

infrared-active modes are Raman inactive, and *vice versa*. The coincidence of bands in the infrared and Raman spectra (Table I), especially those in the low-frequency region which have been assigned to M–O and M–X stretching modes, indicates that the  $M(\text{acac})_2X_2$  complexes exist in solution as the *cis* isomer. The *cis* structure was suggested for the zirconium and hafnium complexes by nmr chemical shift data,<sup>3</sup> and this stereochemistry has been well established for the analogous titanium<sup>37,38</sup> and tin<sup>19,39–41</sup> compounds.

Infrared and Raman spectra of the *cis* isomers should show two M–X stretching vibrations—a symmetric, Raman-polarized mode and an asymmetric

mode. In spectra of the  $M(\text{acac})_2X_2$  complexes the single, rather broad M–X stretching band is generally not resolved. Only in infrared spectra of the solid dichlorides and of  $\text{Hf}(\text{acac})_2\text{Cl}_2$  in dichloromethane were two M–X bands observed, and even in these cases the frequency separation between the symmetric and asymmetric components was only *ca.* 10  $\text{cm}^{-1}$ . Similar small-frequency separations and lack of resolution have been reported in infrared studies of other *cis*-dihalometal acetylacetonates.<sup>14,19,36,37</sup>

Infrared and Raman spectra afford no clue to the stereochemistry of the seven-coordinate  $M(\text{acac})_3X$  complexes because of the low symmetry of the possible geometrical isomers.

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(37) R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Letters*, **3**, 117 (1967).

(38) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).

(39) J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

(40) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc., Sect. A*, 1749 (1966).

(41) W. H. Nelson, *Inorg. Chem.*, **6**, 1509 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
STATE UNIVERSITY OF NEW YORK AT BUFFALO, BUFFALO, NEW YORK 14214

## Electron-Transfer Rate Studies of a Number of Cobalt(II)–Cobalt(III) Systems

BY ROBERT FARINA AND RALPH G. WILKINS

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The kinetics have been studied of the oxidation of  $\text{Co}(\text{terpy})_2^{2+}$  by a series of cobalt(III) oxidants,  $\text{Co}(\text{bipy})_n(\text{H}_2\text{O})_{6-2n}^{3+}$  and  $\text{Co}(\text{phen})_n(\text{H}_2\text{O})_{6-2n}^{3+}$ ,  $n = 0-3$ , as well as the reaction of  $\text{Co}(\text{py})_4\text{Cl}_2^+$  with a series of cobalt(II) reductants,  $\text{Co}(\text{phen})_3^{2+}$ ,  $\text{Co}(\text{bipy})_3^{2+}$ , and  $\text{Co}(\text{terpy})_2^{2+}$ . The effect of (a) free energy drive, (b) aquo compared with hydroxo species, and (c) electronic configuration on the rates of these outer-sphere reactions could therefore be assessed. The reaction rate constant for the redox reaction between  $\text{Cr}(\text{bipy})_3^{3+}$  and  $\text{Cr}(\text{terpy})_2^{3+}$  exceeded  $3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ .

### Introduction

Outer-sphere redox reactions do not involve bond cleavage during electron transfer and attention has been mainly focused on these types of reactions by the theoreticians.<sup>1</sup> In the present work we have investigated the kinetics of oxidation of a common reductant,  $\text{Co}(\text{terpy})_2^{2+}$ , by a series of cobalt(III) oxidants,  $\text{Co}(\text{bipy})_n(\text{H}_2\text{O})_{6-2n}^{3+}$  and  $\text{Co}(\text{phen})_n(\text{H}_2\text{O})_{6-2n}^{3+}$ ,  $n = 0-3$ , as well as  $\text{Co}(\text{tmp})_3^{3+}$ , tmp = 3,5,6,8-tetramethyl-1,10-phenanthroline. We have also studied the reaction of a common oxidant,  $\text{Co}(\text{py})_4\text{Cl}_2^+$ , by a series of cobalt(II) reductants,  $\text{Co}(\text{phen})_3^{2+}$ ,  $\text{Co}(\text{bipy})_3^{2+}$ , and  $\text{Co}(\text{terpy})_2^{2+}$ . This allows us to examine in a systematic way the effect of (a) free energy drive, (b) the relative reactivity of aquo and hydroxo species, and (c) electronic configuration, specifically low- and high-spin cobalt(II), on the rates of outer-sphere reactions. These systems were chosen because we have useful information on the kinetics of isotopic exchange<sup>2</sup> among  $\text{Co}(\text{phen})_3^{2+}$ – $\text{Co}(\text{phen})_3^{3+}$ ,  $\text{Co}(\text{bipy})_3^{2+}$ – $\text{Co}(\text{bi-}$

$\text{py})_3^{3+}$ , and  $\text{Co}(\text{terpy})_2^{2+}$ – $\text{Co}(\text{terpy})_2^{3+}$  and the lability in neutral and acid media of the cobalt (II) complexes,<sup>3</sup> both important for interpretive purposes.

### Experimental Section

**Materials.**—Crude 2,2'-bipyridine was a gift from Imperial Chemical Industries Ltd., through the courtesy of Dr. A. Jubb. It was purified by heating *in vacuo* at 130° and recrystallizing the sublimate from absolute ethanol. Other chemicals used were commercial products. A number of solid complexes were prepared by literature methods and characterized by their spectra. These included (references refer to preparation and spectra, respectively)  $\text{Co}(\text{bipy})_3(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ ,<sup>4,5</sup>  $\text{Co}(\text{phen})_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ ,<sup>2,6</sup>  $\text{Co}(\text{terpy})_2(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ ,<sup>2,7</sup> *cis*- and *trans*- $\text{Co}(\text{bipy})_2\text{Cl}_3$ .

(2) (a) B. R. Baker, F. Basolo, and H. M. Neumann, *J. Phys. Chem.*, **63**, 371 (1959). (b) H. M. Neumann, private communication, has completed an extensive investigation of the  $\text{Co}(\text{bipy})_3^{2+}$ – $\text{Co}(\text{bipy})_3^{3+}$  and  $\text{Co}(\text{phen})_3^{2+}$ – $\text{Co}(\text{phen})_3^{3+}$  systems using optically active cobalt(III) complexes. Values for  $\Delta H^\ddagger$  (7.7 and 5.1 kcal mole<sup>-1</sup>) and  $\Delta S^\ddagger$  (–27 and –34 eu) were determined in 0.1 M  $\text{KNO}_3$ .

(3) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965); **5**, 622 (1966); R. Farina, R. Hogg, and R. G. Wilkins, *ibid.*, **7**, 170 (1968).

(4) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(5) B. Martin and G. M. Waind, *ibid.*, 4284 (1958).

(6) G. Favini and E. Paglia, *J. Inorg. Nucl. Chem.*, **8**, 155 (1958).

(7) <sup>†</sup>Spectral peaks at 338  $\text{m}\mu$  ( $\epsilon$  2.1  $\times 10^4$ ), 278  $\text{m}\mu$  ( $\epsilon$  4.8  $\times 10^4$ ), and 210–220  $\text{m}\mu$  ( $\epsilon$  6–9  $\times 10^4$ ).

(1) For recent accounts and literature see W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press Co., New York, N. Y., 1966; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 454.

$2\text{H}_2\text{O}$  (violet and green, respectively),<sup>8</sup> *cis*-Co(phen)<sub>2</sub>Cl<sub>3</sub>·3H<sub>2</sub>O (violet)<sup>9</sup> and *trans*-Co(phen)<sub>2</sub>Cl<sub>3</sub>·4H<sub>2</sub>O (green).<sup>10</sup> In the last case it was found necessary to reflux Co(phen)<sub>3</sub>Cl<sub>3</sub> many hours in chloroform to effect complete conversion to the bis form. Co(py)<sub>4</sub>Cl<sub>3</sub>·6H<sub>2</sub>O was prepared by the method of Feenstra and Werner.<sup>11</sup> Cobalt(II) complexes prepared included Co(bipy)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>,<sup>4,12</sup> Co(phen)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>,<sup>13</sup> Co(terpy)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O,<sup>14</sup> and Co(phen)<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O.<sup>14</sup>

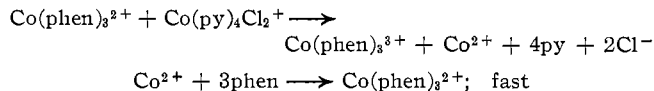
The remaining species were prepared and used *in situ*. The Co(bipy)<sub>2</sub><sup>3+</sup> and Co(phen)<sub>2</sub><sup>2+</sup> ions form in solutions of ligand and excess cobalt(II) ions (mole ratio 1:10). Oxidation by Co<sup>3+</sup>(aq) (in an amount equivalent to ligand) produces Co(bipy)<sub>2</sub><sup>3+</sup> and Co(phen)<sub>2</sub><sup>3+</sup>, respectively. The reactants are left about 1 hr to ensure complete reaction. The Co(III) species have similar broad bands at 510–520 mμ (ε 25) but are sufficiently different at 430 mμ to allow use of this wavelength in the kinetic runs. Co<sup>3+</sup>(aq) was generated by electrooxidation of Co(ClO<sub>4</sub>)<sub>2</sub> in HClO<sub>4</sub> at ~4°. The concentration was estimated spectrally (ε<sub>605</sub> 37).<sup>15</sup> Solutions were stored in a refrigerator. Co(tmp)<sub>3</sub><sup>3+</sup> ion was prepared by oxidation of a solution of cobalt(II) and tmp (1:4) with H<sub>2</sub>O<sub>2</sub>. The solution was boiled until a test for H<sub>2</sub>O<sub>2</sub> was negative. The ion has peaks at 283 mμ (ε 4.6 × 10<sup>4</sup>), 240 mμ (5.5 × 10<sup>4</sup>), and 210 mμ (4.6 × 10<sup>4</sup>). Cr(terpy)<sub>2</sub><sup>2+</sup> and Cr(bipy)<sub>3</sub><sup>2+</sup> ions were prepared in solution by adding an excess of ligand (~3.5 terpy and 15 bipy per chromium atom) to chromium(II) solution in an acetate-acetic acid buffer at pH 4.2. The brown Cr(terpy)<sub>2</sub><sup>2+</sup> ion has maxima at 565 mμ (shoulder, ε<sub>M</sub> 2.0 × 10<sup>3</sup>), 496 mμ (ε<sub>M</sub> 3.8 × 10<sup>3</sup>), and 395 mμ (ε<sub>M</sub> 5.1 × 10<sup>3</sup>). The wine red Cr(bipy)<sub>3</sub><sup>2+</sup> has maxima at 563 mμ (ε<sub>M</sub> 4.3 × 10<sup>3</sup>) and 470 mμ (ε<sub>M</sub> 4.2 × 10<sup>3</sup>). The corresponding Cr(III) complexes have much lower absorption above 500 mμ. Chromium(II) ion was prepared either by electrolytic reduction of chromium(III) or, more conveniently, by dissolving chromium pellets (United Mineral and Chemical Corp.) in 0.3 M HClO<sub>4</sub>, which takes place slowly over several days. The blue solution contains <3% Cr(III), but chloride was produced, which did not however interfere with the redox experiments. Cr(terpy)<sub>2</sub><sup>3+</sup> ion was prepared in solution by chlorine oxidation of Cr(terpy)<sub>2</sub><sup>2+</sup> or from dissolution of solid Cr(terpy)<sub>2</sub>Cl<sub>3</sub>. Handling of chromium(II) species was in the complete absence of oxygen.

**Analyses.**—Bipyridine and phenanthroline were determined in the bis-cobalt(III) complexes by reducing with S<sub>2</sub>O<sub>4</sub><sup>2-</sup> in mildly alkaline solution. After slight acidification, bipy and phen were estimated in the cobalt(II) complex by reaction with ferrous ion and estimation of the resultant tris-iron(II) complex spectrally.

**Anal.** Calcd for *cis*- and *trans*-Co(bipy)<sub>2</sub>Cl<sub>3</sub>·2H<sub>2</sub>O: bipy, 60.8. Found: *cis*, 58.6; *trans*, 59.6. Calcd for *cis*-Co(phen)<sub>2</sub>Cl<sub>3</sub>·3H<sub>2</sub>O: phen, 62.2. Found: 61.5. Calcd for *trans*-Co(phen)<sub>2</sub>Cl<sub>3</sub>·4H<sub>2</sub>O: phen, 60.3. Found: 59.5.

**Kinetic Experiments.**—A glass-Lucite stopped-flow apparatus or occasionally a Cary 14 was used in these experiments. All reactions involving a loss of Co(terpy)<sub>2</sub><sup>2+</sup> were followed at 510 mμ (ε 1.4 × 10<sup>3</sup>). All other cobalt complexes have low absorption in this region. The oxidant was used in sufficient excess to ensure that the reaction went to completion. Fresh solutions of solid Co(terpy)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> in water were used as the source of Co(terpy)<sub>2</sub><sup>2+</sup> ion to avoid excess terpyridine which attacks cobalt(II) products and produces erroneous kinetic traces. In the reaction between Co(terpy)<sub>2</sub><sup>2+</sup> and Co(py)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> low reactant con-

centrations had to be used to produce measurable times. The gain of Co(terpy)<sub>2</sub><sup>3+</sup> was followed at 310 mμ. In reactions of Co(bipy)<sub>3</sub><sup>2+</sup> and Co(phen)<sub>3</sub><sup>2+</sup> with Co(py)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>, the reductant and free ligand were used in excess. The net change



Cl<sub>2</sub><sup>+</sup> → Co(phen)<sub>3</sub><sup>3+</sup> was an increase of optical density at 305 mμ (320 mμ with bipy complex). The Co(phen)<sub>2</sub><sup>2+</sup> + Co(bipy)<sub>2</sub><sup>3+</sup> reaction was followed on a Cary 14 at 430 mμ where most of the absorption is contributed by Co(phen)<sub>2</sub><sup>3+</sup>. The presence of a large excess of Co<sup>2+</sup>(aq) maintains cobalt(II) reactant and product as the mono species. In the reactions at higher acid concentrations, pseudo-first-order kinetics are still observed, but the concurrent loss of Co(terpy)<sub>2</sub><sup>2+</sup> by dissociation must be allowed for, and  $k_{\text{obsd}} = k_{\text{dissociation}} + k_2[\text{Co(III)}]$ . The value of  $k_{\text{dissociation}}$  was determined in separate experiments,<sup>3</sup> thus allowing calculation of the desired second-order redox constant  $k_2$ . The correction for dissociation was considerable at pH ≤ 1.4 at all temperatures. The value of  $k_2$  determined at pH 2.3 was very close to the corrected value determined at pH 1.4 for the Co(terpy)<sub>2</sub><sup>2+</sup> + Co(phen)<sub>3</sub><sup>3+</sup> reaction. The loss of Cr(bipy)<sub>3</sub><sup>2+</sup> was followed at the peak maximum at 563 mμ (ε 4.3 × 10<sup>3</sup>). Oxidation by Co(bipy)<sub>3</sub><sup>3+</sup> and Cr(terpy)<sub>2</sub><sup>3+</sup> was complete with the experimental conditions used, as shown by spectral measurements. The experiments involving Cr(II) complexes were carried out with the rigorous exclusion of oxygen. Sodium perchlorate and perchloric acid were used to adjust the ionic strength and pH. The ionic strength was often 0.05 M but sometimes the value was dictated by requiring a measurable half-life or by the necessity to use high [H<sup>+</sup>] or [Co<sup>2+</sup>]. Errors in  $k_2$  are about ±7% in ΔH\* (±1.0–1.5 kcal mole<sup>-1</sup>) and in ΔS\* (±3–5 eu).<sup>16</sup>

**Redox Potentials.**—These were measured using Pt and saturated calomel electrodes in conjunction with a Radiometer Type TTTIC titrator or, for  $E \leq -0.6$  V, a Leeds and Northrup Universal Type K-3 potentiometer with a high-resistance Leeds and Northrup galvanometer. Equimolar concentrations (~10<sup>-4</sup> M) of the pair of the redox couple were used at the ionic strength of the relevant kinetic experiments. Measurements were made at ~0° (as well as at 25° for the highest species only). With the bis-phenanthroline couple, readings were taken quickly before disproportionation of Co(phen)<sub>2</sub><sup>2+</sup> could occur. The values with an uncertainty of ±0.02 are included in Table I. Those of the tris systems are in satisfactory agreement with the literature.<sup>17</sup> Support for the values was shown by the fact that ferrous ion ( $E = -0.77$  V) did not reduce Co(phen)<sub>3</sub><sup>3+</sup> or Co(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> but was oxidized by Co(phen)(H<sub>2</sub>O)<sub>3</sub><sup>3+</sup> (+Co<sup>2+</sup>(aq)). The presence of Fe<sup>2+</sup>(aq) was detected by bipyridyl solution. The redox potential of Cr(bipy)<sub>3</sub><sup>2+</sup> (-0.34 V) was determined in the presence of N<sub>2</sub>.

## Results and Discussion

Several of the reactions were shown, and the remainder were assumed, to be second order. The rate constants at 0° and the associated enthalpies and entropies of activation are collected in Table I. As it turned out the results with the phenanthroline complexes largely duplicated, but thereby reinforced

(8) F. M. Jaeger and J. A. Van Dijk, *Z. Anorg. Allgem. Chem.*, **227**, 317 (1936).

(9) A. V. Ablov, *Russ. J. Inorg. Chem.*, **6**, 157 (1961).

(10) P. Pfeiffer and B. Werdelmann, *Z. Anorg. Allgem. Chem.*, **263**, 37 (1950).

(11) R. Feenstra and A. Werner, *Ber.*, **39**, 1538 (1905). We find peaks at 635 mμ (ε 37), 510 mμ (ε 28), and 295 mμ (ε 4.0 × 10<sup>3</sup>).

(12) H. L. Schläfer, *Z. Physik. Chem.*, **8**, 377 (1956).

(13) P. Pfeiffer and B. Werdelmann, *Z. Anorg. Chem.*, **261**, 197 (1950).

(14) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962); P. Ellis and R. G. Wilkins, *ibid.*, 299 (1959).

(15) T. J. Conocchioni, G. H. Nancollas, and N. Sutin, *Inorg. Chem.*, **5**, 1 (1966).

(16) A table of detailed data has been deposited as Document No. 9780 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(17) E. Paglia and C. Sironi, *Gazz. Chim. Ital.*, **87**, 1125 (1957), give -0.42 and -0.37 V for Co(phen)<sub>2</sub><sup>2+</sup>-Co(phen)<sub>3</sub><sup>3+</sup> and Co(bipy)<sub>2</sub><sup>2+</sup>-Co(bipy)<sub>3</sub><sup>2+</sup> couples, respectively.

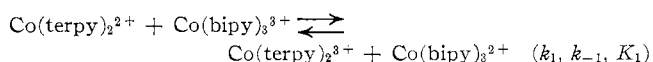
TABLE I  
 REDOX RATE AND POTENTIAL DATA WITH COBALT SYSTEMS AT 0°

Reductant	Oxidant	$k_2$ , $M^{-1} \text{ sec}^{-1} (I)^e$	$k_{\text{calcd}}^d$ , $M^{-1} \text{ sec}^{-1}$	$\Delta H^*$ , kcal mole <sup>-1</sup>	$\Delta S^*$ , eu
Co(terpy) <sub>2</sub> <sup>2+</sup> ( $E^\circ = -0.31$ )	Co(bipy) <sub>3</sub> <sup>3+</sup> ( $E^\circ = +0.34$ )	$6.4 \times 10$ (0.05)	$3.2 \times 10$	8.4	-19
Co(bipy) <sub>3</sub> <sup>2+</sup>	Co(terpy) <sub>2</sub> <sup>3+</sup>	$2.7 \times 10$ (0.05)		8.7	-20
Co(terpy) <sub>2</sub> <sup>2+</sup>	Co(phen) <sub>3</sub> <sup>3+</sup> ( $E^\circ = +0.40$ )	$2.8 \times 10^2$ (0.05)	$1.1 \times 10^3$	6.9	-21
	Co(tmp) <sub>3</sub> <sup>3+</sup>	$4.8 \times 10$ (0.05) <sup>a</sup>		11.7	-8
	Co(bipy) <sub>2</sub> <sup>3+</sup>	$6.8 \times 10$ (0.02) <sup>a</sup>		10.6	-12
	Co(phen) <sub>2</sub> <sup>3+</sup> ( $E^\circ = +0.68$ )	$1.3 \times 10^4$ (0.05) <sup>b</sup>		4.2	-24
	Co(bipy) <sub>3</sub> <sup>3+</sup> ( $E^\circ = +0.84$ )	$3.0 \times 10^4$ (0.05) <sup>b</sup>		4.3	-22
	Co(phen) <sub>3</sub> <sup>3+</sup> ( $E^\circ = +0.84$ )	$6.8 \times 10^2$ (0.05)	$6.4 \times 10^4$	10.8	-6
	Co <sup>3+</sup> (aq) ( $E^\circ = 1.8^\circ$ )	$1.4 \times 10^3$ (0.05)	$6.4 \times 10^4$	10.9	-4
	Co(OH) <sub>2</sub> <sup>2+</sup>	$7.4 \times 10^4$ (1.0)	$2 \times 10^{10}$	3.4	-23
	<i>trans</i> - Co(py) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	$1.7 \times 10^4$ (0.027)		5.1	-20
Co(terpy) <sub>2</sub> <sup>2+</sup>	Co(py) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	$3.0 \times 10^6$ (0.00016)		5.2	-14
Co(bipy) <sub>3</sub> <sup>2+</sup>	Co(py) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	$1.1 \times 10^4$ (0.00016)		5.2	-20
Co(phen) <sub>3</sub> <sup>2+</sup>	Co(py) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	$9.1 \times 10^3$ (0.00016)		8.4	-12
Co(phen) <sub>2</sub> <sup>2+</sup>	Co(bipy) <sub>3</sub> <sup>3+</sup>	0.06 (1.55)		8.7	-30

<sup>a</sup> 95% ethanol solvent. <sup>b</sup> Using the *cis*-dichloro compound. Starting with *trans*, similar  $k_2$  and  $\Delta H^*$ . <sup>c</sup> W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952; D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, 3490 (1964). <sup>d</sup> Calculated on the basis of eq 2. The appropriate isotopic exchange rate constants ( $M^{-1} \text{ sec}^{-1}$ ) at 0° used were: Co(bipy)<sub>3</sub><sup>2+</sup>-Co(bipy)<sub>3</sub><sup>3+</sup>, 9.0; Co(phen)<sub>3</sub><sup>2+</sup>-Co(phen)<sub>3</sub><sup>3+</sup>, 4.8; Co(terpy)<sub>2</sub><sup>2+</sup>-Co(terpy)<sub>2</sub><sup>3+</sup>, 48 (these values were estimated from ref 2 using eq 1); Co(bipy)<sub>2</sub><sup>2+</sup>-Co(bipy)<sub>3</sub><sup>3+</sup> and Co(phen)<sub>2</sub><sup>2+</sup>-Co(phen)<sub>3</sub><sup>3+</sup>, 0.04 (this work); and Co<sup>2+</sup>-Co<sup>3+</sup>, 0.6 (Table II). <sup>e</sup> Ionic strength.

the validity of, the trends shown by the bipyridine complexes.

**A. Electron Transfer between the Highest Cobalt-(II)-Cobalt(III) Species.**—These were the most extensively investigated systems since the rates and redox potentials were easily measurable and direct comparison with the isotopic exchange results<sup>2</sup> was possible. All of the reactions in this group must be outer-sphere redox processes because of the inert character of the cobalt(II)<sup>3</sup> and cobalt(III) complexes. The reaction



was studied in both directions by using sufficient excess of one reagent. The ratio  $k_1/k_{-1}$  (2.2-2.4) varies little over a range of temperature (4-29°) and is in quite satisfactory agreement with the value estimated from the redox potentials ( $K_1 = 3.2 \pm 1.0$  at 25°) and from direct spectrophotometry of equilibrated solutions ( $K_1 = 3.0 \pm 0.5$  at 19°). The small values of  $\Delta H_1$  ( $\Delta H_1^* - \Delta H_{-1}^* = -0.3$  kcal mole<sup>-1</sup>) and  $\Delta S_1$  (+1 eu) show how well this reaction with a small free energy change simulates an isotopic exchange. The oxidation of Co(terpy)<sub>2</sub><sup>2+</sup> by Co(phen)<sub>3</sub><sup>3+</sup> was used to study the effect of ionic strength (using KNO<sub>3</sub> as the added electrolyte) on the rate constant associated with these highly charged reactants. The expected increase in the rate constant with increasing ionic strength is observed. We use expression 1,<sup>18</sup> where  $a$  is the mean

$$\log k_I = \log k_0 + \frac{1.02Z_A Z_B \sqrt{I}}{1 + (0.33 \times 10^8 a \sqrt{I})} \quad (1)$$

(18) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 150.

distance for closest approach. An estimate for  $a/2$  of 5.8 Å was made, this being the radii of the two reacting ions assuming spherical geometry for the reactants.<sup>19</sup> Therefore a plot of  $\log k$  against  $\sqrt{I}/(1 + 3.5\sqrt{I})$  was linear with a slope 6.1 which is agreeably close to the expected product of  $Z_A Z_B$ . However since rather high ionic strengths were used, the agreement may be fortuitous. No attempt was made in this study to investigate the effect of the nature of the anion on the rates of these reactions although this is known to be marked.<sup>2</sup>

A value for the rate constants for the two reactions already considered ( $k_{12}$ ) can be calculated from a theoretical relation which has been derived for outer-sphere redox reactions<sup>20</sup>

$$k_{12} = (k_{11} k_{22} K_{12} f)^{1/2} \quad (2)$$

$$\log f = (\log K_{12})^2 / 4 \log (k_{11} k_{22} / Z^2)$$

Here  $k_{11}$  and  $k_{22}$  are the appropriate isotopic exchange rate constants, e.g., for Co(terpy)<sub>2</sub><sup>2+</sup>-Co(terpy)<sub>2</sub><sup>3+</sup> and Co(bipy)<sub>3</sub><sup>2+</sup>-Co(bipy)<sub>3</sub><sup>3+</sup> in the first reaction we considered, and  $K_{12}$  is the equilibrium constant, which can be derived from the redox potentials,  $\log K_{12} = 16.9\Delta E^\circ$  at 25° or  $18.4\Delta E^\circ$  at 0°. The calculated rate constants are shown in Table I and agreement with the experimental value is good. The  $\Delta H^*$  and  $\Delta S^*$  values for this group are quite close to the corresponding isotopic exchange rate constants.<sup>2b</sup> The effect of heavy methyl substituted in the phenanthroline ring on the rate was investigated using Co(tmp)<sub>3</sub><sup>3+</sup> (tmp: 3,5,6,8-tetramethyl-1,10-phenanthroline). Because of solu-

(19) A. V. Ablov and D. M. Palade, *Russ J. Inorg. Chem.*, **6**, 306 (1961).

(20) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

bility problems the study had to be made in 95% alcohol and so a comparison was made with  $\text{Co}(\text{phen})_3^{3+}$ , also in 95% alcohol. The kinetic constants were very similar for the two systems so that the steric importance of 12 peripheral methyl groups on the ease of electron transfer is small. Indeed the rate constant for  $\text{Co}(\text{phen})_3^{3+}$  in alcohol is similar to that in water but only because of compensating, markedly larger values for  $\Delta H^*$  and  $\Delta S^*$ . Medium effects on the rate of redox reactions have been little studied and would be a fruitful area for research.

**B. Bis-Cobalt(III) Oxidants.**—Our source of the  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{3+}$  and  $\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2^{3+}$  ions was the corresponding dichlorochloride solid which aquates rapidly on dissolution in water.<sup>21</sup> The surprising lability of the systems suggests that *cis*, *trans* rearrangements may also be rapid and that whether we start with green or purple (considered *trans* or *cis*)  $[\text{CoL}_2\text{Cl}_2]\text{Cl}$ , L = bipy or phen, we shall have the same unknown equilibrium mixture in solution. This is supported by recent findings of Vlček,<sup>22</sup> who showed that both *cis*- and *trans*- $[\text{Co}(\text{dipy})_2\text{Cl}_2]\text{Cl}$  aquate to a common diaquo species ( $\epsilon_{610}$  70) which is also obtained by acidification of the carbonate complex. The redox rate constant in our work is the same whether solutions are prepared from the *cis* or *trans* solid and we conclude that the reactant is either pure *cis*- or *trans*- $\text{CoL}_2(\text{H}_2\text{O})_2^{3+}$  or a labile mixture. We were thus unable to look at the effect of stereoisomerism in this series.

Ablov and Palade have determined  $pK$  values of 4.2 and 6.6 at 25°,  $I = 0.25$  for the  $\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2^{3+}$  ion.<sup>19</sup> The solution of *cis*- $[\text{Co}(\text{bipy})_2\text{Cl}_2]\text{Cl}$  in 0.02 *M* HCl has an absorption peak at 505  $m\mu$  ( $\epsilon$  60). In 0.02 *M* NaOH the peak is shifted to 530  $m\mu$  ( $\epsilon$  72).<sup>23</sup> In our redox experiments therefore at pH  $\sim 2$ , we are investigating the diaquo complex and at pH  $\sim 6$  we have mixtures of the mono- and dihydroxo species. The small effect of pH on the rate constant strongly suggests that these are outer-sphere redox reactions since the hydroxo grouping is an effective bridging group and a marked rate-enhancer in inner-sphere reactions.<sup>24</sup> The enhanced rate of the dihydroxo species expected from electrostatic considerations could be offset by a slight decrease in the redox potential when  $\text{H}_2\text{O}$  is replaced by OH.

Unlike the bipyridine analog, the  $\text{Co}(\text{py})_4\text{Cl}_2^+$  ion is remarkably stable to hydrolysis and aquates, with decomposition, with a half-life of some 23 hr at 25°. The relative slowness of substitution in the  $\text{Co}(\text{terpy})_2^{2+}$ ,  $\text{Co}(\text{phen})_3^{2+}$ , and  $\text{Co}(\text{bipy})_3^{2+}$  ions, of the order of seconds or longer,<sup>3</sup> shows that oxidation by  $\text{Co}(\text{py})_4\text{Cl}_2^+$  must be outer sphere. That we must

consider  $\text{Co}(\text{py})_4\text{Cl}_2^+$  as a potential inner-sphere oxidant is shown by its rapid production of  $\text{Co}(\text{EDTA})\text{Cl}_2^-$  when treated with the  $\text{Co}(\text{EDTA})^{2-}$  ion.<sup>26</sup> On the other hand, a solution of  $[\text{Co}(\text{bipy})_2\text{Cl}_2]\text{Cl}$  in water reacted very slowly with  $\text{Co}(\text{EDTA})^{2-}$  to form  $\text{Co}(\text{EDTA})^-$  presumably by an outer-sphere reaction. This again emphasizes the presence and absence of coordinated chloride in fresh solutions of the pyridine and bipyridine complexes, respectively. The enhanced reactivity of  $\text{Co}(\text{py})_4\text{Cl}_2^+$  compared with  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{3+}$  resides in a more positive  $\Delta S^*$  possibly arising from a reduced positive charge product ( $1 \times 2$  compared with  $3 \times 2$ ) for reactants. This oxidant was used to study the relative reductant ability of high-spin<sup>27</sup>  $\text{Co}(\text{bipy})_3^{2+}$  and  $\text{Co}(\text{phen})_3^{2+}$  and low-spin<sup>27</sup>  $\text{Co}(\text{terpy})_2^{2+}$ . The absence of any dramatic differences indicates that spin multiplicity changes, although they must occur in the oxidation of the high-spin cobalt(II) complexes but not the low-spin terpyridinecobalt(II) complex, are relatively unimportant. This is probably because the former complexes can be easily excited from the spin-free to the spin-paired state prior to electron transfer.

**C. Monocobalt(III) Oxidants.**—These complex species have not been previously described. We have prepared them *in situ* by oxidation of the corresponding cobalt(II) mono species with  $\text{Co}^{3+}(\text{aq})$  in the presence of excess  $\text{Co}^{2+}(\text{aq})$ . They are strong oxidants and are probably the tetraaquo species at pH  $\sim 1$ , although we have not investigated this point. The similar rate constant in neutral solution indicates that, with the mono species also, the hydroxo and aquo complexes react at similar rates. Since we have been able to measure the rate constant for the  $\text{Co}(\text{phen})^{2+} + \text{Co}(\text{bipy})^{3+}$  reaction, we can use this value justifiably for the  $\text{Co}(\text{phen})^{2+}$ - $\text{Co}(\text{phen})^{3+}$  isotopic exchange rate constant for application of the Marcus equation. The agreement between calculated and observed rate constants is only fair (Table I) with differences of two orders of magnitude. The rate constant measured for the  $\text{Co}(\text{phen})^{2+}$ - $\text{Co}(\text{bipy})^{3+}$  system is little different at ionic strengths of 1.55 and 0.67 so that using this value in eq 2 instead of one measured at  $I = 0.05$  *M* introduces only a small error and can only in small part account for the large differences. These reactions are also odd in having unusually high  $\Delta H^*$  and  $\Delta S^*$  values of 11 kcal mole<sup>-1</sup> and  $-5$  eu, respectively, compared with the other reactions in the series (4–8 kcal mole<sup>-1</sup> and  $-20$  eu, respectively).

**D. Cobalt(III) Ion Oxidant.**—The rate constant for oxidation of  $\text{Co}(\text{terpy})_2^{2+}$  is only slightly dependent on hydrogen ion concentration from 0.05 to 1.0 *M*, and if we use what is probably the most reliable  $pK$  value

(21) F. Basolo, R. E. Meeker, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **1**, 341 (1955).

(22) A. Vlček, *Inorg. Chem.*, **6**, 1425 (1967).

(23) A similar shift to higher wavelengths is observed when  $\text{Cr}(\text{bipy})_2(\text{H}_2\text{O})_2^{3+}$  is made alkaline: J. Bjerrum and R. G. Inskeep, *Acta Chem. Scand.*, **15**, 82 (1961).

(24) H. Taube and A. M. Zwickel, *Discussions Faraday Soc.*, **29**, 42 (1960), find, for example, similar rate constants for the oxidation of  $\text{Cr}(\text{bipy})_3^{3+}$  by  $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$  and  $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ .

(25) F. Basolo, J. G. Bergmann, R. E. Meeker, and R. G. Pearson, *J. Amer. Chem. Soc.*, **78**, 2676 (1956).

(26) R. Yelin and R. G. Wilkins, *ibid.*, **89**, 5496 (1967).

(27) Magnetic susceptibility measurements on  $\text{Co}(\text{bipy})_2(\text{ClO}_4)_2$  (ref 4) and  $\text{Co}(\text{phen})_3(\text{ClO}_4)_2$  (P. Ellis, R. G. Wilkins, and M. J. G. Williams, *J. Chem. Soc.*, 4456 (1957)) show these are high spin in the solid state and presumably in solution also. The magnetic behavior of  $\text{Co}(\text{terpy})_2\text{Br}_2$  in the solid state is anomalous (D. L. Williams, D. W. Smith, and R. C. Stouffer, *Inorg. Chem.*, **6**, 590 (1967); see also ref 14), but in solution has  $\mu = 2.2$  BM at room temperature (J. Lewis, unpublished data) corresponding to a low-spin complex.

of 0.22 at 25° ( $I = 3.0 M$ )<sup>15</sup> for Co(III), then  $Co^{3+}$ (aq) and  $Co(OH)^{2+}$  must be the main reactants at either end of the  $[H^+]$  scale, and with similar kinetic parameters associated with their reaction these two react by an outer-sphere mechanism. One of the failures in the application of eq 2 is in redox processes where  $Co^{3+}$ (aq) is the oxidant.<sup>28</sup> The reactions considered here are no exception and the difference between experimental and calculated values is some  $10^5$ . A similar situation applies in the oxidation of  $Fe(phen)_3^{2+}$  by  $Co^{3+}$ (aq) where theoretical and experimental rate constants at 25° are,<sup>29</sup> respectively,  $3 \times 10^8$  and  $1.5 \times 10^3 M^{-1} sec^{-1}$ . No sound explanation for the anomalous behavior of cobalt(III) is yet forthcoming but spin multiplicity or some other electronic restrictions may be responsible.<sup>28</sup>

**General Features.**—The replacement of chelated ligand by water in the cobalt(III) complexes leads to an increase in the value of the redox potential (an increase in oxidizing power). This would be expected since the final member of the series,  $Co(H_2O)_6^{3+}$ , is an extremely powerful oxidizing agent.<sup>30</sup> It is observed for example with  $Co(C_2O_4)_3^{3-}$  (+0.57 V) and  $Co(C_2O_4)_2(H_2O)_2^-$  (0.78 V)<sup>31</sup> and with  $Co(NH_3)_6^{3+}$  (+0.06 V) and  $Co(NH_3)_5(H_2O)^{3+}$  (+0.37 V).<sup>32</sup>

The similar reactivity of aquo- and hydroxycobalt(III) complexes and the fairly inert character of the cobalt(II) complexes are convincing evidence that these reactions are outer sphere and the application of Marcus theory to them is satisfactory except for oxidation by  $Co^{3+}$ (aq). One interesting piece of data that we can now compile is the approximate electron-transfer rate constant for a series of cobalt(II)–cobalt(III) systems in which there is progressive ligand replacement by water (Table II). The rate constants and activation parameters are close to one another for all systems. Their calculation from Marcus–Hush Theory<sup>1</sup> is quite difficult, requiring force constant and bond distance data which are not available. The evaluation of  $\Delta S^*$  appears to be easier and for these reactions  $\Delta S^*$

(28) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 164 (1966).

(29) R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1091 (1964).

(30) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952; D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, 3490 (1964).

(31) L. Hin-Fat and W. C. E. Higginson, *ibid.*, Sect. A, 298 (1967).

(32) R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962).

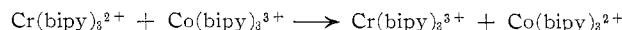
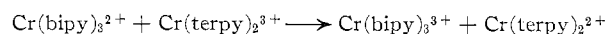
TABLE II  
ELECTRON-TRANSFER RATE CONSTANTS FOR A SERIES OF  
COBALT(II)–COBALT(III) COMPLEX SYSTEMS AT 0° AND  
VARIABLE IONIC STRENGTH

Reductant	Oxidant	$k, M^{-1} \Delta H^*, kcal$		
		$sec^{-1}$	$mole^{-1}$	$\Delta S^*, eu$
$Co(terpy)_2^{2+}$	$Co(bipy)_3^{3+}$	64	8.4	–19
$Co(bipy)_2(H_2O)_4^{2+}$	$Co(bipy)_2(H_2O)_3^{3+}$	2	...	...
$Co(phen)(H_2O)_4^{2+}$	$Co(bipy)(H_2O)_4^{3+}$	0.06	8.7	–30
$Co^{2+}(aq)$	$Co^{3+}(aq)$	0.6 <sup>a</sup>	10.4 <sup>a</sup>	–21 <sup>a</sup>

<sup>a</sup> H. S. Habib and J. P. Hunt, *J. Amer. Chem. Soc.*, **88**, 1668 (1966).

(calcd) is  $-26 eu$ ,<sup>1</sup> which is reasonably close to the experimental values. One perhaps may have anticipated a progressive decrease in rate and increase in  $\Delta H^*$  as one moved down the series and the highly conjugated ligands were replaced by the poorly conducting water but this appears not to be the case. Obviously there is an offsetting factor which almost compensates this effect.

We attempted to extend the study to the corresponding Cr(II)–Cr(III) electron transfer but found that the reactions



were complete within mixing time, thus placing a second-order rate constant at  $\geq 3 \times 10^6 M^{-1} sec^{-1}$  at 25°. Addition or removal of electrons associated with a  $t_{2g}$  orbital is easier than when the  $e_g$  orbital is involved.<sup>1</sup> The ions  $Cr(bipy)_3^{2+}$ <sup>33</sup> and  $Cr(bipy)_3^{3+}$  have  $t_{2g}^4$  and  $t_{2g}^3$  configurations and thus electron transfer is rapid analogous to that between the  $Fe(bipy)_3^{2+}$  ( $t_{2g}^6$ ) and  $Fe(bipy)_3^{3+}$  ( $t_{2g}^5$ ) ions. This situation does not pertain to the cobalt(II)  $t_{2g}^5 e_g^2$  and cobalt(III)  $t_{2g}^6$  complexes, and electron transfer is some  $10^7$  times slower.

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(33) F. Hein and S. Jerzog, *Z. Anorg. Allgem. Chem.*, **267**, 337 (1952).