recombination ($Fe_2S_2 + Fe_2Se_2 \rightleftarrows Fe_4S_2Se_2$) does not appear to be the first event of reaction. As may be seen in Figures 2 and 4, as well as in systems with $N_S \neq N_{Se}$, the first new species to appear are 3,1 and 1,3 rather than 2,2.

Acknowledgment. This research was supported by NIH Grants GM-22352 and GM-28856.

Registry No. $[Fe_2S_2(S\text{-}p\text{-}tol)_4]^{2-}$, 55939-63-4; $[Fe_2SSe(S\text{-}p\text{-}tol)_4]^{2-}$, 77136-59-5; $[Fe_2Se_2(S\text{-}p\text{-}tol)_4]^{2-}$, 74752-89-9; $[Fe_4S_4(S\text{-}p\text{-}tol)_4]^{3-}$, 67724-72-5; $[Fe_4S_3Se(S\text{-}p\text{-}tol)_4]^{3-}$, 77305-58-9; $[Fe_4S_2Se_2(S\text{-}p\text{-}tol)_4]^{3-}$, 77305-56-7; $[Fe_4SSe_3(S\text{-}p\text{-}tol)_4]^{3-}$, 77305-54-5; $[Fe_4Se_4(S\text{-}p\text{-}tol)_4]^{3-}$, 75025-81-9; $[Fe_4S_4(S\text{-}p\text{-}tol)_4]^{2-}$, 51899-68-4; $[Fe_4S_3Se(S\text{-}p\text{-}tol)_4]^{2-}$, 77305-57-8; $[Fe_4S_2Se_2(S\text{-}p\text{-}tol)_4]^{2-}$, 77305-55-6; $[Fe_4SSe_3(S\text{-}p\text{-}tol)_4]^{2-}$, 77305-53-4; $[Fe_4Se_4(S\text{-}p\text{-}tol)_4]^{2-}$, 75025-82-0.

Contribution from the Chemical Laboratories of the University of California,
Santa Barbara, California 93106

Rate and Equilibrium Data for the Protonation of Vaska's Compound and Analogues

RALPH G. PEARSON* and CHARLES T. KRESGE

Received October 30, 1980

Equilibrium constants, K_{H^+}, for the addition of a proton, and K_{HCl}, for the addition of HCl, were measured in methanol for a series of analogues of Vaska's compound, $MY(CO)L_2$. The constants were nearly equal, showing that chloride and methanol are held about equally well in the product complexes. Rhodium(I) complexes are 10 times less basic than the corresponding iridium(I) complexes. A study of the kinetics of the addition reactions showed that chloride ion or solvent added to the metal first, followed by protonation.

The Brønsted acidity of transition-metal hydrides and the related proton basicity of transition-metal complexes are receiving increased attention.[1,2] The role of such hydrides in homogeneous catalysis is a major reason for such interest. The general equation is

$$HML_n + B \rightleftharpoons ML_n^- + BH^+ \tag{1}$$

where both rate and equilibrium constants can be measured in many cases. An additional feature of (1) is that it is an example of reductive elimination in the forward direction and oxidative addition in the reverse direction. The normal oxidation state of the metal is increased by two units upon protonation. Structural changes also occur which show that the oxidation is more than formal.

There is only a modest amount of information available on the effect of changing the metal, M, and the coligands, L, on rates and equilibrium for reaction 1. There is a strong trend for greater basicity in complexes of heavier elements compared to the analogous complexes of the lighter elements. However a recent study of the nucleophilic reactivity of a large number of ML_n showed that no simple pattern existed for rate data.[3] Similar irregularities may be expected for proton basicities.

When ML_n is a square-planar complex of a d^8 metal atom, addition of H^+ is usually accompanied by addition of a second group, X (eq 2). The role played by the group X in determining the rates and equilibria for (2) is not well-known.

$$ML_4 + HX \rightleftharpoons ML_4HX \tag{2}$$

Pioneering studies by Shaw and Deeming[4] on addition of HX in benzene to Vaska's compound and its analogues showed that variations did exist (eq 3). For example $X = Cl^-$ added more strongly than $X = NO_3^-$.

$$IrY(CO)L_2 + HX \rightleftharpoons IrY(CO)L_2HX \tag{3}$$

The addition of acetic acid was reversible and allowed equilibria to be measured as a function of Y and L. Other carboxylic acids also added, with the stronger acids binding to a greater extent.

The complexes $Ir(cod)L_2^+$ and $IrCl(cod)L$, where cod is 1,5-cyclooctadiene, will add HCl and HBr in methanol, but the proton alone will not add.[5] Thus $X = CH_3OH$ is ineffective in oxidative addition to these complexes. Somewhat surprisingly, it was found that the mechanism of addition occurred by X^- adding first, followed by the proton.

The present work was undertaken to get more information on the role of changes in the metal, M, and the coligands, L. An early observation was that, unlike the cod complexes above, Vaska's compound would add the proton only. That is, acids such as CF_3SO_3H and FSO_3H would react. As in the related case of reaction with $CF_3SO_3CH_3$, it is likely that the solvent methanol occupies the sixth position.[6] The kinetics of the addition of H^+ and of HCl were also examined.

Experimental Section

Reagent grade methanol was distilled to remove most of the water present. It was then stored over 3A or 4A molecular sieves under a positive pressure of dry, oxygen-free nitrogen. This was then followed by storage over lumps of calcium hydride, again under a positive pressure of nitrogen.

Reagent grade acetonitrile was predried by stirring with calcium hydride until gas evolution stopped. It was then distilled from P_2O_5 (≤ 5 g/L) in an all-glass apparatus. The first 5% and the last 10% of the distillate were discarded in order to reduce the acrylonitrile content. This was followed by storage under a positive pressure of nitrogen.

Prior to use, the solvents were deoxygenated by bubbling purified nitrogen through them for approximately 1 h. All solvents were handled with use of standard airless techniques (Schlenk tube or serum cap/syringe).

All materials were prepared and stored under prepurified nitrogen. All solutions were prepared and stored under nitrogen in vessels equipped with serum caps to allow for transfer by syringe. Acid and base solutions were freshly prepared prior to each experiment. Trifluoromethanesulfonic acid, HSO_3CF_3 (Aldrich Chemical Co., analytical grade), was used without further purification. Hydrochloric acid and hydrobromic acid (Linde Division, Union Carbide Corp.) solutions were prepared by bubbling gaseous HCl or HBr (anhydrous) through methanol followed by standardization by simple titration.

Tetraethylammonium chloride and bromide (J. T. Baker Chemical Co.), $AgNO_3$ (Mallinckrodt Chemical Co.), $P(OMe)_3$ (Ventron

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(1) For recent work see: Ramasami, T.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 1846.

(2) For recent work see: Walker, H. W.; Kresge, C. T.; Ford, P. C.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 7248. Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *Ibid.* **1979**, *101*, 2027. For reviews of earlier work see: Schunn, R. A. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 203–269. Kaesz, H. D. *Chem. Brit.* **1973**, *9*, 344.

(3) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.

(4) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 1887; **1969**, 1802.

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Chemical Co.) were used without purification. Sodium methoxide was prepared from Na metal and methanol by standard methods followed by standardization by titration.

The following [$MY(CO)L_2$] complexes were prepared by methods in the literature. For M = Ir: $IrCl(CO)(PPh_3)_2$,[7] $IrY(CO)(PPh_3)_2$ (Y = Br, I),[8] $IrCl(CO)(PMePh_2)_2$,[9] $IrY(CO)(PMePh_2)_2$ (Y = Br, I),[10] $IrY(CO)(PMe_2Ph)_2$ (Y = Cl, Br, I),[11] $IrCl(CO)(P\text{-}t\text{-}Bu_2R)_2$ (R = Me, Et),[12] $IrCl(CO)L_2$ (L = $AsPh_3$, $AsMePh_2$),[13] $IrCl(CO)(AsMe_2Ph)_2$.[4] For M = Rh: $RhY(CO)L_2$ (Y = Cl, Br, I; L = PPh_3, $AsPh_3$).[14]

Equilibrium Studies

The extent of protonation of *trans*-[$MY(CO)L_2$] by strong acids to give the corresponding M(III) complex was studied spectrophotometrically on a Cary 118C UV-visible spectrophotometer equipped with a thermostated-cell compartment. Temperature was maintained at 25 ± 0.2 °C during these studies. The extent of conversion to the M(III) species was readily determined spectrally since the yellow Ir(I) and Rh(I) complexes have absorption bands with maxima at ca. 380 and 440 nm, whereas the colorless Ir(III) and Rh(III) products do not absorb in these regions. Thus the decrease in absorbance at these maxima gives directly the amount of the M(I) species converted. The initial concentrations of the [$MY(CO)L_2$] complexes in these experiments were generally in the range of 3×10^{-4}–2×10^{-3} M. Acid concentrations ranged from 2×10^{-3} to 8×10^{-2} M. Several runs under each set of reaction conditions were made in order to establish reproducibility of results (better than ±2%). Nitrogen-saturated methanol was used as the solvent, except for the studies involving $IrY(CO)(PPh_3)_2$ (Y = Cl, Br, I), due to the insolubility of these complexes in methanol. A solvent mixture consisting of 90% methanol and 10% acetonitrile (v/v) was found to be satisfactory. Equilibrium studies involving Ir(I) complexes which were soluble in methanol were also performed with use of this 9:1 methanol/acetonitrile mixture in order to observe the effect of acetonitrile on the results. The equilibrium constants so measured were the same with those found in the 100% methanol studies within experimental error. Also the addition of 1% water had no effect on the measured equilibria and rates. The Ir(I) and Rh(I) complexes are quite stable in methanol and acetonitrile; any decomposition was much slower than the protonation reaction being monitored. All products also appeared to be stable.

In a typical experiment a 2.5-mL aliquot of the M(I) complex was transferred by syringe to a quartz UV-visible cell (1-cm path length); a matched cell containing solvent was in the reference beam. This cell was also equipped with a serum cap and purged with nitrogen. A scan of the spectrum was made. Spectrophotometric titrations were than made by incremental addition of acid solution to the cell. The first optical density measurements were made within 1 min of addition and mixing of the solutions. After this initial scan, optical density measurements were also made after known time intervals. The optical density readings were corrected to the initial volume of the solution by multiplying the optical density readings by the factor, $(V + v)/V$, where V is the initial volume of the solution and v is the volume of the titrant added for the particular optical density reading being considered. These systems were shown by us and others[9] to obey Beer's law. Reactants and products were characterized by comparison of experimental spectra, NMR, UV-visible, and infrared, with published spectra when available.

Nuclear magnetic resonance spectra were recorded at 34 °C on a Varian XL-100 Fourier transform spectrometer. The general procedure was to make a solution of the Ir(I) complex and acid in methanol. This solution was placed into a 5-mm NMR tube. A smaller tube containing D_2O as a lock for the Fourier transform was inserted into the NMR tube. Tetramethylsilane was used as reference.

Infrared spectra (4000–200 cm^{-1}) of the complexes were recorded on a Perkin-Elmer 283 spectrometer. Spectra were calibrated against polystyrene. Spectra of solid samples were taken as KBr pellets. Spectra of solutions were taken in methanol with use of liquid cells with 1-mm spacing between IR-trans II (ZnS) or polyethylene windows.

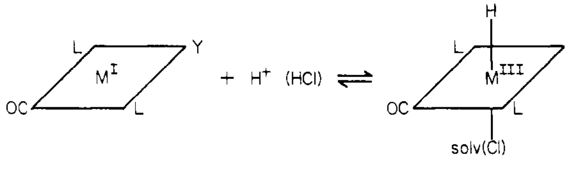
Kinetic Studies

Rates of protonation of $IrY(CO)L_2$ complexes were determined by the rates of disappearance of Ir(I) absorption bands. The kinetic runs were carried out with a Durrum-Gibson D110 stopped-flow spectrophotometer equipped with a thermostated cell (2-cm optical path). The reservoir syringes and observation block containing the mixing chamber were also thermostated. The temperature was maintained at 25 ± 0.2 °C. The measurements were performed in the 370–380-nm range where the molar absorptivities of the $IrY(CO)L_2$ complexes are in the range 1.5×10^3–4.0×10^3 M^{-1} cm^{-1} and that of the solvent and products is negligible. The initial concentration of $IrY(CO)L_2$ in these experiments was generally in the range of 3×10^{-4}–5×10^{-3} M. Kinetic results were the same when the studies were done at ca. 440 nm. The reaction was carried out under pseudo-first-order conditions with the concentration of the acid much larger than that of the metal complex (at least a 10-fold excess). Values of the absorbance of the solution, i.e., the iridium(I) absorption peak, as a function of time were read from the photographs of the reaction traces on the oscilliscope screen. The pseudo-first-order rate constants, k_{obsd}, were obtained from plots of ln $(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances at time t and at infinite time, respectively. Pseudo-first-order rate constants were reproducible to 10% or better. Each reaction was monitored at least six times. Special precautions were taken to exclude oxygen during kinetic (and equilibrium) studies by using inert-atmosphere and serum cap/syringe techniques. Again, reactants and products were characterized by comparison of experimental spectra with published spectra when available.

Results

Detailed NMR and IR studies were made to determine the stereochemistry of addition of HCl to all of the iridium(I) complexes studied.[15] In all cases it was found that stereospecific trans addition had occurred. These results are in complete agreement with earlier results which show trans addition of HX in polar solvents and cis addition in nonpolar solvents and from the gas phase.[16] Hydrogen bromide was also found to add trans to $IrCl(CO)(PPh_3)_2$.

These methods cannot readily be used to determine the stereochemistry of addition of the proton alone. However the general pattern of behavior found for this reaction strongly suggests that the same stereochemistry prevails. Thus all of the reactions reported in this work may be represented by the general equation (4) though there is no direct evidence for the solvent molecule in the sixth position of A.



A (4)

Using CF_3SO_3H as the acid, equilibrium constants were calculated from the relationship in eq 5. The results are given

$$K_{H^+} = \frac{[M(III)]}{[M(I)][H^+]} \qquad (5)$$

in Table I for the iridium complexes. The effects of the substituents L and Y on the basicity is the same as that found for rates and equilibria of a number of oxidative-addition

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(7) Collman, J. P.; Sears, C. T.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 102.

(8) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

(9) Collman, J. P.; Sears, C. T. *Inorg. Chem.* **1968**, *7*, 27.

(10) General method described by: Ball, M. C.; Pope, J. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1802.

(11) Modification of method in ref 4.

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(15) The details are given in: Kresge, C. T. Ph.D. Thesis, University of California, Santa Barbara, 1979.

(16) References 4 and 9. Deeming, A. J.; Shaw, B. L. *Chem. Commun.* **1968**, 751. Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 5325. Blake, D. M.; Kubota, M. *Inorg. Chem.* **1970**, *9*, 989.

Table I. Equilibrium Constants as a Function of Ligands L and Y for $IrY(CO)L_2 + H^+$ in Methanol at 25 °C[a]

L	Y	K_{H^+}, M^{-1}
PPh_3[b]	Cl	1.14×10^2
PPh_3[b]	Br	4.16×10^2
PPh_3[b]	I	7.04×10^2
$PMePh_2$	Cl	3.02×10^2
$PMePh_2$	Br	8.51×10^2
$PMePh_2$	I	1.63×10^3
PMe_2Ph	Cl	6.31×10^2
PMe_2Ph	Br	1.86×10^3
PMe_2Ph	I	3.76×10^3
$AsPh_3$	Cl	2.03×10^2
$AsMePh_2$	Cl	5.16×10^2
$AsMe_2Ph$	Cl	8.68×10^2
P-*t*-$BuMe_2$	Cl	5.98×10^2
P-*t*-$BuEt_2$	Cl	5.02×10^2
P(*t*-Bu)$_2$Me	Cl	4.62×10^2
P(*t*-Bu)$_2$Et	Cl	3.85×10^2

[a] Constancy better than ±5%. [b] In 90:10 methanol/acetonitrile.

Table II. Equilibrium Constants for Rhodium Complexes at 25 °C

compd	K_{H^+}, M^{-1}	compd	K_{H^+}, M^{-1}
$RhCl(CO)(PPh_3)_2$	6.3×10	$RhBr(CO)(AsPh_3)_2$	9.9×10
$RhBr(CO)(PPh_3)_2$	8.7×10	$RhI(CO)(AsPh_3)_2$	1.11×10^2
$RhI(CO)(PPh_3)_2$	1.03×10^2	Rh(diphos)-$(CH_3OH)_2^+$	1.1×10[a]
$RhCl(CO)(AsPh_3)_2$	7.5×10		

[a] Reference 21.

reactions: I > Br > Cl, $P(Me_2Ph)_3 > P(MePh_2)_3 > P(Ph_3)_3$, $AsR_3 > PR_3$.[8,12,16,17] This supports the view that proton basicity and oxidation potential are one and the same parameter for transition-metal bases. For nontransition elements, they are quite independent parameters.

The *tert*-butylphosphine complexes were included in the study in an attempt to probe electronic and steric effects separately. The *tert*-butyl group is more basic than the phenyl group and also more bulky.[18] The results shown in Table I indicate that electronic and steric effects are of comparable importance. Indeed the most notable conclusion to be drawn from Table I is the small range of basicities which covers all of these complexes.

Table II gives the more limited results found for rhodium(I) complexes. Comparison of analogous complexes in Tables I and II shows that the rhodium complexes in all cases are less basic than the iridium analogues. The factors are small, however, ranging from 2 to 10. This reduced basicity of Rh(I) is consistent with a reduced tendency to undergo oxidative-addition reactions compared to Ir(I).[3,19] Because of a lack of analogous complexes, the position of cobalt(I) in the series is not clear. The hydrides $HCo(dmg)_2P(n\text{-}Bu)_3$ and $HRh(dmg)_2P(Ph)_3$ are reported to have pK_a's of 10.5 and 9.5, respectively, in 50:50 water/methanol (dmg is the monoanion of dimethylglyoxime).[1,20] The greater basicity of cobalt(I) may simply be due to the more basic phosphine present as a coligand.

The next series of experiments were measurements of the equilibrium constant for the addition of HCl to a series of Ir(I) complexes (eq 6). The unexpected result was that the degree

$$IrY(CO)L_2 + HCl \rightleftharpoons IrY(CO)L_2HCl \qquad (6)$$

of conversion of iridium(I) to iridium(III) was very much the same at the same concentration of acid, regardless of whether CF_3SO_3H or HCl was used. Furthermore adding a 10-fold excess of $N(n\text{-}Bu)_4Cl$ to a given concentration of HCl had only a modest effect on the Ir(III):Ir(I) ratio. At the concentrations used, HCl and presumably the stronger acid CF_3SO_3H are completely dissociated in methanol.[22]

Table III. Results of Hydrogen Chloride Addition to $IrY(CO)L_2$ at 25 °C

L	Y	K_{HCl}, M^{-1}
PPh_3	Cl	2.20×10^2
PPh_3	Br	6.30×10^2
$PMePh_2$	Cl	6.17×10^2
$PMePh_2$	Br	1.48×10^3
PMe_2Ph	Cl	1.10×10^3
PMe_2Ph	Br	3.06×10^3

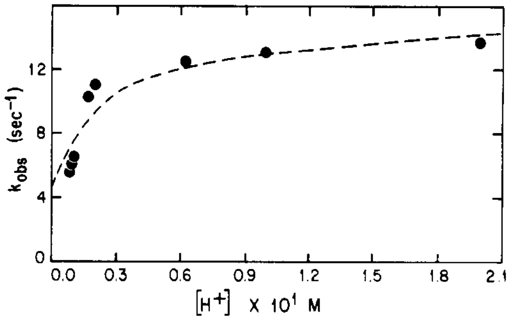

Figure 1. Circles are experimental first-order rate constants for reaction of $IrCl(CO)(PPh_3)_2$ with H^+ in methanol at 25 °C. The dashed line is the computed fit to eq 14.

When the chloride ion is ignored altogether, eq 5 was used to calculate an equilibrium constant, K_{HCl}. The constancy of this number over a range of HCl concentrations was not as good as for K_{H^+} but was satisfactory (±10%). The results given in Table III show that K_{HCl} is 1.5–2.0 times as great as K_{H^+}. The only reasonable interpretation is that the solvolytic equilibrium (eq 7) has an equilibrium constant near unity;[23]

$$IrY(CO)L_2HCl + CH_3OH \rightleftharpoons IrY(CO)L_2H(CH_3OH)^+ + Cl^- \qquad (7)$$

that is, the free energy is nearly the same whether a chloride ion or a solvent molecule is trans to the hydride ligand.

For comparison, the solvolysis reaction (8) has an equilibrium

$$Ir(NH_3)_5Cl^{2+} + H_2O \rightleftharpoons Ir(NH_3)_5(H_2O)^{3+} + Cl^- \qquad (8)$$

rium constant[24] of 8×10^{-5} M at 95 °C. Also reaction 7 must be labile at room temperature, whereas (8) has a half-life of hours even at 95 °C. Considering the difference in charges and the strong trans effect of a hydride ligand, these differences are not unreasonable.

Oxidative additions of HX to analogues of Vaska's compound are clearly quite different from those of $Ir(cod)L_2^+$ and IrCl(cod)L where solvent cannot take the place of X^-. This is also understandable since the diolefin ligand will stabilize the iridium(I) oxidation state. An anionic ligand can provide the extra driving force needed to go to iridium(III).

The kinetics of addition of H^+ and HCl to $IrCl(CO)(PPh_3)_2$ and $IrBr(CO)(PPh_3)_2$ were studied in 90:10 methanol/acetonitrile.

The pseudo-first-order rate constants found are shown as a function of acid concentration in Figures 1–4. In all cases

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(17) The anomalous order Cl > Br > I found for rates of reaction with methyl iodide is discussed in Kubota, M. *Inorg. Chim. Acta* **1973**, *7*, 195.

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(22) Harned, H.; Thomson, H. *J. Am. Chem. Soc.* **1936**, *58*, 761. Kolthoff, J.; Guss, L. *Ibid.* **1944**, *66*, 1484.

(23) While it is easy to show that concentrated solutions of $IrY(CO)L_2HCl$ contain coordinated chloride ion, we were unable to devise a method for assaying free and bound Cl^- in dilute solutions.

(24) Lamb, A. B.; Fairhall, L. T. *J. Am. Chem. Soc.* **1923**, *45*, 378.

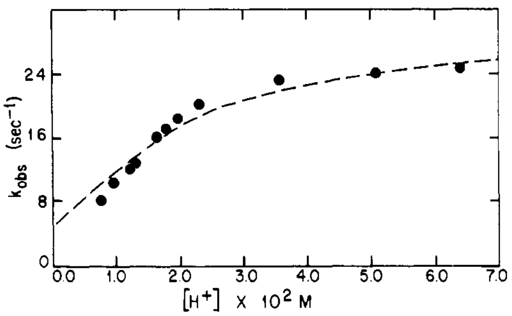

Figure 2. First-order rate constants for reaction of $IrCl(CO)(PPh_3)_2$ with HCl.

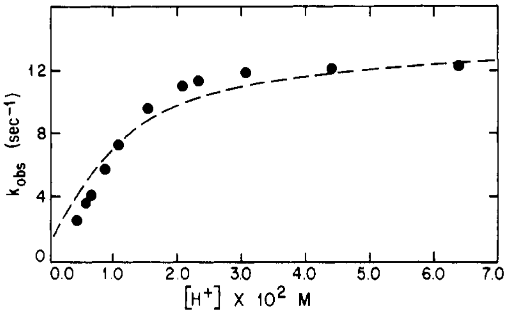

Figure 3. First-order rate constants for reaction of $IrBr(CO)(PPh_3)_2$ with H^+.

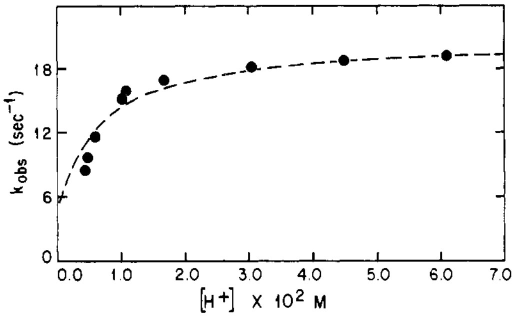

Figure 4. First-order rate constants for reaction of $IrBr(CO)(PPh_3)_2$ with HCl.

the rate constant leveled off and reached a nearly constant value at high concentrations of acid. Measurements at very low hydrogen ion concentrations were not possible because of the small extent of protonation.

A limiting rate at high acid concentration can be explained by one of two mechanisms. In the first, a preequilibrium exists between the proton and the metal complex, represented by M (eq 9 and 10). The slow step would be the addition of X^-

$$M + H^+ \rightleftharpoons MH^+ \quad \text{fast} \tag{9}$$

$$MH^+ + X^- \rightleftharpoons MHX \quad \text{slow} \tag{10}$$

or of solvent. However this mechanism is inconsistent with the results. The slow step measured has a large spectral change, whereas (9) and not (10) would be expected to give the large spectral change. Also extrapolation back to zero time was found to give an optical density equal to that of the starting complex, M.

The alternative mechanism is in goood agreement with the results (eq 11 and 12). Applying the steady-state approximation to the concentration of MX^- gives the rate law for the approach to equilibrium (eq 13 and 14). It must be assumed

$$M + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MX^- \tag{11}$$

$$MX^- + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MHX \tag{12}$$

Table IV. Rate Data for Reaction of $IrY(CO)(PPh_3)_2$ with H^+ and HCl at 25 °C in Methanol[a]

reactants Y	k_1, s^{-1}	k_{-2}, s^{-1}	k_{-1}/k_2, M	$k_1k_2/k_{-1}k_{-2}$
Cl, H^+ i	16	4.6	0.030	114
Cl, HCl ii	41	4.6	0.040	220
Br, H^+ iii	16	1.8	0.021	416
Br, HCl iv	22	5.0	0.007	630

[a] Correlation coefficient (eq 14): (i) 0.994, (ii) 0.956, (iii) 0.856, (iv) 0.998.

$$\frac{dx}{dt} = k_{obsd}(x_e - x) \tag{13}$$

$$k_{obsd} = \frac{k_1k_2[H^+] + k_{-1}k_{-2}}{k_{-1} + k_2[H^+]} \tag{14}$$

that solvent molecule can take the place of X^- in eq 11.

Figures 1–4 show dashed lines which are the result of a linear regression analysis fitting eq 14 to the experimental data. Table IV gives the rate constants calculated in this way. The limiting rate constant at high acid concentration is k_1. The intercept at zero acid is k_{-2}. Since we also know the equilibrium constant, K_{H^+} or K_{HCl}, the ratio of k_{-1}/k_2 can be found as well (eq 15). The values of k_1 calculated for the addition

$$K_{H^+} (K_{HCl}) = k_1k_2/k_{-1}k_{-2} \tag{15}$$

of H^+ and of HCl to a given complex show that Cl^- is 1.5–2.5 times as effective as methanol in reaction 11.

The mechanism of oxidative addition for Vaska's compounds thus seems to be identical with that found earlier for the cyclooctadiene complexes.[5] Addition of an anion, or of solvent, precedes the protonation step. Presumably this addition of a ligand increases the election density available at the sixth coordination site. The five-coordinated halide species, MX^-, have actually been isolated in the case of $Ir(cod)I_2^+$.[25] No such species have been isolated for $IrY(CO)L_2$.

While the acidity of $IrY(CO)L_2HX$ is nearly independent of whether X is Cl^- or methanol, this will not be the case for all ligands. Some experiments with HBr showed little difference between K_{HBr} and K_{HCl}. However the addition of excess trimethyl phosphite to a reaction mixture of $IrCl(CO)(PPh_3)_2$ and CF_3SO_3H greatly increased the formation of Ir(III). The apparent equilibrium constant became 4.2 × 10^3, an increase of 37-fold. $P(OMe)_3$ is a good ligand but a poor proton base. The product is assumed to be $IrHCl(CO)(PPh_3)_2P(OMe)_3^+$, but some replacement of Cl^- by phosphite could also have occurred.

An extreme case of the role of the ligand, X, trans to H is afforded by the complex $IrHCl_2(CO)(PMe_2Ph)_2$, B, which is isomeric to the adduct, A, described in the present work. This isomer B has H trans to CO, as well as trans Cl_2 and trans phosphines. It will not lose HCl even in boiling sodium methoxide solution.[4] This shows that a very strongly held group X, in this case CO, can greatly influence oxidative addition and the basicity of iridium(I) complexes.

The kinetics of addition of several nonmetal hydrides, HX, to $IrY(CO)L_2$ in toluene have been reported by Walper and Kelm.[26] It was found that a concerted addition of HX took place. Such a result is reasonable in a nonpolar solvent where dissociation of HX is very small. The product of addition has H and X in a cis configuration. For HCl, the isomer formed,

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C, is different from either A or B, since H is trans to the group Y and not to CO.

Acknowledgments. This work was supported in part by a grant (No. CH77-27417) from the National Science Foundation. Thanks are also due to Mathey-Bishop for the loan of precious metals.

Registry No. $IrCl(CO)(PPh_3)_2$, 15318-31-7; $IrBr(CO)(PPh_3)_2$, 15842-08-7; $IrI(CO)(PPh_3)_2$, 19472-16-3; $IrCl(CO)(PMePh_2)_2$, 15318-32-8; $IrBr(CO)(PMePh_2)_2$, 19354-07-5; $IrI(CO)(PMePh_2)_2$, 42482-35-9; $IrCl(CO)(PMe_2Ph)_2$, 21209-82-5; $IrBr(CO)(PMe_2Ph)_2$, 21209-83-6; $IrI(CO)(PMe_2Ph)_2$, 21209-87-0; $IrCl(CO)(AsPh_3)_2$, 23954-42-9; $IrCl(CO)(AsMePh_2)_2$, 52720-84-0; $IrCl(CO)(AsMe_2Ph)_2$, 21209-84-7; $IrCl(CO)(P\text{-}t\text{-}BuMe_2)_2$, 36466-98-5; $IrCl(CO)(P\text{-}t\text{-}BuEt_2)_2$, 36490-55-8; $IrCl(CO)(P(t\text{-}Bu)_2Me)_2$, 34365-68-9; $IrCl(CO)(P(t\text{-}Bu)_2Et)_2$, 34365-70-3; $RhCl(CO)(PPh_3)_2$, 15318-33-9; $RhBr(CO)(PPh_3)_2$, 17070-17-6; $RhI(CO)(PPh_3)_2$, 21006-49-5; $RhCl(CO)(AsPh_3)_2$, 16970-35-7; $RhBr(CO)(AsPh_3)_2$, 38581-34-9; $RhI(CO)(AsPh_3)_2$, 55222-24-7; HCl, 7647-01-0.

Contribution from the Department of Physical Chemistry
and Center for Marine Research, "Rudjer Bošković" Institute, Zagreb, Croatia, Yugoslavia

Precipitation and Complex Formation of Zirconium(IV) with Maleic and Phthalic Acids at 25 °C[1a]

HALKA BILINSKI,*[1b] NEVENKA BRNIČEVIĆ,[1b] and ZDENKA KONRAD[1c]

Received October 9, 1980

The precipitation of zirconium from aqueous solution of zirconyl chloride (1 mM) and potassium maleate (0.2–100.0 mM) and also with potassium phthalate (0.1–50 mM) was investigated at pH 2–11, at 25 °C, by using the tyndallometric technique. In the precipitation diagram two soluble regions have been observed, where zirconium forms complexes with maleate and phthalate anions. Electrophoretic and pH measurements were used to study soluble complexes. The evidence for the existence of zirconium-hydrolyzed anions has been obtained. In the precipitation region the following precipitates were identified: $Zr(OH)_3(OOCCH{=}CHCOOH)$ (I), $Zr(OH)_3(OOCC_6H_4COOH)$ (II), and zirconium hydroxide. Infrared spectra were used to characterize the mode of coordination of carboxylate ligands. From physical and infrared spectral data it was concluded that these solid complexes are of polymeric nature.

Introduction

Complexes of zirconium with dibasic carboxylic acids have been studied, as seen in the literature, mostly in a solid form. Complexes having coordinated one[2–4] and two phthalic acid molecules[5] were isolated, but no detailed interpretation of physical and spectral properties has been given. Although Intorre and Martell[6] have been emphasizing for 20 years that very few ligands are known which form water-soluble complexes with zirconium stable at high pH, there was little research in that direction. Zirconium hydrolysis[7,8] and zirconium oxalate[9] have been investigated in detail. Interesting biological experiments with zirconium[10] have inspired us to continue the zirconium research, particularly with respect to the complex formation with oxygen donor ligands such as phthalate and maleate ions.

Experimental Section

Zirconium oxychloride octahydrate, $ZrOCl_2(H_2O)_8$, was used to make a stock solution. It was analyzed for zirconium by complexometric titration with titriplex III. Solutions of maleic acid (0.2 mol dm^{-3}), potassium hydrogen phthalate (0.5 mol dm^{-3}), phthalic acid (0.1 mol dm^{-3}), and potassium hydroxide (0.5 mol dm^{-3}) were prepared from Merck, Darmstadt, p.a. chemicals. For determination of precipitation diagrams, the method described earlier by Težak et al.[11] was used. For quantitative determination of the composition of the solid phases, precipitates were left to settle and then filtered, washed with water, and dried in a desiccator.

Table I. Chemical Composition of the Precipitate Formed between Zr(IV) and Maleic Acid at Different pH Values

[Zr], mM	[maleic acid], mM	[KOH], mM	pH	% found		
				C	H	Zr
1	40	40	2.2	17.09	2.48	35.08
1	4	9	3.75	9.57	2.47	44.99
1	2	6.5	4.2	7.85	2.38	46.27
10	20	30	2.3	16.07	2.52	36.01
10	20	40	2.6	15.25	2.55	36.80
10	20	60	5.5	12.23	2.51	42.65
10	20	80	6.6	8.57	3.04	47.77

In electrophoretic experiments, a solution of radioactive zirconium was used. The solutions of $^{95}Zr(^{95}Nb)$ were prepared from the original solution of $^{95}Zr(^{95}Nb)$ in oxalic acid (The Radiochemical Centre Ltd., Amersham), by evaporation to dryness, with addition of concentrated nitric acid and hydrogen peroxide several times.[12] After evaporation, the appropriate supporting electrolyte was added to the residue. The specific activities of these solutions were 1 μCi/20 μL (20 μL was the solution volume applied at the starting point of each electrophoretic strip).

Turbidity measurements, used in precipitation studies, were performed with a Zeiss tyndallometer attached to a Pulfrich photometer. For infrared spectra, a Perkin-Elmer 257 spectrophotometer was used (KBr pellets and Nujol mulls). X-ray photographs were taken in 0.3-mm capillaries, with a Philips 57.54-mm camera and an exposure time of 1.5 h.

The electrophoretic experiments were performed as described previously,[13] except that the temperature of the gasoline was maintained constant by means of an ultrathermostat.[14,15] The concentration of potassium hydrogen maleate and potassium hydrogen phthalate varied from 1 × 10^{-2} to 4 × 10^{-2} mol dm^{-3}. The details of the experimental conditions were published earlier.[16]

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(1) (a) This work has been presented in part of the 5th Meeting of the Chemists of Croatia, Zagreb, Yugoslavia, Feb 14–16, 1977. (b) Department of Physical Chemistry. (c) Center for Marine Research.

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