35	5.39	2.86×10^2
0.03	1.85	5.29	7.44×10^1

[a]Concentrations are initial values in molar units. [b]The ionic strength was controlled to 1.00 M ($LiClO_4$); the temperature was controlled to 25.0 ± 0.1 °C; wavelength employed to follow this reaction was 410 nm; $k_3 = k_{obs}/[Cr(II)]$.

TABLE 8. Kinetic data for the fourth reaction observed in the Cr(II) reduction of $[Co(bpy)_3]^{3+}$

$[H^+]^a$	$[Co(bpy)_3]^{3+} \times 10^3\,^a$	$[Cr(II)] \times 10^2\,^a$	k_{obs} $(s^{-1})^{b,c}$
0.03	1.35	5.41	4.33×10^{-1}
0.10	1.35	5.41	6.30×10^{-1}
0.30	1.35	5.42	1.07
0.40	1.35	5.40	1.24
0.50	1.35	5.40	1.46
0.03	0.85	5.29	4.33×10^{-1}
0.10	1.35	8.08	6.30×10^{-1}

[a]Concentrations are initial values in molar units. [b]The ionic strength was controlled to 1.00 M ($LiClO_4$). [c]The temperature was controlled to 25.0 ± 0.1 °C.

stant of 46.3 ± 0.2 s^{-1}. The rate constant for the second observed reaction is (1.38 ± 0.02) × 10^2 s^{-1} over the Cr(II) concentration range of 2–8 × 10^{-2} M, [Co(III)] = 1.35 × 10^{-3} M, and the range of H^+ concentrations is 0.03 to 0.10 M. It is probable that this constant masks a more complicated process (*vide infra*). The third reaction observed was followed by studying a slower increase in absorbance and it exhibited both a chromium(II) and a direct hydrogen dependence. The rate constant for this reaction is $k_{obs} = k'_3 + k''_3[H^+]$ where $k'_3 = 53 \pm 3$ $M^{-1}\,s^{-1}$ and $k''_3 = (4.6 \pm 0.2) \times 10^2$ $M^{-2}\,s^{-1}$. Results of this study are listed in Table 7. The fourth reaction was studied at 400 nm and was found to be dependent only on the hydrogen ion concentration (Table 8). The rate constant for this reaction is $k_{obs} = k'_4 + k''_4[H^+]$ where $k'_4 = 0.39 \pm 0.02$ s^{-1} and $k''_4 = 2.16 \pm 0.06$ $M^{-1}\,s^{-1}$. Finally, a much slower reaction was followed at 465 nm with μ = 1.0 M ($LiClO_4$) at 25 °C on a UV–Vis spectrophotometer. This reaction (k_5 = 8.70 × 10^{-5} s^{-1}) was independent of the hydrogen ion concentration and appears to be associated with decomposition processes.

Since there is a real possibility that free 2,2′-bipyridine liberated in the first stages of an expected outer-sphere reduction might be responsible for the subsequent series of reactions, we looked at the Cr(II) reduction of $[Co(bpy)_3]^{3+}$ in the presence of added free 2,2′-bipyridine (8.44 × 10^{-4} M) in 0.10 M $HClO_4$ at μ = 1.00 M ($LiClO_4$) and 25 °C. The same four reactions were detected as described above but the presence of this additional amount of free ligand had a specific effect on the magnitude of the rate constants observed. The first and third reactions became much faster, whereas the second one (the suspected autocatalysis process) was inhibited. There was no effect on the rate constant of the fourth reaction (see Table 9). These observations will have to be accounted for in the development of possible mechanisms (*vide infra*).

We also had to consider the possibility that some or all of the observed reactions were due to the direct interaction of Cr(II) with free 2,2′-bipyridine liberated in an outer-sphere process. Therefore, we also studied the Cr(II) reduction of 2,2′-bipyridine itself over the $HClO_4$ concentration range 0.03 to 0.10 M (μ = 1.00 M ($LiClO_4$) at 25 °C). Two fast reactions were observed on the stopped-flow instrument. The first showed an increase in absorbance at 400 nm with a rate constant $k = 3.17 \times 10^3$ $M^{-1}\,s^{-1}$ and the second showed a decrease in absorbance at 360 nm with a rate constant $k = 2.47 \times 10^1$ $M^{-1}\,s^{-1}$, both with $[H^+]$ = 0.10 M. Both reactions were dependent on the Cr(II) and hydrogen

TABLE 9. Kinetic data for the series of reactions following the Cr(II) reduction of $[Co(bpy)_3]^{3+}$ in the presence of added 2,2′-bipyridine[a]

Reaction	$[Co(bpy)_3]^{3+}$ [b]	[Cr(II)] [b]	[bpy] [b]	k
1	1.35×10^{-3}	5.40×10^{-2}	8.44×10^{-4}	$6.93 \times 10^{1} s^{-1}$
2	1.35×10^{-3}	5.40×10^{-2}	8.44×10^{-4}	$5.13 \times 10^{1} s^{-1}$
3	1.35×10^{-3}	5.40×10^{-2}	8.44×10^{-4}	$2.57 \times 10^{2} M^{-1} s^{-1}$
4	1.35×10^{-3}	5.40×10^{-2}	8.44×10^{-4}	$6.30 \times 10^{-1} s^{-1}$

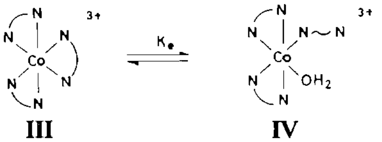
[a] The temperature was controlled to 25.0 ± 0.1 °C and the ionic strength was controlled to 1.00 M ($LiClO_4$). [b] Concentrations are initial values in molar units.

ion concentrations, and neither of them corresponds to any of the reactions observed in the Cr(II) reduction of $[Co(bpy)_3]^{3+}$.

A blank experiment was performed by oxidizing 5×10^{-2} M Cr(II) in the presence of a saturated solution of free 2,2′-bipyridine (8.44×10^{-4} M) in 0.10 M $HClO_4$. Product studies showed that less than 2% of the bipyridine was incorporated into the metal complex as $Cr(bpy)(H_2O)_4^{3+}$ upon air oxidation.

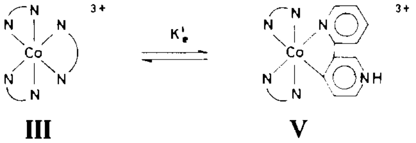
Discussion

The complicated nature of the kinetics and the observation of an auto-catalyzed step suggests a mechanism involving radical ions. The initial reduction product of the reaction between $[Co(bpy)_3]^{3+}$ and Cr(II) could not have been free ligand, $[Co(OH_2)_6]^{2+}$ and $[Cr(OH_2)_6]^{2+}$ (the expected outer-sphere products). If this were the case, all subsequent reactions would arise from reactions between bpy and $[Co(OH_2)_6]^{2+}$ (an equilibrium), bpy and $[Cr(OH_2)_6]^{3+}$ (far too slow) or bpy and $[Cr(OH_2)_6]^{2+}$ (which we have established is not the case). We have observed that the decomposition of $[Co(bpy)_3]^{3+}$ leading to loss of 2,2′-bipyridine is light catalyzed. This suggests that a rapidly attained light-induced equilibrium between a chelated and unidentate 2,2′-bipyridine ligand on the Co(III) complex is not unreasonable (eqn. (1)). However, complex IV cannot exist on any large scale since we have been unable to find any spectroscopic evidence for it. Also, reactions performed in the dark lead to the same products as those carried out under bright illumination.



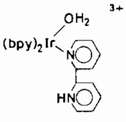
III IV (1)

An alternative mechanism is one having an equilibrium between normal $[Co(bpy)_3]^{3+}$ and a cyclometallated structure as in eqn. (2).

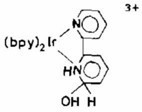


III V (2)

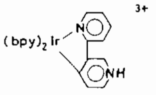
Monodentate 2,2′-bipyridine ligands have been proposed before as reaction intermediates in the aquation [16] of $[Fe(bpy)_3]^{2+}$, for example, and it has been claimed that such a species is present in the reaction [17] of bpy with $[Al(Me_2SO)_6]^{3+}$. It has also been suggested that a monodentate bipyridyl complex may exist as one of the products of the aquation of *cis*-$[Cr(bpy)_2(H_2O)(Cl)]^{2+}$ as evidenced by ion-exchange chromatography [18]. Studies of the photolysis of $Ru(bpy)_3^{2+}$ in DMF indicate that an intermediate monodentate bpy species is formed in solution prior to formation of the final product, $[Ru(bpy)_2(SCN)_2]$ [19]. Attempts to isolate this material as a crystalline solid were not successful [20]. There is evidence for formation of a species containing monodentate bpy in the photolysis of $Ru(bpy)_3^{2+}$ in aqueous solution but again it was not possible to isolate the complex [21]. An early report by Watts *et al.* [20] in 1977 of a monodentate bpy (structure IV) in the protonated $[Ir(bpy)_3]^{3+}$ cation based on spectral evidence and the observation of a pK_a of 3.0 for the free nitrogen atom, was subsequently challenged by Gillard *et al.* [22] in 1979. These workers instead formulated the complex as a 'covalent hydrate' (structure VII). It eventually became clear that there are three forms, two yellow and one red, of the cation formally designated as $[Ir(bpy)_3]^{3+}$. One of the yellow ones is the usual tris-chelated complex, originally prepared in 1974 by Flynn and Demas [23]. The other yellow one is the protonated species first synthesized by Watts *et al.* [20]. The evidence is now overwhelmingly in favor of a cyclometallated structure for this compound (structure VIII). Two crystal structures have been reported on this species [24, 25], as well as one on the red compound which was found to be the deprotonated cyclometallated complex [26]. In addition, NMR studies including one employing 500 MHz proton and 125 MHz carbon-13 spectros-



VI



VII



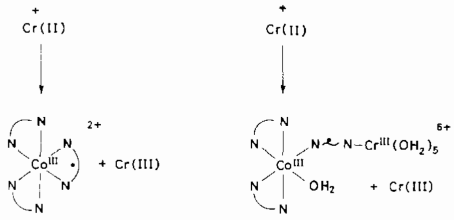
VIII

copy were consistent with this interpretation [27, 28]. A cyclometallated 2,2′-bipyridine ligand has been observed to bridge two metal centers in triosmium clusters [29]. In view of the definite assignment of cyclometallated structures for the iridium and osmium complexes, the postulation of a similar mode of bonding in a cobalt intermediate (complex V) is not unreasonable. Indeed, others have likewise suggested cyclometallated intermediates in mechanistic studies [30–34].

An outer-sphere attack by Cr(II) on III and an inner-sphere attack at the free N atom of IV or V is a reasonable next step.

$$\underset{\textbf{III}}{Co(bpy)_3^{3+}} \underset{(H^+,H_2O)}{\overset{K\text{ or }K'_e}{\rightleftharpoons}} \qquad (3)$$

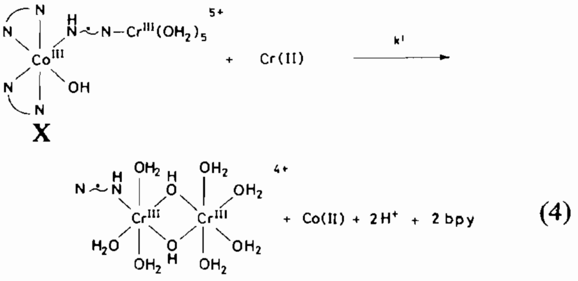
$$\underset{\textbf{IV}}{Co(bpy)_2(o\text{-}bpy)(H_2O)^{2+}} \text{ or } \underset{\textbf{V}}{Co(bpy)_2(bpyH)^{3+}}$$



IX **X**

After reduction, it is necessary to assume that the electron remains largely confined in ligand type orbitals on the 2,2′-bipyridine moiety forming ligand radical intermediates, IX and X. Precedence for this type of behavior may be found in studies of the magnetic and optical properties of tris-bpy complexes [29], particularly those of chromium [35–38] and vanadium [39,40], as well as in bis-bpy complexes of iridium containing cyclometallated ligands [41–48]. These studies indicated that the reduction of $[Cr(bpy)_3]^{3+}$ to $[Cr(bpy)_3]^{2+}$ is a metal-centered process, i.e. Cr(III) is reduced to Cr(II). However, the second reduction to yield $[Cr(bpy)_3]^+$ is not only ligand-centered but it also causes transfer of a metal electron to the ligands [49,50] to yield a complex formulated as $[Cr^{III}(bpy)(bpy^-)_2]^+$ rather than $[Cr^{II}(bpy)_2(bpy^-)]^+$. A quantitative calculation was performed to interpret this behavior [50] but it can also be understood qualitatively by considerations of π-backbonding, i.e. Cr(II) can be stabilized by good π-accepting ligands such as a neutral bpy in $[Cr(bpy)_3]^{2+}$. However, the π-accepting ability of a coordinated reduced bpy is sufficiently diminished that it causes the oxidation of the metal center to Cr(III) via transfer of a metal electron to an additional coordinated bpy. In the case of the cobalt–radical ion complexes, **IX** and **X**, the electron must remain on the ligand orbitals during the timescale of the reaction since cobalt(II) is very labile and its complexes normally fall apart rapidly.

The radical binuclear, **X**, is then attacked by another Cr(II) in an inner-sphere manner at the water oxygens to give the dihydroxo binuclear intermediate, **XI**. This species is very similar to the usual O_2 oxidation product of $[Cr(OH_2)_6]^{2+}$, that is, the familiar green dimer, $[(OH_2)_4Cr(OH)_2Cr(OH_2)_4]^{4+}$ and the surprising observation may be not so much that a dihydroxy-bridged complex is an observed product of this reaction but that dimeric redox products of Cr(III) have been isolated only very infrequently. It may be that they will be found to be a common product of radical-mediated electron transfers. Dimeric products of chromium(II) reductions have been reported by Kuperferschmidt and Jordan [51] but in their work the dimer arose as a result of attack of excess Cr(II) on the double bond of the free ligand in solution. In the present study, it appears that the second electron transfer step leading to the dimer is faster than the first so no intermediate is detected and there is no evidence for reduction of the coordinated ligand in the product.



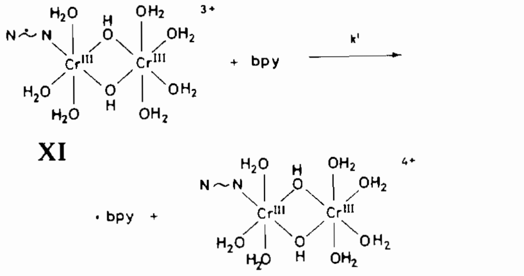
X

XI

The $[Co(bpy)_2(OH_2)_3]^{3+}$ product obtained may arise in part from the decomposition of some of the $[Co(bpy)_2(bpy\cdot)]^{2+}$ species to yield $[Co(bpy)_2(OH_2)_2]^{3+}$ and bpy·.

The first observed reaction is independent of the Cr(II) concentration which means that, as postulated above, reduction has already occurred. This reaction is markedly accelerated by the presence of added 2,2′-bipyridine. It can be reasonably attributed to transfer of the electron from the coordinated 2,2′-bipyridine to free 2,2′-bipyridine (eqn. (5)).

We were unable to test the order of any of the reactions with respect to bpy concentration since the ligand was not very soluble in aqueous solution. The values quoted in Table 9 were for addition of a saturated bpy solution. The rate constants obtained under these conditions were reproducible but attempts to use less concentrated solutions gave kinetic results which were subject to large variation.

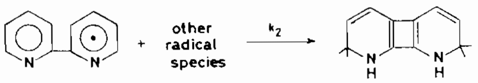


XI

XII

(5)

The second observed reaction is auto-catalyzed and is attributed to the annihilation of a 2,2′-bipyridine radical by reaction with another radical species to give reduced 2,2′-bipyridine – an observed product (compound **II**). This reaction is inhibited by added 2,2′-bipyridine which is to be expected if an equilibrium is established between free 2,2′-bipyridine and its radical ion. The overall reaction for this step is given by eqn. (6). Due to the autocatalytic nature of this process, a detailed kinetic investigation is not possible.

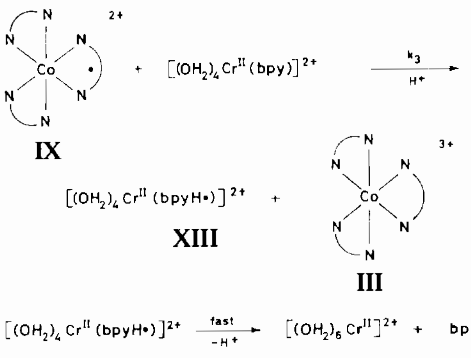


(6)

II

There is considerable evidence that the protons on the C3 and C3′ positions of coordinated 2,2′-bipyridine have enhanced acidities as a result of high steric strain. The crystal structure of $[Ru(bpy)_3]^{2+}$ first illustrated this effect [52], and it was later confirmed by NMR studies [53]. Constable and Seddon found that addition of deuterated sodium methoxide and methanol to a solution of $[Ru(bpy)_3]^{2+}$ in dimethylsulfoxide resulted in slow deuterium–hydrogen exchange at the 3,3′-positions of the ligated bipyridines [53]. There is similar evidence [54] for weakly acidic character of the C3 and C3′ hydrogens in $[Os(bpy)_3]^{2+}$. Our observed product, compound **II**, has a bond between the C3 and C3′ carbons which may result from the enhanced reactivity at these positions and may mean that it originates from a coordinated bpy of one of the radical ions, **IX**, **XI** or **XIII**.

The third observed reaction is Cr(II) dependent and is also accelerated by the addition of free 2,2′-bipyridine. A possible mechanistic explanation is that this step involves a reaction between the minor component of the initial reduction process, **IX**, and a chromium(II)–bipyridine complex (eqn. (7)), the reduced species of which rapidly decomposes to yield the bpy radical and $[Cr(OH_2)_6]^{2+}$. The reaction shows a direct acid dependence which may indicate that the coordinated bpy has a tendency to pick up a proton upon reduction to give **XIII**.



IX

XIII

III

(7)

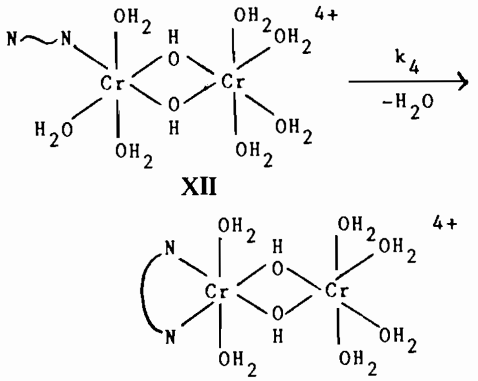
XIII

The step regenerates the original $[Co(bpy)_3]^{3+}$ starting material which may go through the cycle again. Thus, we may obtain more than 100% of the final $[Cr_2(bpy)(OH)_2(OH_2)_6]^{4+}$ complex based on the amount of $[Co(bpy)_3]^{3+}$ used if an excess of Cr(II) is present. When free bpy is added, the labile $[Cr^{II}(OH_2)_4(bpy)]^{2+}$ concentration is increased, resulting in an increase in the rate of reaction. The rate law for this step is

$$\frac{-d[\text{complex } \mathbf{IX}]}{dt} = (k'_3 + k''_3[H^+])[\text{complex } \mathbf{IX}] \times [Cr(II)]$$

where $k'_3 = 53 \pm 3\ M^{-1}\ s^{-1}$ and $k''_3 = (4.6 \pm 0.2) \times 10^2\ M^{-2}\ s^{-1}$ as determined from the intercept and slope of the plot of the acid dependence of the reaction (Table 7).

We ascribe the fourth observed reaction which is independent of Cr(II) and unaffected by the addition of free 2,2′-bipyridine to ring closure of the 2,2′-bipyridine ligand on the chromium(III) binuclear complex to give the observed product (eqn. (8)). This reaction exhibits a direct acid dependence possibly because protonation of the departing water molecule makes it a better leaving group.



XII

I

(8)

The rate law for this last step is

$$\frac{-d[\text{complex } \mathbf{XII}]}{dt} = (k' + k''[H^+])[\text{complex } \mathbf{XII}]$$

where $k'_4 = 0.39 \pm 0.02\ s^{-1}$ and $k''_4 = 2.16 \pm 0.06\ M^{-1}\ s^{-1}$ as determined from the intercept and slope of the plot of the acid dependence of the reaction (Table 8).

Confirmation or modification of our suggested mechanism for this new class of autocatalyzed reactions must await further thermal redox studies on polypyridyl complexes. Preliminary studies on the Cr(II) reduction of $[Cr(bpy)_3]^{3+}$ in our laboratory indicates that a similar series of steps are involved in this process, including an autocatalysis step. We are also currently examining cyclometallated oxidants in an attempt to discover if such species are involved as intermediates in the $[Co(bpy)_3]^{3+}$ and $[Cr(bpy)_3]^{3+}$ reactions with Cr(II).

Acknowledgements

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