stance that sublimes easily at 50° (15 mm). In the solid state, it is stable in air at room temperature and it begins to decompose at about 65° without melting. The nmr spectrum is very similar to the one reported for tris(π-allyl)rhodium and is consistent with two sets of π-allyl groups in the ratio 1:2. The mass spectrum shows the presence of parent peaks corresponding to the expected masses 316 and 314.

The compound reacts readily with carbon monoxide, giving air-unstable substances which slowly transform to $[Ir(CO)_3]_4$.

Experimental Section

A 1 *M* solution of C_3H_5MgCl (0.02 mole) in THF was added to a benzene solution (20 ml) of $Ir(acac)_3$[3] (1 g or 0.002 mole). The yellow solution became orange immediately.

The reaction mixture was then warmed at 50° for 10 hr, the excess of Grignard reagent was decomposed with carbon dioxide, and, after evaporation of the solvents under vacuum, the mixture was extracted with *n*-hexane. Then the crude product, obtained by evaporation, was sublimed: it gave white crystals of camphoraceous odor (0.125 g or 20% yield). *Anal.* Calcd for $C_9H_{15}Ir$: C, 34.27; H, 4.79; Ir, 60.94. Found: C, 34.04; H, 4.46; Ir, 59.8.

The mass spectrum was recorded on an LKB 9000A spectrometer at electron accelerating voltage of 70 v.

The nmr spectrum was recorded on a Perkin-Elmer R10 spectrometer at 60 Mc in CCl_4 solution, using TMS as internal standard. The set of peaks of intensity 1 consists of signals at 4.9 ppm (τ_1, multiplet), at 7.26 ppm (τ_2, doublet), and at 7.45 ppm (τ_3, doublet) with $J_{12} \sim 8.6$ cps and $J_{13} = 11.1$ cps.

The set of peaks of intensity 2 gives τ_1 at 6.6 ppm (multiplet), τ_2 at 7.24 ppm (doublet), and τ_3 at 8.4 ppm (doublet) with $J_{12} = 6.8$ cps and $J_{13} = 9.5$ cps.

The infrared spectrum was recorded on a Perkin-Elmer 621 spectrophotometer in CCl_4 solution. In the C–H stretching region there are bands at 3051 (s), 2992 (s), 2912 (m), and 2905 (w) cm^{-1}, in the corresponding bending region there are bands at 1472 (s), 1456 (s), and 1385 (m) cm^{-1}.

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The Kinetics of Some Oxidation–Reduction Reactions Involving Silver(II)[1]

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Although many oxidation–reduction reactions are catalyzed by silver ions,[3,4] rate constants for only very few silver(II) oxidations have been reported. Kirwin, *et al.*,[5,6] have studied the reaction between silver(I) and cobalt(III) as part of an investigation of the silver(I)-catalyzed oxidation of chromium(III) by cobalt(III). From their data they were able to estimate the rate constant for the silver(I)–cobalt(III) reaction.[6] We have studied the effect of silver(I) on the rate of oxidation of iron(II) by cobalt(III).[7] These studies afford another determination of the rate constant for the silver(I)–cobalt(III) reaction and, in addition, provide a check on the mechanism proposed by Kirwin, *et al.*, for the silver(I)-catalyzed oxidation of chromium(III) by cobalt(III). For the purpose of comparison with these systems we have also measured the rate of oxidation of cobalt(II), iron(II), manganese(II), and vanadium(IV) by silver(II).

Experimental Section

Materials.—Cobalt(II) perchlorate solutions were prepared by dissolving reagent grade cobalt carbonate in perchloric acid of the desired concentration. Solutions containing cobalt(III) were prepared by electrooxidation of the cobalt(II) solutions. About 30–40% yield of cobalt(III) was usually obtained after prolonged electrolysis at 0°. Iron(III) perchlorate was purified by recrystallization. Solutions of iron(II) were prepared by electroreduction of the iron(III) solutions. Silver(II) oxide was prepared according to the method described in the literature.[8] Solutions of silver(II) were prepared by dissolving the solid in 4 *M* perchloric acid at −15 to −20°. Most of the solid was reduced to the +1 oxidation state upon dissolution. Vanadium(IV) was prepared by electrolysis of a solution of vanadium pentoxide in perchloric acid using a platinum gauze cathode. Manganese(II) solutions were prepared by dissolution of manganese metal in 4 *M* perchloric acid. The other chemicals were used without further purification.

Analyses.—Solutions for the stopped-flow and equilibrium measurements were prepared with triple distilled water. The cobalt(II) and cobalt(III) solutions were analyzed spectrophotometrically (ϵ_{max}[cobalt(II)] = 4.84 at 509 mμ and ϵ_{max}[cobalt(III)] = 37.0 at 605 mμ). The concentration of cobalt(II) was also checked by titration with EDTA using methyl thymol blue as indicator. The concentration of silver(I) in the stock solutions was determined by the Volhard method. Silver(II) oxide was analyzed for silver[8] and its oxidizing power was checked by adding the solid to an excess of iron(II) and titrating the excess iron(II) as described below. Solutions of silver(II) were analyzed spectrophotometrically[5,9] (ϵ_{max}[silver(II)] = 140 at 470 mμ). The analyses were performed concurrently with stopped-flow runs. The concentrations of iron(II) and iron(III) in the stock solutions were determined by titration with standard cerium(IV) sulfate using ferroin as indicator. The iron(III) was reduced to iron(II) with a Jones reductor. The concentration of vanadium(IV) in the stock solution was determined by titration with permanganate at 80° and was checked spectro-

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[3] See, for example, reviews by (a) W. K. Wilmarth and A. Haim in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, pp 194–200, and (b) J. A. McMillan, *Chem. Rev.*, **61**, 65 (1961).

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[9] The spectrum of silver(II) in 4 *M* perchloric acid is in agreement with reported values[5] in 3 *M* perchloric acid. No changes in the shape of the band in the region 540–560 mμ or the charge-transfer band (380 mμ) was observed at the higher acidity.

photometrically (ϵ_{max}[vanadium(IV)] = 16.5 at 760 mμ). Manganese(II) was determined spectrophotometrically as permanganate after oxidation with potassium periodate.

Kinetic Measurements.—The reactions were studied using the stopped-flow apparatus which has been described previously.[10] The iron(II)–cobalt(III) reaction was followed at 605, 405, 300, and 285 mμ. The disappearance of cobalt(III) coincided with the appearance of iron(III) (no optical density changes were observed at 330 and 247 mμ, the isosbestic points for the over-all reaction). The reactions of iron(II), vanadium(IV), and manganese(II) with silver(II) were studied by mixing a solution containing the reducing agent with a solution containing silver(II) and silver(I). The silver(I) was added to the silver(II) solution in order to suppress the formation of appreciable amounts of silver(III) by the disproportionation reaction

$$2\text{Ag(II)} \rightleftharpoons \text{Ag(I)} + \text{Ag(III)}$$

The silver(II) oxidation of cobalt(II) was studied at 470 mμ, the wavelength where silver(II) has maximum absorbance. The absorbance of silver(II) is greater at all wavelengths than that of either cobalt(II) or cobalt(III), and hence only the disappearance of silver(II) was observed. The reaction between vanadium(IV) and cobalt(III) was studied using a Cary Model 14 spectrophotometer. The reaction was followed at 760 mμ and at 405 mμ, the absorption maxima of vanadium(IV) and cobalt(III), respectively.

Results

The oxidation of iron(II) by cobalt(III) was studied in the presence of excess silver(I) and iron(II). The reactions to be considered are

$$\text{Co(III)} + \text{Ag(I)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Co(II)} + \text{Ag(II)} \quad K_1 \qquad (1)$$

$$\text{Ag(II)} + \text{Fe(II)} \xrightarrow{k_2} \text{Ag(I)} + \text{Fe(III)} \qquad (2)$$

$$\text{Co(III)} + \text{Fe(II)} \xrightarrow{k_3} \text{Co(II)} + \text{Fe(III)} \qquad (3)$$

At sufficiently high iron(II) concentrations the rate constant for the disappearance of cobalt(III) is

$$k_{\text{obsd}} = \frac{0.693}{t_{1/2}[\text{Fe(II)}]} = k_3 + \frac{k_1[\text{Ag(I)}]}{[\text{Fe(II)}]} \qquad (4)$$

The values of k_{obsd} are presented in Table I. A plot of the left-hand side of eq 4 *vs.* [Ag(I)]/[Fe(II)] yielded a straight line of slope k_1 and intercept k_3. The values of k_1 and k_3 calculated from this plot are 41 ± 3 M^{-1} sec^{-1} and 330 ± 7 M^{-1} sec^{-1}, respectively.

The oxidation of cobalt(II) by silver(II) was studied in the presence of excess cobalt(II) and silver(I). Under these conditions the rate constant for the approach to equilibrium is

$$k_{\text{obsd}} = \frac{0.693}{t_{1/2}} = k_1[\text{Ag(I)}] + k_{-1}[\text{Co(II)}] \qquad (5)$$

The values of k_{obsd} are presented in Table II. A plot of k_{obsd} *vs.* [Co(II)] at [Ag(I)] = 1.16 × 10^{-2} M yields a straight line. The value of k_{-1} calculated from the slope of this plot is (1.75 ± 0.05) × 10^3 M^{-1} sec^{-1}. The intercept of the plot at the above Ag(I) concentration is too small to give a good estimate of k_1. However, from the value of k_{obsd} = 32.2 ± 3 sec^{-1} at [Ag(I)] = 2.01 × 10^{-1} M and [Co(II)] = 1.42 × 10^{-2} M we calculate that k_1 = 37 ± 4 M^{-1} sec^{-1}. The equilibrium constant of reaction 1, $K_1 = k_1/k_{-1}$, is calculated to be 2.3 × 10^{-2} in 4 M perchloric acid at 25.0°

TABLE I

KINETIC DATA FOR THE SILVER(I)-CATALYZED OXIDATION OF IRON(II) BY COBALT(III) IN 4 M PERCHLORIC ACID AT 25.0°

[Fe(II)] × 10^2, M	[Ag(I)] × 10^2, M	[Co(II)] × 10^3, M	[Co(III)] × 10^3, M	k_{obsd} × 10^{-2}, M^{-1} sec^{-1}
2.77	0	3.35	1.35	3.30
2.35	2.10	7.90	2.10	3.57
1.38	1.45	3.87	0.83	3.84
2.77	5.14	3.60	1.10	4.13
0.69	2.32	2.00	0.50	5.14
1.70	10.7	8.65	1.35	6.47
0.83	5.53	2.00	0.50	6.90
1.39	11.6	2.00	0.50	6.82
0.74	7.25	3.87	0.83	7.46
0.37	4.44	2.12	0.38	8.00
1.60	21.0	9.00	1.00	8.49
1.94	25.7	3.60	1.10	8.73
0.69	11.6	2.00	0.50	11.1
0.45	9.32	2.12	0.38	11.3
0.85	19.6	8.65	1.35	13.7
1.18	30.0	6.50	3.50	16.5
0.83	31.2	2.00	0.50	17.8
0.27	17.0	3.40	1.30	34.0

TABLE II

OBSERVED RATE CONSTANTS FOR THE OXIDATION OF COBALT(II) BY SILVER(II) IN 4 M PERCHLORIC ACID AT 25.0°

[Co(II)] × 10^3, M	[Ag(II)] × 10^4, M[a]	k_{obsd}, sec^{-1}
23.0	9.3	38.1
17.2	7.5	30.5
11.6	6.0	20.9
5.7	4.7	10.1
3.4	4.5	6.4
9.3	4.2	16.2
14.2	4.1[b]	32.2

[a] [Ag(I)] = 1.16 × 10^{-2} M unless otherwise indicated. [b] [Ag(I)] = 2.01 × 10^{-1} M.

Rate constants for the iron(II)–silver(II), vanadium(IV)–cobalt(III), vanadium(IV)–silver(II), and manganese(II)–silver(II) reactions are presented in Table III together with rate constants for some other reactions of interest.

Discussion

The value of k_1 determined from the effect of silver(I) on the rate of the iron(II)–cobalt(III) reaction (41 ± 3 M^{-1} sec^{-1}) is in good agreement with the value obtained in the more direct measurement (37 ± 4 M^{-1} sec^{-1}) but is a factor 3 lower than the value calculated by Kirwin, *et al.*,[6] from the effect of silver(I) on the rate of the chromium(III)–cobalt(III) reaction. However, inspection of ref 6 shows that the higher value of k_1 reported there is due to the omission of a stoichiometric factor 3 from the rate equations for the silver(I)-catalyzed reaction. When this factor is introduced the rate constant obtained by Kirwin, *et al.*, becomes 37 ± 7 M^{-1} sec^{-1} in 3 M perchloric acid at 25.0°, in good agreement with the value determined in the present study. This agreement provides further support for the mechanisms proposed for the silver(I) catalysis of the chromium(III)–cobalt(III) and iron(II)–cobalt(III) reactions.

The equilibrium constant for reaction 1 can be calcu-

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[10] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

TABLE III

RATE CONSTANTS FOR SILVER(II) AND COBALT(III) OXIDATIONS IN 4 M PERCHLORIC ACID AT 25.0°

Reductant	$k_{\text{Ag(II)}}$, M^{-1} sec^{-1}	$k_{\text{Co(III)}}$, M^{-1} sec^{-1}	$\frac{k_{\text{Ag(II)}}}{k_{\text{Co(III)}}}$	$\frac{k_{\text{Ag(I)}}}{k_{\text{Co(II)}}}$
V(IV)	5×10^3	1.37[a]	3.6×10^3	8×10^1
Cr(III)	1.5×10^3 [b]	≤ 4[c]	$\geq 4 \times 10^2$	≥ 9
Mn(II)	3×10^4	1.0×10^2 [d]	3×10^2	7
Fe(II)	4×10^5 [e]	3.3×10^2	1.2×10^3	3×10^1
Co(II)	1.75×10^3	20[f]	0.9×10^2	2
Ce(III)	5×10^3 [g]	10[h]	5×10^2	1×10^1

[a] The vanadium(IV)–cobalt(III) reaction has also been studied by D. R. Rosseinsky and W. C. E. Higginson, *J. Chem. Soc.*, 31 (1960). Their value for the rate constant is in good agreement with the value determined in the present work after allowance is made for the effect of temperature and perchloric acid concentration on the reaction rate. [b] 3 M $HClO_4$: ref 6. [c] Calculated from the data reported in ref 6. [d] 3 M $HClO_4$: H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964). [e] At high iron(II) concentrations (*e.g.*, [Fe(II)] $\sim 1 \times 10^{-1}$ M and [Ag(II)] $\sim 2 \times 10^{-3}$ M) some slower secondary reactions were observed. These reactions, which may be associated with dimeric reactants or products, were not investigated in detail. [f] H. S. Habib and J. P. Hunt, *J. Am. Chem. Soc.*, **88**, 1668 (1966). [g] Calculated from the data reported by W. C. E. Higginson, *et al.*[4] [h] 1 M $HClO_4$: L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

lated from the formal oxidation potentials of the silver(I)–silver(II) and cobalt(II)–cobalt(III) couples. The formal potentials of these couples are 2.00 v in 4 M perchloric acid[11,12] and 1.84 v in 4 M nitric acid,[13] respectively, at 25°. We have determined[14] the formal potential of the cobalt(II)–cobalt(III) couple to be 1.92 ± 0.02 v in 4 M perchloric acid at 25°.[15,16] From these potentials we calculate that $K_1 = (4 \pm 2) \times 10^{-2}$, in satisfactory agreement with the equilibrium constant obtained from the kinetic measurements.

The rates of oxidation of vanadium(IV), chromium(III), manganese(II), iron(II), cobalt(II), and cerium(III) by silver(II) and cobalt(III) are compared in Table III. It will be seen that the silver(II) oxidations proceed about 10^2 to 10^4 times more rapidly than do the corresponding cobalt(III) oxidations. Moreover, since the equilibrium constant for the oxidation of cobalt(II) by silver(II) is known, we can calculate the relative rates of oxidation of silver(I) and cobalt(II) in the reverse of the above reactions. The results of these calculations are presented in the last column of Table III. It is apparent from this column that the reductions by silver(I), despite their more unfavorable free energy changes, proceed at least as rapidly as the reductions by cobalt(II). The relatively rapid rates of reduction by silver(I) and oxidation by silver(II) suggest that silver(I) is likely to be more efficient than cobalt(II) as a catalyst of oxidation–reduction reactions, a conclusion consistent with the widespread use of silver(I) as an electron mediator.

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[13] A. A. Noyes and T. J. Deahl, *ibid.*, **59**, 1337 (1937).

[14] In order to avoid the precipitation of potassium perchlorate during the potential measurements, the saturated potassium chloride solution in the calomel electrode was replaced by a saturated sodium chloride solution. The cobalt(III) solution was separated from the calomel electrode by a perchloric acid bridge in order to suppress the reaction of cobalt(III) with chloride ions. Silver(I) was added as a potential mediator[13] in some measurements.

[15] D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, 3490 (1964), report a value of 1.95 ± 0.1 v for the formal potential of the cobalt(II)–cobalt(III) couple in 4 M perchloric acid at 25°. This value was calculated from the heat and entropy changes of the iron(II)–cobalt(III) reaction.

[16] The lower value of the potential in 4 M nitric acid suggests that extensive complex formation occurs between cobalt(III) and nitrate ions.

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The Synthesis of Perfluorovinylborazines[1]

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Prior to this investigation, a limited number of halogen derivatives of borazine were known. The B-trihaloborazines $(HNBX)_3$ where the boron hydrogen atom was replaced by either fluorine, chlorine, bromine, or iodine had been prepared.[2–6] Only two partially halogenated alkyl derivatives had been reported. Leffler had prepared N-(β,β,β-trifluoroethyl)borazine, $(CF_3CH_2NBH)_3$,[7] and a partially chlorinated alkyl derivative B-(β-chloroethoxy)borazine, $(HNBOCH_2CH_2Cl)_3$ was prepared by Niedenzu, Dawson, and George.[8]

No definitive studies had been reported on the synthesis and properties of borazine derivatives where a perfluoroalkyl group was bonded to either boron or nitrogen at the time this work was started. Since then Gutmann and his co-workers have prepared a series of N-fluoroalkylborazines and B-fluoroarylborazines.[9] Stafford and Stone,[10] however, had described the preparation and certain properties of perfluorovinylborane compounds.

These investigators had observed that organoboron compounds, having halogen atoms in the organo groups bonded to boron, readily decompose to form the more stable boron trihalides. The perfluorovinyl boron compounds, notably trisperfluorovinylborane, decomposed to perfluorovinyldifluoroborane and boron trifluoride on heating to 100° for 5 hr.

It was expected that a perfluorovinyl group bonded to a boron of a six-membered boron–nitrogen ring system would comprise a more stable system with

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[1] Presented at the 3rd International Symposium on Fluorine Chemistry, Aug 30–Sept 2, 1965, Munich, Germany.

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