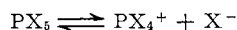


tem. Estimates of the exchange barrier for  $C_6H_5PF_5^-$  and for  $C_2H_5PF_5^-$  in these sulfoxide solutions are  $>25$  and  $<12$  kcal., respectively. The significant difference here between  $CH_3PF_5^-$  and  $C_2H_5PF_5^-$  must be steric in origin, whereas the greater stability of  $C_6H_5PF_5^-$  may reflect the higher effective nuclear charge on phosphorus in the aryl derivatives and the resultant greater stability of aryl pentafluorophosphate anions.

**Donor Behavior.**—A pentacoordinate phosphorus compound may function as a donor either (1) through ionization



as established for phosphorus(V) chloride and bromides or (2) through nonbonding electron pairs on the ligands. There is no evidence of such behavior for phosphorus pentafluoride but all of the mono-, di-, and trialkyl and -aryl derivatives of  $PF_5$  give evidence of donor activity, although our data do not distinguish between mechanisms (1) and (2).

Strong acceptor molecules such as  $BF_3$ ,  $SbF_5$ , and  $PF_5$  form crystalline, colorless 1:1 complexes with the various types of alkyl and aryl phosphorus fluorides. The dialkyl derivatives form more stable complexes than the monoalkyl derivatives. For example, the dissociation pressure of  $(CH_3)_2PF_3 \cdot PF_5$  is  $<1$  mm. at  $25^\circ$ , whereas the dissociation pressure of  $CH_3PF_4 \cdot PF_5$  is 10 mm. at  $-61^\circ$ . Boron trifluoride forms a relatively stable complex with  $(CH_3)_2PF_3$  but is immiscible with  $CH_3PF_4$  at  $-120^\circ$ . The aryl phosphoranes consistently form less stable complexes with  $SbF_5$  and  $PF_5$  than do the analogous alkyl phosphoranes.

It is tempting to conclude that these fluoride complexes consist, at least in the solid state, of  $RPF_3^+$  or  $R_2PF_2^+$  and  $MF_x^-$  aggregates. However, we have no evidence to support this formulation nor to exclude an alternative scheme based on fluorine bridge bonding.

#### Experimental

**Reagents.**—Purification of the phosphoranes was effected by distillation from sodium fluoride. All organic solvents were rigorously dried by standard procedures. Special procedures were necessary for dimethyl sulfoxide. Commercial samples were distilled and then dried further with a molecular sieve. This yielded material free of absorption in the OH infrared stretching region and free of proton n.m.r. resonance in the water region<sup>6</sup>; however, the conductivity was greater after molecular sieve treatment. A final distillation under reduced pressure, ca. 300 mm., gave sulfoxide free of water and with minimal conductivity. Commercial boron trifluoride was used without purification. Arsenic trifluoride, sulfur tetrafluoride, antimony pentafluoride, and phosphorus pentafluoride were purified by distillation.

**Reactions with Donor Molecules.**—Dimethylformamide (100 mmoles) was added to a solution of  $C_6H_5PF_4$  (50 mmoles) in 60 ml. of ethyl ether. Considerable heat was evolved, and the solution on cooling yielded colorless crystals. *Anal.* Calcd. for  $C_6H_5PF_4 \cdot OCHN(CH_3)_2$ : C, 42.0; H, 4.67; F, 29.6. Found: C, 41.9; H, 5.37; F, 28.6. A similar procedure was followed with pyridine and  $C_6H_5PF_4$  to give colorless crystals. *Anal.* Calcd. for  $C_6H_5PF_4 \cdot NC_5H_5$ : C, 50.2; H, 3.82; F, 28.9. Found: C, 50.2; H, 4.41; F, 29.1. These stoichiometries were also confirmed tensimetrically in a vacuum system; dissociation pressures of the crystalline solids were 1 mm. or less at  $25^\circ$ .

(6) This region was identified by adding water to the dimethyl sulfoxide.

**Reactions with Acceptor Molecules.**—In a vacuum system, gaseous  $(CH_3)_2PF_3$  was introduced into a reaction vessel containing 0.5 g. of  $SbF_5$ . When no further absorption occurred as evidenced by a static pressure reading, the vessel was evacuated. The product was a colorless crystalline solid. *Anal.* Calcd. for  $(CH_3)_2PF_3 \cdot SbF_5$ : C, 6.11; P, 9.27; Sb, 36.4. Found: C, 7.17; P, 9.31; Sb, 36.1. A similar procedure was employed to make  $C_2H_5PF_4 \cdot SbF_5$ . *Anal.* Calcd. for  $C_2H_5PF_4 \cdot SbF_5$ : P, 8.78; Sb, 34.5. Found: P, 7.69; Sb, 33.4. The  $BF_3 \cdot (CH_3)_2PF_3$  complex was prepared in a vacuum system by reaction of liquid  $(CH_3)_2PF_3$  with gaseous  $BF_3$  at  $\sim -30^\circ$ ; the dissociation pressure was  $\sim 1$  mm. at  $25^\circ$  and may account for the high phosphorus and carbon analysis. *Anal.* Calcd. for  $(CH_3)_2PF_3 \cdot BF_3$ : C, 12.4; B, 5.83; P, 16.7. Found: C, 14.1; B, 5.64; P, 18.54. Stoichiometries of other systems, e.g.,  $RPF_4$  and  $R_2PF_3$  with  $PF_5$ , were determined tensimetrically in a vacuum system. The dissociation pressure of  $CH_3PF_4 \cdot PF_5(c)$  conformed to the equation  $\log p_{mm} = 9.89 - 1882/T$  over the temperature range  $-78$  to  $-20^\circ$ .

**Acknowledgment.**—We wish to thank Dr. R. Schmutzler of the Explosives Department for generous samples of the fluorophosphoranes.

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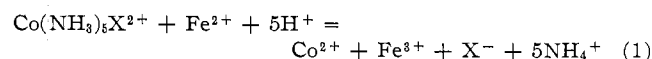
### Kinetics and Mechanisms of Reactions of Iron(II) and Acidopentaamminecobalt(III) Ions<sup>1</sup>

BY JAMES H. ESPENSON

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Dominating current work on oxidation-reduction reactions of metal complexes in solution is the question of the mechanism by which the over-all electronic change occurs. Such systems involving one-equivalent changes have been studied extensively in the past decade.<sup>2-5</sup>

Reactions proving particularly useful for learning about mechanisms of electron transfer have been those of divalent metal ions with monoacido complexes of pentaamminecobalt(III), and of pentaquo- and pentaamminechromium(III). The metal ions studied as reducing agents have included especially chromium(II), and also vanadium(II), europium(II), as well as complexed forms of these. Recent work<sup>6</sup> reported on the reducing agent  $Co(CN)_5^{3-}$ . In the present study some analogous reactions of iron(II) are considered.



Two related reactions have been studied previously: the reaction of iron(II) with trisoxalatocobalate(III)

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

(3) D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

(4) J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

(5) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(6) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.* **85**, 2517 (1963).

TABLE I  
SECOND-ORDER RATE CONSTANTS FOR REACTIONS OF IRON(II)  
ION WITH COBALT(III) COMPLEXES<sup>a</sup>

Oxidizing agent	Temp., °C.	No. of runs	$k^b \times 10^3$ , $M^{-1} \text{ sec.}^{-1}$
Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup>	25.0	13	1.35 ± 0.06
	35.0	3	2.87 ± 0.04
	45.0	3	5.37 ± 0.06
Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>2+</sup>	15.0	2	0.325
	20.0	2	0.477
	25.0	2	0.726
Co(NH <sub>3</sub> ) <sub>5</sub> F <sup>2+</sup>	25.0	5	6.6 ± 0.3
	35.0	2	15.1
	45.0	2	31.4
Co(NH <sub>3</sub> ) <sub>5</sub> O <sub>2</sub> CCH <sub>3</sub> <sup>2+</sup>	25.0	1	<0.05
Co(NH <sub>3</sub> ) <sub>5</sub> NCS <sup>2+</sup>	25.0	1	<0.003
Co(NH <sub>3</sub> ) <sub>5</sub> N <sub>3</sub> <sup>2+</sup>	25.0	<i>c</i>	8.8
Co(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>3-</sup>	20.3	<i>d</i>	9 × 10 <sup>5</sup>
Co(NH <sub>3</sub> ) <sub>5</sub> C <sub>2</sub> O <sub>4</sub> H <sup>2+</sup>	25.0	7 <sup>e</sup>	3.8 ± 0.1 <sup>f</sup>

<sup>a</sup> Ionic strength = 1.00 *F* with LiClO<sub>4</sub>, except as noted.

<sup>b</sup> Corrected for the simultaneous aquation reaction for chloro and bromo reactions, as explained in the text. Uncertainties listed are average deviations of individual *k* values from the mean.

<sup>c</sup> From ref. 8. <sup>d</sup> From ref. 7, extrapolated to zero ionic strength.

<sup>e</sup> [H<sup>+</sup>] varied from 0.10 to 0.31 *M*; ionic strength 0.52 *F*. <sup>f</sup> The rate equation is  $k'[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}][\text{Fe}^{2+}]/[\text{H}^+]$ ; the value quoted is *k'*, in sec.<sup>-1</sup>.

ion<sup>7</sup> and with azidopentaamminecobalt(III) ion.<sup>8</sup> The relation of this earlier work with iron(II) to the present studies will be discussed.

### Experimental

**Reagents.**—Iron(II) solutions were prepared from hydrated solid iron(II) perchlorate (G. F. Smith), which contains some iron(III) and appreciable perchloric acid. The iron(III) was reduced with primary standard grade iron, and iron(II) was analyzed by titration with cerium(IV). Stock solutions were stored under purified nitrogen in contact with iron metal. Complexes of the pentaamminecobalt(III) series used in this work were prepared from standard recipes given in the literature.<sup>4</sup> Aqueous solutions of these complexes exhibited visible spectra in quantitative agreement with published data.<sup>4</sup> Conductivity water was used in all preparations and reaction solutions.

**Kinetic Experiments.**—The progress of reaction was followed spectrophotometrically, using the absorption peak of the cobalt(III) complex in the vicinity of 5000 Å. Solutions of all reagents except iron(II) were introduced into a cylindrical spectrophotometer cell with a 10-cm. optical path. The solution and cell were thoroughly purged with purified nitrogen introduced *via* a long hypodermic needle piercing a rubber cap. The sealed cell was brought to reaction temperature in a regulated bath, then positioned in the spectrophotometer cell compartment in a water-filled jacket of a special holder maintained at the reaction temperature. The desired volume of iron(II) solution, also at the same temperature, was introduced with a calibrated syringe which had been first flushed with nitrogen. Either continuous or intermittent absorbance readings were made with a Cary Model 14 spectrophotometer.

### Results

Kinetic data obey a rate equation first order with respect to both the cobalt(III) complex and iron(II).

$$-d[\text{Co}^{\text{III}}]/dt = k[\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{Fe}^{2+}] \quad (2)$$

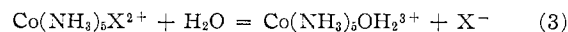
Concentration conditions were chosen such that iron(II) was always in considerable excess, which was often sufficient (≥40-fold) to ensure pseudo-first-order rate

TABLE II  
ACTIVATION PARAMETERS FOR REACTIONS OF COBALT(III)  
COMPLEXES WITH IRON(II)

Oxidizing agent	$\Delta H^*$ , kcal./mole <sup>a</sup>	$\Delta S^*$ , cal. mole <sup>-1</sup> deg. <sup>-1b</sup>
Co(NH <sub>3</sub> ) <sub>5</sub> F <sup>2+</sup>	13.7	-23
Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup>	12.5	-30
Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>2+</sup>	13.3	-28
Co(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>3-</sup>	12.0 <sup>c</sup>	0

<sup>a</sup> Estimated uncertainty ± 1.2 kcal. <sup>b</sup> Estimated uncertainty ± 5 e.u. <sup>c</sup> Reference 7.

behavior. These reactions (eq. 1) are generally sufficiently slow that the aquation reaction



occurs to an appreciable extent; the relative effect of aquation is minimized at high iron(II) concentration. Where pseudo-first-order kinetics are observed, the method of Guggenheim was used to treat the rate data using a constant time interval of 2-3 half-lives.<sup>9</sup> In the other instances, a second-order equation was used, and the rate plots were linear to ≥75% reaction.

An extensive series of runs was performed in the case of the chloro complex to establish this rate equation. With the other complexes, the dependence upon iron(II) was often assumed rather than verified experimentally. Initial concentrations of the cobalt(III) complexes generally lay in the range 0.001-0.005 *M*; iron(II), 0.01-0.09 *M*, with 0.002 *M* cobalt(III) and 0.08 *M* iron(II) the concentrations generally employed.

Table I reports the kinetic data for these reactions. The observed second-order rate constant for reaction 1 has been corrected for the simultaneous occurrence of reaction 3 in those instances (Cl<sup>-</sup> and Br<sup>-</sup>) where aquation contributes appreciably. This correction, which lies in the range 2-8% for the chloro complex, and 11-15% for the bromo complex, was made using published values of the first-order rate constants and their activation energies for reaction 3: Cl<sup>-</sup>,  $k_{\text{aq}} = 1.7 \times 10^{-6} \text{ sec.}^{-1}$  at 25°,  $E_a = 24 \text{ kcal.}$ ; Br<sup>-</sup>,  $k_{\text{aq}} = 6.3 \times 10^{-6} \text{ sec.}^{-1}$  at 25°,  $E_a = 24 \text{ kcal.}$

In the case of the chloro complex, runs were also performed to establish independence of the rate upon [H<sup>+</sup>] and [Cl<sup>-</sup>]. The latter ion is present in each experiment as the anion accompanying the cobalt(III) complex and is also a product of the reaction being studied. Experiments done here prove that low concentrations of Cl<sup>-</sup>, at least up to 0.015 *M*, are without effect on that reaction.

Lack of deviation of the rate data from second-order behavior in the other instances establishes that their accompanying anions<sup>10</sup> are also without effect at these low concentrations.

The reaction rate of the unidentate binoxalato complex depends inversely upon [H<sup>+</sup>] in the range 0.10-0.31 *M*. The protonated complex is the predominant form in these solutions.

Table II summarizes the activation parameters which

(9) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

(10) The anion accompanying each complex was perchlorate ion, with these exceptions: Cl<sup>-</sup>, Cl<sup>-</sup>; Br<sup>-</sup>, Br<sup>-</sup>; F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>.

(7) J. Barrett and J. H. Baxendale, *Trans. Faraday Soc.*, **52**, 210 (1956).  
(8) A. Haim, *J. Am. Chem. Soc.*, **85**, 1016 (1963).

characterize these systems. Values of  $\Delta H^*$  were obtained from slopes of plots of  $\log k/T$  vs.  $1/T$ .

### Discussion

Reactions of  $\text{Cr}^{2+}$  with  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  proceed by means of an "inner-sphere" transition state,<sup>3,5</sup> since the chromium(III) product is invariably  $\text{CrX}^{2+}$ . In many reactions of  $\text{Co}(\text{CN})_5^{3-}$  a product criterion based on the inertness of the cobalt(III) product also establishes an inner-sphere mechanism.<sup>6</sup> Unfortunately, this clear-cut criterion is not available with most reducing agents, since their oxidized forms are substitution labile.

In these instances the relative reaction rates of the azido and thiocyanato complexes may provide a more useful criterion indicating operation of an inner-sphere mechanism.<sup>8,11</sup> Provided nitrogen-bonded thiocyanate ion is the stable product, an inner-sphere mechanism should show a great preference for the symmetrical  $\text{N}_3^-$  over  $\text{NCS}^-$ . The available data are summarized in Table III. This criterion would place iron(II) ion in the inner-sphere category. The mechanism for vanadium(II) and europium(II) remains undecided by this criterion, as the lower ratios in these cases may be due to an inner-sphere reaction *via* the sulfur end of the thiocyanate ion or to outer-sphere reaction. Other arguments have been advanced, however, to suggest that vanadium(II) reacts by an outer-sphere pathway.<sup>4,12</sup> The reducing agent  $\text{Co}(\text{CN})_5^{3-}$ , for which the inner-sphere path has been clearly established<sup>6</sup> (the product criterion is valid in this instance), would appear to be exceptional. Actually, this is due to sulfur-bonded thiocyanate ion being the stable configuration of the  $\text{Co}(\text{CN})_5\text{SCN}^{2-}$  product, as the work of Burmeister has established.<sup>13</sup>

TABLE III  
RELATIVE RATES OF REDUCTION AT 25° OF AZIDO AND  
THIOCYANATO COMPLEXES

Oxidizing agent	Reducing agent	$k_{\text{N}_3^-}/k_{\text{NCS}^-}$	Ref.
$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	$\text{Cr}^{2+}$	$10^4$	4
$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	$\text{V}^{2+}$	27	4
$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	$\text{Eu}^{2+}$	300	4
$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	$\text{Fe}^{2+}$	$\geq 3 \times 10^3$	This work
$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	$\text{Cr}(\text{dipy})_2^{2+}$	4	4
$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	$\text{Co}(\text{CN})_5^{3-}$	1.6	6
$\text{Cr}(\text{OH}_2)_6\text{X}^{2+}$	$\text{Cr}^{2+}$	$4 \times 10^4$	3, 11

The relative reaction rates of the halide ion complexes  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  with  $\text{Fe}^{2+}$  studied in this work provide an interesting comparison with earlier work. These rate constants decrease with increasing atomic number of  $\text{X}^-$ . These values trend in the same direction as those for europium(II) ion as the reducing agent, but are just opposite to those observed for chromium(II) as a reactant in the same series.<sup>4</sup> As these authors pointed out, this does not imply, however, that a mechanism involving an inner-sphere transition state is not operating here, and the azido-thiocyanate

criterion suggested above may provide a better indication of mechanism.

There is the additional point that applies to the iron-(II) reactions studied here: it is an unjustified assumption to assert that a given reducing agent reacts with each member of a series of related complexes along similar pathways, for there are instances where this is certainly not the case.<sup>4,6</sup>

The rate equation for the reaction of  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$  and  $\text{Fe}^{2+}$  written in terms of the predominant species takes the form  $k'[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}][\text{Fe}^{2+}]/[\text{H}^+]$ . This rate law is consistent with bimolecular reaction of  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$  and  $\text{Fe}^{2+}$ ;  $k'$  is identified as the product of this bimolecular rate constant and the acid dissociation quotient of the binoxalato complex.<sup>14</sup> The reason the basic oxalato form reacts preferentially may lie in the nature of the reaction product. Since chelated  $\text{FeC}_2\text{O}_4^+$  is the stable configuration, it is energetically profitable, in forming the bridged transition state, for both coordinating positions on the oxalate ion to be available to the incoming iron-(II) ion.

An alternative pathway for this reaction, kinetically indistinguishable from that suggested previously, is provided by reaction of  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$  and  $\text{FeOH}^+$ . Since the stable iron(III) product in solutions at these acid concentrations is  $\text{Fe}^{3+}$  and not  $\text{FeOH}^{2+}$ , this path appears to offer no particular energetic advantage for facilitating the electron-transfer process.

**Acknowledgment.**—The author wishes to express his appreciation to Professors A. Haim, J. Halpern, E. L. King, and H. Taube for helpful discussions concerning this work.

(14) Were the acid dissociation quotient  $Q_a$  of the binoxalato complex known, the true second-order rate constant for reaction of  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$  and  $\text{Fe}^{2+}$  would be calculable. Although the numerical value of  $Q_a$  is not known, it is sufficiently small that in the range of  $[\text{H}^+]$  studied here, 0.1–0.3 M, the protonated form of this cobalt(III) complex predominates.

CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS  
COMPANY, REDSTONE ARSENAL RESEARCH DIVISION,  
HUNTSVILLE, ALABAMA

### The Preparation of N,N-Difluorosulfamide

BY ROBERT A. WIESBOECK AND J. K. RUFF

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The successful fluorination of urea with elementary fluorine to difluorourea in aqueous media<sup>1</sup> prompted a study of the fluorination of sulfamide under similar conditions. It was found that at 0 to  $-5^\circ$  N,N-difluorosulfamide was produced when an unbuffered aqueous solution of sulfamide was subjected to fluorination.

(11) R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964).

(12) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

(13) J. L. Burmeister, *Inorg. Chem.*, **3**, 919 (1964).

(14) V. Grakauskas, paper presented before the Division of Industrial and Engineering Chemistry, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.