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The Cr(II) Reduction of Pentane-2,4-dionatobis(ethylenediamine)cobalt(III). An Apparent Failure of the Product Criterion for Assigning Inner-sphere Mechanisms

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Abstract

The Cr(II) reduction of $[Co(bipy)_2(ptdn)]^{2+}$ (bipy = 2,2′-bipyridine and ptdn = pentane-2,4-dione) proceeded too rapidly to be detected by the stopped-flow method and a lower limit of 3 × 10^4 M^{-1} s^{-1} (μ = 0.10 M ($LiClO_4$)) and $[H^+]$ = 0.030 M was calculated for this reaction. Product studies established that both $[Cr(bipy)(OH_2)_4]^{3+}$ and $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ were formed. The ratio of products obtained was strongly dependent on the mixing technique used. Under conditions of excess chromium(II), more than the stoichiometric amount of Cr(III) products were isolated, indicating that some degree of substitution was occurring. Blank experiments established that the products obtained could have arisen from an outer-sphere reaction followed by capture of the free ligands by Cr(II). A synergistic effect between the acac and bipy ligands appears to be operating. Two reactions were observed on the stopped-flow instrument. Both are ascribed to ring-closure of bipy on Cr(III). The reaction to give $[Cr(bipy)(OH_2)_4]^{3+}$ was characterised by $k^{25\,°C}$ = 5.06 × 10^{-1} s^{-1} with activation parameters $\Delta H^\ddagger$ = 9.9 ± 0.3 kcal/mol, and $\Delta S^\ddagger$ = –26.8 ± 0.9 e.u. The second reaction was ascribed to the formation of $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ from $[Cr(bipy)(ptdn)(OH_2)_3]^{2+}$ and had $k^{25\,°C}$ = 5.83 × 10^{-2} s^{-1}; $\Delta H^\ddagger$ = 4.93 ± 0.06 kcal/mol, $\Delta S^\ddagger$ = –47.6 ± 0.2 e.u. The final reaction was attributed to breakdown of the Cr(III) products. It occurred very slowly with $k^{25\,°C}$ = 4.6 × 10^{-6} s^{-1} (all values quoted at μ = 0.10 M ($LiClO_4$) and $[H^+]$ = 0.030 M).

Introduction

The first observation of the inner-sphere pathway was made in 1953 by Taube, Myers and Rich [1]. The presence of the bridging atom, in the first instance, a chloride, between the metal centres in the activated complex, was established by taking advantage of the labile and inert characteristics of the participating oxidant, $[Co(NH_3)_5Cl]^{2+}$ and reductant, Cr(II). This study established the so-called 'product criterion' for proving the existence of an inner-sphere mechanism, *i.e.* if the bridging ligand is transferred from the oxidant to the reductant faster than can be accounted for by substitution processes, then an inner-sphere mechanism must be operating. Over the last three decades, this criterion has been invoked hundreds of times in mechanistic redox assignments [2].

In this work, we report an apparent failure of the 'product criterion' in assigning mechanism. Earlier [3], we reported that the Cr(II) reduction of $[Co(bipy)_2(ptdn)]^{2+}$ (bipy = 2,2′-bipyridine, ptdn = pentane-2,4-dione, also called acetylacetone and abbreviated acac) proceeded in part by a di-bridged inner-sphere pathway, giving $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ as the major product of reduction. Product studies showed that the substitution of bipy and of ptdn on Cr(III) was slow and could not account for the observation of the final product. Also, substitution of bipy on $[Cr(ptdn)(OH_2)_4]^{2+}$ and of ptdn on $[Cr(bipy)(OH_2)_4]^{3+}$ was very much slower than formation of $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ in the kinetic medium. The incorporation of bipy in the first co-ordination sphere of Cr(II) was somewhat favoured, giving some $[Cr(bipy)(OH_2)_4]^{3+}$ upon oxidative quenching. Very little ptdn was captured by Cr(II) in a similar experiment employing this ligand [4]. We now wish to report the full study on this system including our experiments on the capture of bipy and ptdn by Cr(II) when these ligands are *simultaneously* in the reaction mixture. Apparently, there is a synergistic effect operating which highly favors the production of the 'di-bridged product', $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$, upon quenching this solution with dioxygen. The results of this work serve to illustrate the point that it is not only necessary to do substitution experiments on Cr(III) but also, especially with chelating ligands such as bipy, it is

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necessary to do quenching experiments with Cr(II) before assigning an inner-sphere mechanism.

Experimental

Reagents

All reagent solutions were prepared in water which was de-ionized and doubly distilled as described earlier [5]. Lithium perchlorate solutions were made by dissolving anhydrous grade $LiClO_4$ (G. Frederick Smith Chemical Co.) in the purified water. The resulting solution was filtered through a 0.47 μ Durapore filter (Millipore Filter Corporation). Triplicate portions of this stock solution (~2.2 M) were then standardized by determining titrimetrically the amount of hydrogen ion released from an Amberlite IR-120(H) analytical grade resin (BDH Chemicals Ltd.). Perchloric acid solutions (~2.2 M) were prepared from doubly distilled 70% perchloric acid purchased from the G. Frederick Smith Chemical Company; these were standardized against sodium hydroxide. Chromium(II) perchlorate solutions were prepared by reduction of $[Cr(OH_2)_5](ClO_4)_3$ (G. Frederick Smith Chemical Co.) in aqueous perchloric acid solution (0.20 M) using zinc–mercury amalgam. These solutions were stored and handled using standard syringe techniques in an atmosphere of high-purity argon. The concentration of Cr(II) was determined every three days by a standardization procedure described earlier [6].

Preparation of Pentane-2,4-dionatobis(2,2′-bipyridine)cobalt(III)

The compound was prepared by the method of Kashiwabara and Douglas [7] except that sodium perchlorate was used instead of sodium iodide to effect precipitation. The resulting red crystals were dissolved in water and were purified by ion-exchange chromatography on a Bio-Rex cation exchange resin in the sodium ion form (Bio-Rad Laboratories). Elution with 0.05 M NaCl solution moved the desired red band away from all impurities. The resin containing the red complex was then separated physically by transferring it to another column. The complex was eluted by washing the resin with a saturated solution of sodium chloride.

Upon addition of a small amount of a saturated sodium perchlorate solution, red crystals appeared. These were filtered, washed with ether and allowed to air dry at the pump. The crystals were twice recrystallized from the deionized, doubly-distilled water before use. *Anal.* Calcd. for $[Co(C_5H_7O_2)(C_{10}H_8N_2)_2](ClO_4)_2$: C, 42.0; H, 3.64; N, 7.84. Found: C, 41.8; H, 3.60; N, 7.77%.

Product Analyses

The product studies were performed at ambient temperatures by dissolving 140 μmol of $[Co(bipy)_2(ptdn)](ClO_4)_2$ in 50 ml of 0.05 M $HClO_4$ and then adding a slight excess of Cr(II) (141–146 μmol). The results were initially found to fluctuate wildly. This was eventually found to be a consequence of the mixing procedure. A method of rapid mechanical mixing was ultimately devised to circumvent this problem and allow the attainment of reproducible results. Product studies with a two-fold excess of Cr(II) over Co(III) were also performed. After ten minutes when the reaction had gone to completion, the solution was aerated for five to ten minutes to oxidise any excess Cr(II). The reaction mixture was subsequently diluted three-fold, and submitted to an ion-exchange procedure on Sephadex SP-C25-120 strongly acidic cation exchange resin (Sigma Chemical Company). The eluent obtained upon charging the column and washing it with water was collected and analysed spectrophotometrically to determine if free ligands were present. The solution was found to contain both the ligands pentane-2,4-dione and 2,2′-bipyridine.

Elution of the various compounds of the reaction mixture was accomplished by using different concentrations of NaCl in 0.004 M $HClO_4$. Initially, a solution containing a 0.050 M NaCl/0.004 M $HClO_4$ was used and the concentration was gradually increased up to 0.20 M NaCl/0.004 M $HClO_4$ to move more highly charged cations. The lower portion of the first reddish-orange band (which was darker than the upper portion) was collected and was found to contain a chromium complex. However, in the chromate analysis, a small amount of cobalt(II) always appeared. These two species could be separated by passing the diluted eluent through a second column, then slowly moving them apart by addition of a dilute NaCl solution. The band containing the chromium complex was physically removed from the column and was placed in a second column, whereupon the desired species was eluted in concentrated form by the addition of a saturated NaCl solution. A saturated aqueous solution of $NaClO_4$ was added to effect precipitation. Needle-shaped red and green crystals were formed in very small yield. These were collected by filtration and dried in the air. The red and green crystals were separated physically. There was insufficient material obtained to do detailed characterization studies on these isomers. The green crystals dissolved in water to give a red solution. The red crystals were analysed. *Anal.* Calcd. for $[Cr(C_5H_7O_2)(C_{10}H_8N_2)(H_2O)_2](ClO_4)\cdot 2H_2O$: C, 33.2; H, 3.50; N, 5.16. Found: C, 32.7; H, 3.42; N, 4.90%.

All the chromium(III) and cobalt(III) materials were characterized by UV-visible spectroscopy. The extinction coefficients were calculated on the

TABLE I. Kinetic Data for the First Reaction Observed in the Reduction of $[Co(bipy)_2(ptdn)]^{2+}$ by Chromium(II).

Temp. °C[a]	$[H^+]$	$(LiClO_4)$	10^{-4}[Co(III)][b]	10^{-2}[Cr(II)][b]	k_{obs} (s^{-1})
25.0	0.030	0.10	2.52	1.17	5.06×10^{-1} [c]
	0.030	0.20	2.52	1.16	1.54
	0.030	0.20	2.52	2.28	1.52
	0.060	0.20	2.52	1.16	7.70×10^{-1}
	0.100	0.20	2.52	1.16	5.13×10^{-1}
35.0	0.030	0.10	2.52	1.17	8.66×10^{-1} [c]
45.0	0.030	0.10	2.52	1.17	15.4×10^{-1} [d]

[a] The temperature was controlled to ±0.1 °C or better. [b] Concentrations in molar units. [c] Average of three runs. [d] Average of two runs.

TABLE II. Kinetic Data for the Second Reaction Observed in the Reduction of $[Co(bipy)_2(ptdn)]^{2+}$ by Chromium(II).

Temp. °C[a]	$[H^+]$	$\mu(LiClO_4)$	$10^{-4} \times$ [Co(III)]	$10^{-2} \times$ [Cr(II)][b]	k_{obs} (s^{-1})
25.0	0.030	0.10	2.52	1.17	5.83×10^{-2} [c]
	0.030	0.20	2.52	1.16	2.48×10^{-1}
	0.030	0.20	2.52	2.28	2.49×10^{-1}
	0.060	0.20	2.52	1.16	2.04×10^{-1}
	0.100	0.20	2.52	1.16	1.93×10^{-1}
35.0	0.030	0.10	2.52	1.17	7.76×10^{-2} [d]
45.0	0.030	0.10	2.52	1.17	1.05×10^{-1} [c]

[a] The temperature was controlled to 0.1 °C or better. [b] Concentrations in molar units. [c] Average of two runs. [d] Average of three runs.

basis of cobalt and chromium concentrations which were determined spectrophotometrically. In order to make these measurements, chromium(III) was analysed as chromate and cobalt as $[Co(SCN)_4]^{2-}$ using the standard procedure of Kitson [8].

Kinetic Measurements

The rate of reduction of $[Co(bipy)_2(ptdn)]^{2+}$ by Cr(II) was determined by observing the change in absorbance as the reaction proceeded, using a Dionex Model D-110 Stopped-Flow Spectrophotometer. The kinetic traces were displayed on a Nicolet Explorer II Digital Oscilloscope. The temperature of the water bath on the stopped-flow instrument was measured using a 0–50 °C ASTM mercury thermometer calibrated by NBS procedures (Fisher Scientific Co.). The bath temperature was adjusted by circulating water from a Lauda NB-D water bath connected to an electronic relay (Lauda R-10) and controlled by a mercury thermocouple.

Physical Measurements

The ultraviolet and visible spectra were measured either on a Hitachi EPS-3T Spectrophotometer or on a Perkin-Elmer Model 330 instrument. The CHN analyses were done by Guelph Chemical Laboratories Ltd.

Results

The kinetic data obtained for the reduction of $[Co(bipy)_2(ptdn)]^{2+}$ by Cr(II) are given in Tables I and II. All kinetic runs at different temperatures were done at 0.10 M ionic strength ($LiClO_4$). This was necessitated by the very low solubility of the complex. The acid and chromium dependencies were determined with some difficulty in 0.20 M ionic strength at 25.0 °C.

The actual reduction of $[Co(bipy)_2(ptdn)]^{2+}$ by Cr(II) occurred extremely rapidly and could not be observed on the stopped-flow apparatus even at the lowest possible concentrations of $[Co(bipy)_2(ptdn)]^{2+}$ (2.55×10^{-5} M) and [Cr(II)] (1.17×10^{-2} M).

On the stopped-flow instrument, two reactions were detected after the initial reduction. The first one was studied at 540 nm. It was detected by observing a rapid decrease in absorbance on the oscilloscope. The second one exhibited a slower increase in absorbance at 420 nm. Both reactions

TABLE III. Kinetic Data for the Third Reaction Observed in the Reduction of $[Co(bipy)_2(ptdn)]^{2+}$ by Chromium(II).

Temp. °C[a]	$[H^+]$	$[LiClO_4]$	$10^{-4}[Co(III)]$[b]	$10^{-2}[Cr(II)]$[b]	k_{obs} (s^{-1})
25.0	0.031	0.10	6.0	1.51	4.62×10^{-6}
	0.051	0.10	6.0	1.51	2.57×10^{-6}
	0.050	0.10	6.0	1.00	2.76×10^{-6}
45.0	0.031	0.10	6.0	1.51	6.24×10^{-6}
	0.051	0.10	6.0	1.22	5.50×10^{-6}
	0.051	0.10	6.0	1.00	5.68×10^{-6}

[a] The temperature was controlled to ±0.1 °C or better. [b] Concentrations in molar units.

TABLE IV. Activation Parameters Calculated for the First Two Observed Reactions between $[Co(bipy)_2(ptdn)]^{2+}$ and Cr(II) at $[H^+] = 0.030$ M.

Reaction	$k^{25°C}(s^{-1})$	$\Delta H^{\ddagger}$ (kcal/mol)[a]	$\Delta S^{\ddagger}$ (e.u.)[a]
$[Cr(bipy)(OH_2)_5]^{3+} \rightarrow [Cr(bipy)(OH_2)_4]^{3+}$	5.06×10^{-1}	9.9 ± 0.3	−26.8 ± 0.9
$[Cr(bipy)(ptdn)(OH_2)_3]^{2+} \rightarrow [Cr(bipy)(ptdn)(OH_2)_2]^{2+}$	5.83×10^{-2}	4.93 ± 0.06	−47.6 ± 0.2

[a] Errors given are standard errors calculated from the least-squares best fit to the kinetic data.

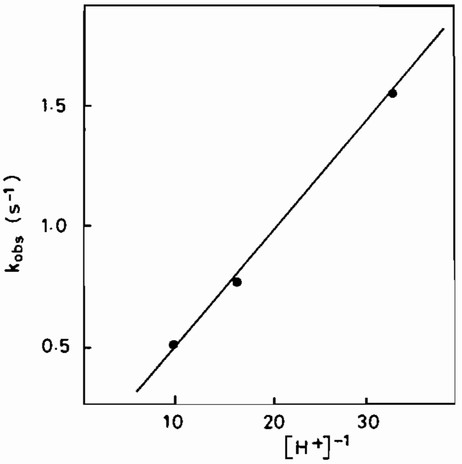

Fig. 1. Plot of the inverse acid dependence of reaction 1 observed in the Cr(II) reduction of $[Co(bipy)_2(ptdn)]^{2+}$.

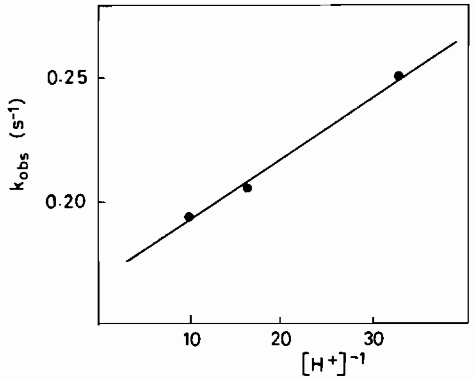

Fig. 2. Plot of the invese acid dependence of reaction 2 observed in the Cr(II) reduction of $[Co(bipy)_2(ptdn)]^{2+}$.

were characterized by a slight inverse hydrogen ion dependence (see Figs. 1 and 2), and no dependence on the concentration of Cr(II). These data indicate that the initially formed reduction products exist as equilibrium mixtures of protonated and unprotonated forms and the latter are more reactive. The form of the rate law for both of these reactions is

$$-\frac{d[Cr(III)]}{dt} = \left[a + \frac{b}{[H^+]}\right][Cr(III)] \qquad (1)$$

A computer least squares fit to the line in Fig. 1 for the first reaction gave an intercept, a = 5.7×10^{-2} s^{-1} and a slope b = 4.4×10^{-2} M^{-1} s^{-1}. For the second reaction represented in Fig. 2, a = 1.7×10^{-1} s^{-1} and b = 2.4×10^{-3} M^{-1} s^{-1}. The activation parameters for these reactions at $[H^+] = 0.030$ M are collected in Table IV.

A third extremely slow reaction was studied on the UV-visible spectrophotometer at 256 nm with $\mu = 0.1$ M ($LiClO_4$) at 25 and 45 °C (see Table III). This reaction took about a week to complete and was also found to be inversely dependent on the hydrogen-ion concentration.

TABLE V. Electronic Spectral Parameters of Cr(III) Complexes with Pentane-2,4-Dionato and 2,2′-Bipyridine Ligands.

Complex	λ_{max} (ϵ_{max}) nm (M^{-1} cm^{-1})	Number of Determinations
$[(OH_2)_2Cr(bipy)(ptdn)]^{2+}$	520 (36 ± 1)	4
	386 (354 ± 5)	4
	332sh (8600 ± 5)	4
	320sh (11,600 ± 40)	4
	306 (15,600 ± 300)	4
	245 (13,800 ± 200)	
$[(OH_2)_4Cr(bipy)]^{3+}$	528 (21 ± 1)	3
	442sh (23 ± 1)	3
	412sh (59 ± 4)	3
	388sh (82 ± 7)	3
	247 (5,900 ± 400)	3
	307 (8,500 ± 700)	3
$[(OH_2)_4Cr(ptdn)]^{2+}$ [a]	553 (26.8 ± 0.3)	
	392 (209 ± 1)	
	326 (8,150 ± 70)	
	253 (4,310 ± 30)	

[a] Values taken from ref. 4.

The spectral properties of the $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ complex isolated from the product studies were found to be closely approximated by the superposition of the spectra of $[Co(bipy)(OH_2)_4]^{3+}$ and $[Cr(ptdn)(OH_2)_4]^{2+}$ as expected (see Table V). The possibility that the spectrum is a result of a mixture of these latter two species is discounted because only a single band appeared on the column and several different product analyses gave identical spectral parameters. In addition, the CHN analysis (*vide supra*) indicates that one of each ligand is present in the solid product.

This compound accounted for 59 ± 4% of the reaction product by analysis of the total chromium in this band at 25 °C, under conditions of a ratio of Co(III) to Cr(II) of 1:1 (see Table VI). The upper portion of the reddish-orange band was found to be a mixture of $[Cr(bipy)(ptdn)(H_2O)_2]^{2+}$ and $[Cr(bipy)(H_2O)_4]^{2+}$. The eluent from this part of the band was passed through a second column containing SP Sephadex to effect a complete separation. The second band to be eluted was found to contain the $[Cr(bipy)(H_2O)_4]^{3+}$ ion by UV-visible spectral analysis. This species formed 39 ± 3% of the reaction product based on the amount of the initial cobalt(III) complex used.

Other product studies were accomplished using a cobalt to chromium ratio of 1:2 by reacting 116 μmol of $[Co(bipy)_2(ptdn)]^{2+}$ with 235 μmol of Cr(II). This resulted in the production of 95 ± 2% of $[Cr(bipy)(ptdn)(OH_2)_4]^{2+}$ and 27 ± 3% of $[Cr(bipy)(OH_2)_4]^{3+}$ based on the initial cobalt(III) complex used. Obviously, not all of these complexes could have arisen from the electron transfer process itself (*vide infra*). The column performed under conditions of chromium excess contained two additional bands at the top of resin bed. The lower of these bands contained the blue $[Cr(OH_2)_6]^{3+}$ and the upper was the green chromium(III) dimer; both these species arise from the air oxidation of excess chromium(II) in the solution. To determine if any of these substituted products could arise from substitution of free ligand on Cr(III) after the act of electron transfer, a product analysis of a reaction mixture which had been set aside for a week at ambient temperature was also performed. Only $[Cr(OH_2)_6]^{3+}$ and the green dimer were isolated after this period of time.

In an effort to determine how much Cr(II) interfered with the observed product distribution, another product study was performed under a five-fold excess of chromium(II). This resulted in the isolation of 97 ± 2% of the red $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ and 77% of the purple $[Cr(bipy)(OH_2)_4]^{2+}$ (see Table VI). These results and those of the 2:1 studies imply that if excess Cr(II) is present, essentially all of the available pentane-2,4-dione will be incorporated into the final product. However, even under conditions of five-fold excess of Cr(II), some free 2,2′-bipyridine remains in solution.

Addition of excess added 2,2′-bipyridine into the reaction mixture under 2:1 conditions at 45 °C gave 69 ± 1% of the $[Cr(bipy)(OH_2)_4]^{3+}$ material as compared to only 32 ± 3% when all the free ligand originated from the cobalt(III) compound (see Table VI). A similar experiment was performed

TABLE VI. Product Analysis Data for the Cr(II) Reduction of $[Co(bipy)_2(ptdn)]^{2+}$.

Temp. (°C)	[Cr(II)] μmol used	$[Co(bipy)_2(ptdn)]^{2+}$ μmol used	[bipy] μmol used	ptdn μmol used	$[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$		$[Cr(bipy)(OH_2)_4]^{3+}$	
					μmol recovered[a]	% recovered[a]	μmol recovered[a]	% recovered[a]
25.0	172	168			100 ± 7	59 ± 4	66 ± 4	39 ± 3
45.0	146	145			86 ± 5	59 ± 3	46 ± 6	32 ± 4
25.0	235	116			139 ± 3	95 ± 2	43 ± 6	27 ± 3
35.0	336	168			159 ± 3	94 ± 2	50 ± 4	29 ± 3
45.0	242(288)	119(141)			110 ± 1(129 ± 1)	92 ± 1	36 ± 4(47 ±1)	32 ± 3
45.0	724	145			140 ± 3	97 ± 2	112 ± 9	77 ± 6
45.0	219	110	221		109 ± 2	99 ± 2	76.0 ± 0.6	69 ± 1
45.0	219	110		110	116 ± 5	104 ± 4	14 ± 5	13 ± 4
45.0	280		280	140[b]	115 ± 3	82 ± 2[b]	60 ± 4	43 ± 3

[a] All values are averages of 3–6 runs, and all error limits give the actual spread of the measured data. The limits are *not* standard deviations which would be much smaller. [b] These values should be interpreted with some caution because of the extreme volability of free pentane-2,4-dione.

using pentane-2,4-dione as the added ligand. It is interesting to note that very little or none of this free ligand was incorporated into the $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ product and the amount of $[Cr(bipy)(OH_2)_4]^{3+}$ was *reduced* by about one-half (see Table VI).

A final series of product experiments were performed in which no cobalt(III) complex was used. The same concentrations of pentane-2,4-dione, 2,2′-bipyridine and Cr(II) were introduced as would be present under the 2:1 conditions commonly employed (see Table VI). It was found that 82 ± 2% of the $[Cr(bipy)(ptdn)(H_2O)_2]^{2+}$ and 43 ± 3% $[Cr(bipy)(OH_2)_4]^{3+}$ products were produced at 45 °C. This compares with 92 ± 1% of the former and 32 ± 3% of the latter when the same quantities of ligands were introduced by the cobalt(III) complex. Thus, at least 10% of the red $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ complex cannot be accounted for exclusively by substitution on Cr(II) alone. This implies that some of the product might, indeed, arise from an inner-sphere pathway.

Discussion

In an earlier communication on this work [3], we reported that the reaction of Cr(II) and $[Co(bipy)_2(ptdn)]^{2+}$ proceeded partly by a di-bridged attack of Cr(II) on an oxygen atom of a pentane-2,4-dione ring and simultaneously on the nitrogen of a transient mono-coordinated 2,2′-bipyridine ligand. The $[Cr(bipy)(OH_2)_4]^{3+}$ product was attributed to inner-sphere attack on only the mono-coordinated 2,2′-bipyridine molecule.

We have now performed an extensive series of product studies which establishes that capture of these chelated ligands by air oxidation of excess Cr(II) may also produce significant amounts of these compounds. There is no substitution of either pentane-2,4-dione or 2,2′-bipyridine on $[Cr(OH_2)_6]^{3+}$ during the reaction times employed in these experiments (⩽5 min.). The data in Table VI indicate that there is a strong synergistic effect operating with the two ligands. In all of the experiments in which excess Cr(II) is present, almost all of the available pentane-2,4-dione is consumed to produce $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ at the expense of $[Cr(bipy)(OH_2)_4]^{3+}$. The exception is the series of experiments in which excess ptdn was added. This resulted only in a marginal increase in the production of $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ but, surprisingly it also significantly depressed the appearance of $[Cr(bipy)(OH_2)_4]^{3+}$. Under conditions in which 2,2′-bipyridine is in excess, most of the pentane-2,4-dione is captured by Cr(II) to produce $[Cr(bipy)(ptdn)(OH_2)_4]^{2+}$ even when it is added as the free ligand, along with 2,2′-bipyridine (see final entry in Table VI). Thus,

TABLE VII. Kinetic Parameters for the First and Second Observed Reactions Calculated from the Plots of Figs. 1 and 2.

Reaction	k' (s^{-1})	kK_a (Ms^{-1})	k (s^{-1})[a]
$[Cr(bipy)(OH_2)_5]^{3+} \rightarrow [Cr(bipy)(OH_2)_4]^{3+}$	5.7×10^{-2}	4.4×10^{-2}	90
$[Cr(bipy)(OH_2)_5]^{2+} \rightarrow [Cr(bipy)(ptdn)(OH_2)_2]^{2+}$	1.67×10^{-1}	2.4×10^{-3}	5

[a] Calculated by assuming K_a is about 5×10^{-4}. See text.

if the product studies were performed with an excess of Cr(II) there would be no way to distinguish a true inner-sphere reaction from an outer-sphere process followed by capture of the liberated ligands during air oxidation of the excess Cr(II), and the product criterion for assigning redox mechanisms fails under these conditions.

There is also the possibility that the reaction does proceed either wholely or in part by an outer-sphere path, with the initially liberated bipy and ptdn ligands becoming attracted to free Cr(II) in solution. If these $[Cr(bipy)(ptdn)(OH_2)_2]^{1+}$ complexes react with $[Co(bipy)_2(ptdn)]^{2+}$ also by an outer-sphere process to give $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ and more free ligands, this could equally well account for the observed product distribution, even in the studies performed under equimolar conditions of oxidant and reductant. Alternatively, 2,2′-bipyridine could combine with Cr(II) to give $[Cr(bipy)(OH_2)_4]^{2+}$ which could react with $[Co(bipy)_2(ptdn)]^{2+}$ by an inner-sphere attack at the pentane-2,4-dione ring to give $[Cr(bipy)(ptdn)(OH_2)_4]^{3+}$ as the final product. There is little doubt but that at least one of these processes does, in fact, occur to some extent at least. If the solutions containing $[Cr(OH_2)_6]^{2+}$ and $[Co(bipy)_2(ptdn)]^{2+}$ are not rapidly stirred as they are combined, one obtains about 81 ± 5% of the red $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ and only 16 ± 1% of the purple $[Cr(bipy)(OH_2)_4]^{3+}$ complex at ambient temperatures. Incomplete mixing produces erratic results whereas very rapidly mixed solutions lead to the reproducible values listed in Table VI. Still, one cannot conclude on the basis of the product studies alone that the reaction proceeded by the inner-sphere routes.

The redox step itself proceeded too rapidly to be detected on the stopped-flow instrument even at the lowest possible concentrations of reactants ($[Co(bipy)_2(ptdn)]^{2+} = 2.55 \times 10^{-5}$ M, $[Cr(II)] = 1.17 \times 10^{-2}$ M) so that we calculate a lower limit of the rate constant to be 3×10^4 M^{-1} s^{-1} ($\mu = 0.10$ M ($LiClO_4$) and $[H^+] = 0.030$ M). Two fast reactions were observed, however, and both of them showed absorbance changes in the visible region. Since both exhibit first-order kinetics, they are most reasonably attributed to changes in ligand binding to chromium(III). By analogy to similar reductions of pentane-2,4-dione complexes of cobalt, the ring closure involving this ligand on chromium(III) will be too rapid to observe. The two reactions observed on the stopped-flow instrument were both assigned to ring closure involving the 2,2′-bipyridine ligand. The slow one, with $k_2 = 5.83 \times 10^{-2}$ s^{-1} at 25 °C should probably be assigned to closure of the 2,2′-bipyridine ring on the $[Cr(bipy)(ptdn)(OH_2)_2]^{2+}$ complex, since the presence of a pentane-2,4-dionato ligand on Cr(III) should decrease its electrophilicity. The fast reaction, with $k_1 = 5.06 \times 10^{-1}$ s^{-1} is then assigned to a similar ring-closure reaction to give $[Cr(bipy)(OH_2)_4]^{3+}$ from the monodentate precursor $[Cr(bipy)(OH_2)_5]^{3+}$. This assignment is supported by the fact that these reactions are both inversely dependent on the $[H^+]$. The ring-closure should be faster when the pyridine N is not protonated. If the primes represent reaction of the protonated species, then the rate law derived for these ring closure steps is

$$-\frac{d[Cr(III)]}{dt} = \left[\frac{k'[H^+] + kK_a}{K_a + [H^+]}\right][Cr(III)] \qquad (2)$$

where [Cr(III)] represents the total concentration of the protonated and unprotonated forms of the respective chromium(III) complex (either $[Cr(bipy)(ptdn)(OH_2)_3]^{2+}$ or $[Cr(bipy)(OH_2)_5]^{3+}$). The pK_a for free 2,2′-bipyridine [9] is 5.62×10^{-6} and although co-ordination to chromium(III) would likely increase this value, it is likely that a good approximation is still that $[H^+] \gg K_a$ and eqn. 2 reduces to the form of the observed eqn. 1. Values of k' and kK_a are collected in Table VII. Assuming that co-ordination to a metal lowers the pK_a by about two units [10], then K_a for the $[Cr(bipy)(OH_2)_5]^{3+} \rightleftarrows [Cr(bipyH)(OH_2)_5]^{4+}$ and the $[Cr(bipy)(ptdn)(OH_2)_3]^{2+} \rightleftarrows [Cr(bipyH)(ptdn)(OH_2)_3]^{3+}$ reactions would be about 5×10^{-4}. Thus, we can estimate that the rates of reduction of the protonated species are about 90 s^{-1} and 5 s^{-1}, respectively. From these data we see that the ring closure of the unprotonated complex proceeds faster than that of the protonated species, as expected. The extremely slow reaction observed on the spectrophotometer was attributed to the decomposition of the Cr(III) products. At the completion of this reaction, a product analysis showed that only $[Cr(OH_2)_6]^{3+}$ was present.

The possibility that the observed reactions could arise from the Cr(II) reduction of free 2,2′-bipyridine was discounted by following the reaction between these two species separately. Two fast reactions were observed on the stopped-flow instrument but both were found to be dependent on the concentration of [Cr(II)], unlike the two reactions associated with the cobalt complex. The first showed an increase in absorbance with a rate constant of $k = 3.17 \times 10^3\ M^{-1}\ s^{-1}$ at 400 nm and the second showed an absorbance decrease at 360 nm with $k = 2.47 \times 10^1\ M^{-1}\ s^{-1}$ at 25.0 °C. Both reactions displayed a hydrogen ion dependence. The results of this study will be reported later.

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