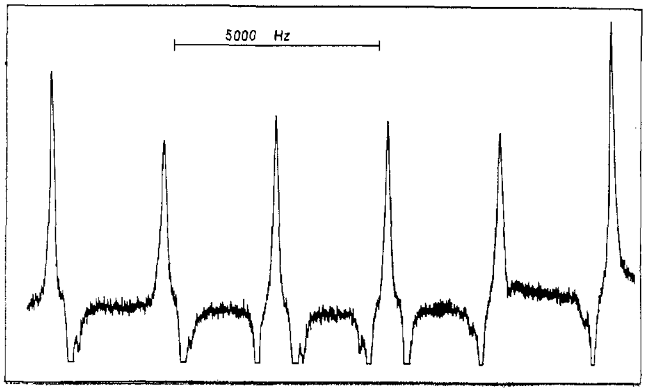


Figure 2.—The ^{19}F nmr spectrum of IF_6^+. Inverted peaks are 2500-Hz modulation side bands from base-line stabilization circuitry.

the parent fluoride and the cations SF_3^+,[18] SOF_3^+,[20] and SeF_3^+.[21] However, it is comparable to the recently observed positive shifts occurring on formation of the halogen fluoro cations ClF_2^+ and BrF_2^+.[22] The IF_6^+ peak position found in the broad-line study of IF_6^+-AsF_6^- solid was −126 ± 16 ppm from CF_3CO_2H (−46 ± 16 ppm from $CFCl_3$), in reasonable agreement with our value.[10]

The signal is split into a sextet by coupling of the six equivalent fluorines to ^{127}I (spin $^5/_2$, 100% abundance). The value of the coupling constant (J_{I-F}) is 2730 ± 15 Hz. This is the first instance of the direct measurement of an iodine–fluorine coupling constant. Only for IF_7 itself has the ^{127}I–F coupling constant been reported, obtained by computer fitting of the spectrum which is partially collapsed by quadrupole relaxation.[11] It was calculated to be 2100 Hz with an error of less than 10%, significantly lower than the coupling constant determined here. It is interesting to note that comparison of the cation SeF_3^+ with other neutral Se(IV) fluorides similarly shows a large increase in the ^{77}Se–^{19}F coupling constant.[21]

It can be seen that although the peaks of the sextet have equal intensities, their widths and thus heights are not all the same (Figure 2). The two outside peaks are sharpest, followed by the two center peaks, with the second and fifth signals being the broadest. The "sharp" outside peaks are in fact fairly broad, having a width at half-height of 1.1 × 10^2 Hz, and the broadest peaks have a width of 1.7 × 10^2 Hz. Broadening of the peaks occurs because of quadrupole relaxation of the iodine. Multiplet line contours for the resonance of equivalent nuclei coupled to a high-spin nucleus undergoing quadrupole relaxation have been calculated by Suzuki and Kubo as a function of the parameter α.[23] For a nucleus of spin $^5/_2$

$$\alpha = \frac{125}{3}\frac{1}{T_1}\frac{1}{2\pi J}$$

where T_1 is the relaxation time of the quadrupole nucleus and J is the coupling constant to the nuclei being observed. The spectrum we obtain is best described by that calculated for $\alpha = 250$.[23] Cooling the sample from 34 to 0° causes the IF_6^+ peaks to broaden somewhat further, as expected for coupling to a nucleus undergoing quadrupole relaxation. In contrast, were the broadening of the room-temperature peaks caused by a chemical-exchange process, cooling the sample would slow the exchange and cause the peaks to narrow.

Quadrupole relaxation of a high-spin nucleus occurs if there is an electric field gradient at the nucleus. For an ion of O_h symmetry, such as IF_6^+, the electric field gradient at the iodine will be zero and quadrupole broadening would not be expected to occur. In fact, the broadening is quite large, and a well-resolved spectrum is seen only because of the large value of the ^{127}I–^{19}F coupling constant. Similar results have been previously reported for highly symmetric species. The ^{17}O nmr spectrum of MnO_4^- shows considerable broadening and the six components caused by coupling of ^{17}O to ^{55}Mn ($I = {}^5/_2$) form one peak envelope with six maxima.[24] Although quadrupole relaxation of ^{17}O itself contributes to the broadening, it was not possible to describe the band shape solely in terms of this effect. A significant broadening caused by quadrupole relaxation of ^{55}Mn also had to be taken into account to fit the observed spectrum. Quadrupole relaxation of the central nucleus has been explained by deformation of the ion, producing an electric field gradient at the nucleus. This can be due to collisions with other molecules in solution, which cause momentary distortions of symmetry.[24,25]

Acknowledgments.—We wish to thank Professor Z. Luz of the Weizmann Institute of Science for helpful discussions.

[20] M. Brownstein, P. A. W. Dean, and R. J. Gillespie, *Chem. Commun.*, 9 (1970).

[21] M. Brownstein and R. J. Gillespie, to be submitted for publication.

[22] M. Brownstein and J. Shamir, submitted for publication.

[23] M. Suzuki and R. Kubo, *Mol. Phys.*, **7**, 201 (1963).

[24] M. Broze and Z. Luz, *J. Phys. Chem.*, **73**, 1600 (1969).

[25] R. A. Dwek, Z. Luz, and M. Shporer, *ibid.*, **74**, 2232 (1970).

Contribution from the Department of Chemistry,
The University of Chicago, Chicago, Illinois 60637

The Reaction of Hydridopentacyanocobaltate(III) with Ferricyanide

By Jack Halpern* and Marijan Pribanić

Received July 12, 1971

While the hydridopentacyanocobaltate(III) ion, $Co(CN)_5H^{3-}$, has been found to exhibit pronounced reactivity toward substrates such as free radicals[1] and conjugated olefins[2] to which it can transfer a hydrogen atom, it appears to be intrinsically rather unreactive toward simple "electron transfer" type oxidants such as ferricyanide. Reactions of the latter type are, however, frequently promoted by OH^- and occur readily at sufficiently high pH. Under these conditions $Co(CN)_5H^{3-}$ was found to react with $Fe(CN)_6^{3-}$ in aqueous solution in accord with the stoichiometry

$$Co(CN)_5H^{3-} + 2Fe(CN)_6^{3-} + OH^- \longrightarrow [(NC)_5FeCNCo(CN)_5]^{6-} + Fe(CN)_6^{4-} + H_2O \quad (1)$$

---

[1] J. Kwiatek and J. K. Seyler, *Advan. Chem. Ser.*, **No. 70**, 207 (1968).

[2] J. Halpern and L. Y. Wong, *J. Amer. Chem. Soc.*, **90**, 6665 (1968).

This paper describes a study of the kinetics of this reaction and discusses its mechanism. Of related interest are recent studies of the OH^--promoted reactions of $Co(CN)_5H^{3-}$ with benzoquinone[3] and with $Hg(CN)_2$,[4] as well as the original characterization by Haim and Wilmarth[5] of the $[(NC)_5FeCNCo(CN)_5]^{6-}$ ion as the product of reaction of $Co(CN)_5{}^{3-}$ with $Fe(CN)_6{}^{3-}$.

Experimental Section

Materials.—Starting solutions of the desired composition were prepared by dissolving analytical reagent grade cobalt(II) chloride, potassium cyanide, potassium hydroxide, potassium ferricyanide, and potassium chloride (used to adjust the ionic strength) in distilled water with rigorous exclusion of oxygen (achieved by purging with nitrogen which had been passed twice through acidified chromium(II) perchlorate solutions in contact with amalgamated zinc).

Solutions of $Co(CN)_5H^{3-}$ were prepared by hydrogenation of corresponding solutions of $Co(CN)_5{}^{3-}$ according to eq 2 in a glass-lined Parr Series 4500 stirred autoclave, pressurized with approximately 20 atm of H_2, as previously described.[2,6] Under these conditions the equilibrium of reaction 2 lies sufficiently far to the right (and the reverse reaction following release of the hydrogen pressure is sufficiently slow) that interference from reaction of residual $Co(CN)_5{}^{3-}$ was negligible.

$$2Co(CN)_5{}^{3-} + H_2 \rightleftharpoons 2Co(CN)_5H^{3-} \qquad (2)$$

Kinetic Measurements.—The kinetics of the reaction were followed by monitoring the decrease in the concentration of $Fe(CN)_6{}^{3-}$ spectrally at 418 nm. A Cary 14 spectrophotometer with a thermostated (±0.2°) cell compartment was used for these measurements, as well as to record reactant and product solution spectra. The reactions were initiated by injecting, with a hypodermic syringe, a calibrated small volume of a standardized stock solution of $Co(CN)_5H^{3-}$ (typically 0.010 ml of 0.030 *M* $Co(CN)_5H^{3-}$) into a serum-capped spectrophotometer cell filled with a solution containing the other reaction components and thermally equilibrated to the reaction temperature.

Results and Discussion

Stoichiometry.—The following observations provide quantitative confirmation of the stoichiometry described by eq 1.

(1) Several spectral titrations, in which solutions, initially containing *ca.* 0.2 *M* OH^- and $Fe(CN)_6{}^{3-}$ concentrations ranging from 4.5×10^{-3} to 1.5×10^{-3} *M*, were titrated with $Co(CN)_5H^{3-}$ and the spectral changes at 300 and 408 nm (corresponding to absorption maxima of $Fe(CN)_6{}^{3-}$) were monitored, exhibited sharp end points at $Fe(CN)_6{}^{3-}:Co(CN)_5H^{3-}$ ratios of 2.02 ± 0.05 in agreement with eq 1.

(2) The final solution spectrum in each case was in quantitative agreement with that reported by Haim and Wilmarth[5] (and confirmed by us) for $[(NC)_5FeCNCo(CN)_5]^{6-}$ prepared by an alternate route, namely, the stoichiometric reaction of $Co(CN)_5{}^{3-}$ with $Fe(CN)_6{}^{2-}$.

Kinetics.—Kinetic measurements were performed over the temperature range 3–35° and over a wide range of solution compositions encompassing the initial concentration ranges: 1.8×10^{-6}–1.8×10^{-4} *M* $Co(CN)_5H^{3-}$, 1.8×10^{-4}–1.8×10^{-3} *M* $Fe(CN)_6{}^{3-}$, 5.0×10^{-3}–2.0×10^{-1} *M* OH^-, 0–0.10 *M* CN^-, 0–0.01 *M* $Fe(CN)_6{}^{4-}$, 0.11–2.0 *M* ionic strength (adjusted with KCl).

The kinetic results conformed accurately to the rate law described by eq 3. Under the conditions of our measurements, with $Fe(CN)_6{}^{3-}$ in excess over $Co(CN)_5H^{3-}$ and with the OH^- concentration sufficiently high to remain essentially constant throughout each reaction, the observed kinetic behavior was always pseudo first order (over at least 4 half-lives) in accord with eq 4, where $k_{obsd} = k_5[OH^-]$.

$$-d[Fe(CN)_6{}^{3-}]/dt = -2d[Co(CN)_5H^{3-}]/dt = 2k_5[Co(CN)_5H^{3-}][OH^-] \qquad (3)$$

$$-d \ln [Co(CN)_5H^{3-}]/dt = k_{obsd} \qquad (4)$$

The kinetic measurements are summarized in Table I.

TABLE I

SUMMARY OF KINETIC DATA

Temp, °C	Initial concn, *M*			Ionic strength, *M*	10^2k_{obsd}, sec^{-1}	k_5, M^{-1} sec^{-1}
	$10^5[Co(CN)_5H^{3-}]$	$10^3[Fe(CN)_6{}^{3-}]$	$[OH^-]$			
25.0	1.8	1.8	0.10	1.0	1.7	0.17
25.0	4.5	1.8	0.10	1.0	1.7	0.17
25.0	9.0	1.8	0.10	1.0	1.6	0.16[a]
25.0	18.0	1.8	0.10	1.0	1.6	0.16
25.0	1.8	0.18	0.10	1.0	1.6	0.16
25.0	5.0	5.0	0.10	1.0	1.5	0.15
25.0	9.0	1.8	0.0050	1.0	0.086	0.17
25.0	9.0	1.8	0.010	1.0	0.17	0.17
25.0	9.0	1.8	0.025	1.0	0.44	0.18
25.0	9.0	1.8	0.050	1.0	0.79	0.16
25.0	9.0	1.8	0.20	1.0	3.16	0.16
25.0	9.0	1.8	0.10	0.11	0.35	0.035
25.0	9.0	1.8	0.10	0.25	0.54	0.054
25.0	9.0	1.8	0.10	0.50	0.81	0.081[b]
25.0	9.0	1.8	0.10	1.5	2.0	0.20[b]
25.0	9.0	1.8	0.10	2.0	2.5	0.25
3.0	9.0	1.8	0.10	1.0	0.50	0.050
14.0	9.0	1.8	0.10	1.0	0.63	0.063
20.0	9.0	1.8	0.10	1.0	1.2	0.12
29.0	9.0	1.8	0.10	1.0	2.0	0.20
35.0	9.0	1.8	0.10	1.0	2.5	0.25

[a] Unaffected by the addition of up to 0.1 *M* CN^- or up to 0.01 *M* $Fe(CN)_6{}^{4-}$. [b] Unchanged when NaCl was used instead of KCl to adjust the ionic strength.

At constant temperature and ionic strength k_5 is seen to be substantially independent of the initial concentrations of $Co(CN)_5H^{3-}$, OH^-, and $Fe(CN)_6{}^{3-}$ and unaffected by the addition of CN^- or $Fe(CN)_6{}^{4-}$. The values of k_5, determined over the temperature range 3–35°, yielded a good Arrhenius plot from which the following activation parameters were computed: $\Delta H^{\ddagger} = 8.0 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -35 \pm 2$ cal mol^{-1} deg^{-1}.

Mechanism.—The observed kinetics are most plausibly interpreted in terms of a mechanistic scheme, similar to that proposed for other OH^--promoted reactions of $Co(CN)_5H^{3-}$,[3,4] *i.e.*, involving the pentacyanocobaltate(I) ion, $Co(CN)_5{}^{4-}$, generated by the rate-determining step

$$Co(CN)_5H^{3-} + OH^- \xrightarrow{k_5} Co(CN)_5{}^{4-} + H_2O \qquad (5)$$

followed either by the rapid reaction sequence

$$Co(CN)_5{}^{4-} + Fe(CN)_6{}^{3-} \longrightarrow [(NC)_5FeCNCo(CN)_5]^{7-} \qquad (6a)$$

$$[(NC)_5FeCNCo(CN)_5]^{7-} + Fe(CN)_6{}^{3-} \longrightarrow [(NC)_5FeCNCo(CN)_5]^{6-} + Fe(CN)_6{}^{4-} \qquad (6b)$$

or, alternatively, by the sequence

$$Co(CN)_5{}^{4-} + Fe(CN)_6{}^{3-} \longrightarrow Co(CN)_5{}^{3-} + Fe(CN)_6{}^{4-} \qquad (7a)$$

$$Co(CN)_5{}^{3-} + Fe(CN)_6{}^{3-} \longrightarrow [(NC)_5FeCNCo(CN)_5]^{6-} \qquad (7b)$$

---

(3) J. Hanzlik and A. A. Vlcek, *Inorg. Chem.*, **8**, 669 (1969).

(4) H. S. Lim and F. C. Anson, *ibid.*, **10**, 103 (1971).

(5) A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).

(6) J. Halpern and M. Pribanić, *Inorg. Chem.*, **9**, 2616 (1970).

Our kinetic data do not distinguish between these two mechanistic variants which become equivalent if, as is indeed expected to be the case, the intermediate of the first mechanism, $[(NC)_5FeCN(CN)_5]^{7-}$, dissociates rapidly into $Fe(CN)_6^{4-}$ and $Co(CN)_5^{3-}$. The nature of the ionic strength dependence and the large negative $\Delta S^{\ddagger}$ are consistent with the proposed rate-determining step between two negative ions.

Our value of k_5 (8.1×10^{-2} M^{-1} sec^{-1} at 25°, $\mu = 0.5$ M) is in reasonably good agreement with the corresponding value (9.6×10^{-2} M^{-1} sec^{-1} at 24°, $\mu = 0.5$ M adjusted with $NaClO_4$ instead of KCl) determined by Lim and Anson[4] from kinetic measurements on the reaction of $Co(CN)_5H^{3-}$ with $Hg(CN)_2$. However, as already pointed out by Lim and Anson,[4] this value is too low to accommodate a mechanism encompassing eq 5 as a step, such as that proposed by Hanzlik and Vlcek,[3] for the much faster reaction of $Co(CN)_5H^{3-}$ with benzoquinone. The origin of this discrepancy is unclear and warrants further investigation.

In contrast to the reaction with $Hg(CN)_2$[4], the reaction of $Co(CN)_5^{4-}$ with $Fe(CN)_6^{3-}$ (eq 6a or 7a) is too fast for significant competition from the back-reaction of eq 5 (*i.e.*, from eq 8) to be observed even at our lowest $Fe(CN)_6^{3-}$ concentrations (*ca.* 1.8×10^{-4} M). Since, based on an earlier direct determination,[7] $k_{-5} = 1.1 \times 10^5$ sec^{-1}, we conclude that the rate constant for the reaction of $Co(CN)_5^{4-}$ with $Fe(CN)_6^{3-}$ (eq 6a or 7a) must be at least 10^{10} M^{-1} sec^{-1}, *i.e.*, essentially diffusion controlled. Combination of the values

$$Co(CN)_5^{4-} + H_2O \xrightarrow{k_{-5}} Co(CN)_5H^{3-} + OH^- \qquad (8)$$

k_5 and k_{-5}, cited above, yields a value of about 20 for the pK_a of $Co(CN)_5H^{3-}$ which, thus, is an extremely weak acid.

Acknowledgments.—Support of this work through grants from the National Institutes of Health and from the National Science Foundation is gratefully acknowledged. M. P. also thanks the U. S. Government Fulbright–Hays Program for a travel grant and the University of Zagreb for a leave of absence.

[7] G. D. Venerable II and J. Halpern, *J. Amer. Chem. Soc.*, **93**, 2176 (1971).

Contribution from the Department of Chemistry,
Harvey Mudd College, Claremont, California 91711

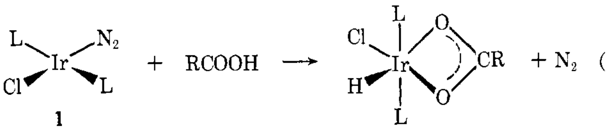
Hydridocarboxylato Complexes of Iridium

By Sally A. Smith,[1] Daniel M. Blake,
and Mitsuru Kubota*

Received July 12, 1971

The formation of hydrido–transition metal complexes by the oxidative addition of protonic acids to complexes of transition metals in low oxidation states is relevant to the elucidation of fundamental processes involved in reactions which are homogeneously catalyzed.[2] The oxidative addition of hydrogen halides HX to square-planar d^8 complexes *trans*-$Ir(CO)X(P(C_6H_5)_3)_2$ leads to formation of the hydrido complexes $IrH(CO)X_2(P(C_6H_5)_3)_2$.[3] While it is expected that carboxylic acids, RCOOH, should form hydridocarboxylato complexes, $IrH(CO)X(RCOO)(P(C_6H_5)_3)_2$, such complexes have not been isolated except for acids in which R is CF_3 or C_2F_5.[4] The formation of hydrido complexes by oxidative addition of protonic acids to d^{10} complexes is observed when the acid is strong or when the conjugate base of the acid is a good ligand.[5] The extent of protonation of four-coordinated iridium(I) complexes by carboxylic acids has been related to the basicity of the iridium complex and the pK_a of the carboxylic acid.[6] Due to extensive dissociation, the carboxylatohydrido complexes have not been isolated. That the carboxylato group is a good ligand for iridium(III) is indicated by the isolation of complexes formed by substitution of the chloro ligands using silver carboxylates.[7] Details for the synthesis of these compounds have not been presented. Carboxylato ligands form strong bonds in related complexes. For example, monodentate carboxylato complexes are formed in oxidative addition reactions of carboxylic acids with d^8 complexes of ruthenium.[8] These reactions, however, do not form hydrido derivatives. Hydridocarboxylatotris(triphenylphosphine)ruthenium(II) complexes have been prepared by the reactions of $RuCl_2(P(C_6H_5)_3)_3$, the sodium salt of a carboxylic acid, and hydrogen in methanol.[9]

Carboxylic acids have been found in the present study to react with *trans*-$IrCl(N_2)(P(C_6H_5)_3)_2$ to form hydridocarboxylato complexes **2** (L is triphenylphosphine).



1 **2** (1)

Analytical results for all compounds are given in Table I. Pertinent ir spectral data for these complexes are presented in Table II. The Ir–H stretching frequencies in the 2221–2304-cm^{-1} region are much higher than those in related iridium(III) hydrido complexes[10] or related ruthenium(II) hydridocarboxylato complexes.[9] The high frequencies may be attributed to the low trans labilizing properties of the carboxylato ligand. The assignment of the Ir–H stretching frequencies was confirmed by running a reaction of the dinitrogen complex **1** with deuterioacetic acid. The product **2A′** has a band at 1655 cm^{-1} which is assigned to the Ir–D stretching frequency (ν(Ir–H)/ν(Ir–D) = 1.392). The far-ir data in the Ir–Cl stretching region, namely, the absence of absorption in the 250–275-cm^{-1} region, indicate that Cl is not trans to a hydrido or triphenylphosphine ligand.[10] The symmetric and asymmetric carboxylato frequencies in the

---

[1] National Science Foundation Undergraduate Research Participant.

[2] J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

[3] L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, **83**, 2784 (1961).

[4] H. Singer and G. Wilkinson, *J. Chem. Soc. A*, 2516 (1968).

[5] D. M. Roundhill, P. B. Tripathy, and B. W. Renoe, *Inorg. Chem.*, **10**, 727 (1971).

[6] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1802 (1969).

[7] R. M. Slade and B. L. Shaw, unpublished work cited in ref 6.

[8] B. F. G. Johnson, R. D. Johnston, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 689 (1971).

[9] D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *ibid.*, *A*, 2610 (1969).

[10] (a) D. M. Blake and M. Kubota, *Inorg. Chem.*, **9**, 989 (1970); (b) D. M. Blake and M. Kubota, *J. Amer. Chem. Soc.*, **92**, 2578 (1970).