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Ionic Equilibria in Mixed Solvents. III. Hydrolysis of Copper(II) Ion in a 0.2 Mole Fraction Dioxane–Water Mixture

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Received December 12, 1967

The hydrolytic reaction of copper(II) ion was studied at 25° in a 0.2 mole fraction (55.01% w/w) dioxane–water mixture containing 3 *M* $LiClO_4$ as an ionic medium. A partially hydrolyzed solution of copper(II) perchlorate was gradually acidified by addition of perchloric acid from a buret or by generating hydrogen ions coulometrically, the total copper(II) concentration being kept constant. Total copper(II) concentrations of 0.005735, 0.01466, 0.02624, and 0.03489 *M* were studied. The emf data obtained can be explained in terms of the formation of $CuOH^+$ (log $^*\beta_{1,1} = -7.60 \pm 0.02$) and $Cu_2(OH)_2{}^{2+}$ (log $^*\beta_{2,2} = -10.95 \pm 0.05$).

Introduction

In studies of hydrolysis of copper(II) ion in aqueous solutions, a number of investigators have assumed that the principal reaction is the formation of the mononuclear $CuOH^+$ complex. However, more extensive studies have shown that the formation of polynuclear complexes is important. The formation of the binuclear complex, $Cu_2(OH)_2{}^{2+}$, was first reported by Hagisawa[1] in aqueous copper(II) sulfate solutions in 1939. In 1943 Pedersen[2] assumed the formation not only of $Cu_2(OH)_2{}^{2+}$ but also of the complexes $CuOH^+$ and Cu_2OH^{3+} in order to explain his data. On the other hand, Berecki-Biedermann[3] found only the $Cu_2(OH)_2{}^{2+}$ complex in 3 *M* $NaClO_4$ medium. Perrin[4] reported the formation of $Cu_3(OH)_4{}^{2+}$ and a series of $Cu_n(OH)_{2n-2}{}^{2+}$ ($n \geqslant 4$) complexes together with the $Cu_2(OH)_2{}^{2+}$ complex, on the basis of the "core + links" hypothesis,[5] but he did not find any mononuclear species.

The present study deals with the hydrolytic reaction of copper(II) ion in a 0.2 mole fraction (55.01% w/w) dioxane–water mixture containing 3 *M* $LiClO_4$ as an ionic medium.

Neglecting solvation by dioxane and omitting hydrated water molecules, the hydrolytic reaction of copper(II) ion may be written as

$$q\mathrm{Cu}^{2+} + p\mathrm{H_2O} = \mathrm{Cu}_q(\mathrm{OH})_p{}^{(2q-p)+} + p\mathrm{H}^+ \tag{1}$$

where the equilibrium constant is defined as

$$^*\beta_{p,q} = [\mathrm{Cu}_q(\mathrm{OH})_p{}^{(2q-p)+}][\mathrm{H}^+]^p/[\mathrm{Cu}^{2+}]^q \tag{2}$$

Here the brackets denote the concentration of the relevant species.

Symbols

h	Hydrogen ion concentration at equilibrium
H	Analytical excess of hydrogen ions = $[ClO_4^-] - 2B - [Li^+]$
B	Total concentration of copper(II)
b	Concentration of free copper ions
Z	Average number of hydrogen ion set free per copper atom = $(h - H)/B$
p	Number of OH groups bound to hydrolyzed species
q	Number of Cu atoms present in hydrolyzed species
$^*\beta_{p,q}$	Equilibrium constant of the formation of $Cu_q(OH)_p{}^{(2q-p)+}$
E	Emf

Experimental Section

Reagents.—Copper(II) perchlorate was prepared from copper(II) oxide and perchloric acid.

Copper(II) oxide was made from copper(II) nitrate as follows. Reagent grade copper(II) nitrate was recrystallized twice from water, and crystals were heated in a porcelain dish until no more appreciable NO_2 vapor was evolved and then were ignited in an electric furnace at about 800° for several hours. Copper(II) oxide, thus prepared, was dissolved in an excess of hot perchloric acid, the solution was filtered, and copper(II) perchlorate crystals were collected. The stock solution of copper(II) perchlorate contained about 0.2 *M* $HClO_4$.

The copper content of the stock solution was determined by electrodeposition of copper in an H_2SO_4–HNO_3 solution. The acid concentration in the stock solution was determined in the following manner. An aliquot (about 50 ml) of aqueous 3 *M* $LiClO_4$ solution containing about 10^{-3} $HClO_4$ was gradually neutralized coulometrically. As the volume change was negligible during the coulometric titration, the end point was determined by means of a plot of $10^{E/59.15}$ *vs.* microfaradays passed (Gran plot[6]). Then a small amount of the stock solution of copper(II) perchlorate was added to the vessel from a weight buret and the solution was acidified by the use of a coulometer. The amount of acid present in the stock solution was easily estimated from a similar plot of $10^{E/59.15}$ *vs.* microfaradays.

The ion-exchange method for determining the total perchlorate concentration agreed satisfactorily with the sum of equivalent concentrations of copper(II) and hydrogen ions in the solution.

Lithium perchlorate was prepared as described by Biedermann and Ciavatta.[7]

Dioxane was purified by the method described elsewhere.[8]

Apparatus. Glass Electrodes and pH Meter.—Beckman No. 40498 glass electrodes were used in combination with a Radiometer PHM-4d (Copenhagen).

The Wilhelm-type half-cell described by Forsling, Hietanen, and Sillén[9] was used for emf measurements.

A coulometric analyzer (Leeds and Northrup Co., Philadelphia, Pa.) was employed as a current source. Constant currents of 0.643 and 6.43 mA were used; the currents were held constant to ±0.1 and ±0.05%, respectively.

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(1) H. Hagisawa, *Bull. Inst. Phys. Res. Tokyo, Rikagaku Kenkyusho Iho,* **18,** 275 (1939).

(2) K. J. Pedersen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.,* **20** (7), 1 (1943).

(3) C. Berecki-Biedermann, *Arkiv Kemi,* **9,** 175 (1956).

(4) D. D. Perrin, *J. Chem. Soc.,* 3189 (1960).

(5) L. G. Sillén, *Acta Chem. Scand.,* **8,** 299 (1954).

(6) G. Gran, *Analyst,* **77,** 661 (1952).

(7) G. Biedermann and L. Ciavatta, *Acta Chem. Scand.,* **15,** 1347 (1961).

(8) H. Ohtaki, *Inorg. Chem.,* **6,** 808 (1967).

(9) W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.,* **6,** 901 (1952).

All emf measurements were performed at 25.00 ± 0.01° in a paraffin oil thermostat in a room thermostated at 25 ± 1°.

Methods of Investigation.—The hydrolytic equilibria were studied by the measurement of the hydrogen ion concentration of a series of copper(II) perchlorate solutions at 25° using a glass electrode. During a potentiometric titration B was kept constant. The values of B studied were 0.005735, 0.01466, 0.02624, and 0.03489 M.

Preparation of the Test Solution.—The hydrolysis of copper(II) ion has been studied by previous workers by adding an alkaline solution to an acidic copper(II) solution. In the present case, however, a preliminary experiment showed that the solubility of copper(II) hydroxide in a 0.2 mole fraction dioxane–water mixture seemed much less than that in aqueous solutions: the maximum Z in the aqueous dioxane solution was found to be about 0.01 of the Z reported in aqueous solutions.[3] Furthermore, copper hydroxide precipitates rather slowly with a small excess of alkali. In order to avoid the formation of any precipitate during a titration and to obtain reproducible results, a "back-titration" procedure[8,10] was carried out: a clear test solution saturated with copper(II) hydroxide precipitates was prepared and titrated with an acid solution.

An aliquot of 3 M $LiClO_4$ in a 0.2 mole fraction dioxane–water mixture containing a small amount of $HClO_4$ (*ca.* 10^{-3} M) was taken in a polyethylene bottle (A), and 100 ml of copper(II) perchlorate in $LiClO_4$ (total $[ClO_4^-] = 3$ M) in the same solvent containing $HClO_4$ (*ca.* 10^{-3} M) was placed in a three-neck Pyrex flask (B). Nitrogen gas, free from carbon dioxide and preequilibrated with the solvent, was passed through both solutions to expel carbon dioxide from the solutions. A direct current was supplied between platinum electrodes to produce lithium hydroxide electrolytically in the polyethylene bottle. After passing current overnight under the continuous bubbling of nitrogen gas, the current was stopped and a stopcock situated between the anode and cathode chambers was closed. A portion of the solution in the polyethylene bottle was transferred to flask B by turning another stopcock between the polyethylene bottle and flask B, with the help of the pressure of nitrogen gas, until a pale green precipitate was formed in the copper(II) perchlorate solution. The solution was stirred at least 3 days by means of a magnetic stirrer with a Teflon-covered stirring bar under an atmosphere of nitrogen. The solution was filtered through a G3 glass filter with a layer of fine platinum powder into a flask (C), in which the air had been replaced by nitrogen gas. The solution was filtered again through a G4 glass filter with a platinum layer into the final flask (D), into which a continuous flow of nitrogen gas was introduced through a 50-ml buret. The clear solution thus obtained was sucked into the 50-ml buret. An aliquot of the solution was used for the determination of the copper(II) content in the solution. Another portion of the solution was used for the potentiometric titration.

The total concentration of copper(II) in the test solution was determined gravimetrically by means of copper(II) salicylaldoximate.[11]

Emf Measurements.—The general composition of a test solution may be written as: B Cu(II), H H^+, $(3 - 2B - H)$ Li^+, 3 M ClO_4^-, where H, the analytical excess of hydrogen ion, may be negative. The test solutions were titrated with a solution of the composition: B Cu(II), H_0 H^+, $(3 - 2B - H_0)$ Li^+, 3 M ClO_4^-, except that for $B = 0.005735$ M titrations were carried out coulometrically. The coulometric circuit consisted of

$$(-)\mathrm{Pt}\left|\begin{array}{c}2.90\ M\ \mathrm{LiClO_4}\ \text{and}\\ 0.10\ M\ \mathrm{AgClO_4}\ \text{in}\\ \text{aqueous solution}\end{array}\right|\begin{array}{c}3.00\ M\ \mathrm{LiClO_4}\ \text{in}\\ 0.2\ \text{mole fraction}\\ \text{aqueous dioxane}\end{array}\left|\ \text{test solution}\ \right|\mathrm{Pt}(+)$$

Emf measurements were performed by means of the cell

$$(-)\mathrm{GE}\,|\,\text{test solution}\,|\,\mathrm{Ref}(+) \qquad (3)$$

where GE denotes a glass electrode and Ref the reference half-cell,

$$\left|\begin{array}{c}3.00\ M\ \mathrm{LiClO_4}\ \text{in}\\ 0.2\ \text{mole fraction}\\ \text{aqueous dioxane}\end{array}\right|\begin{array}{c}2.99\ M\ \mathrm{LiClO_4}\ \text{and}\\ 0.01\ M\ \mathrm{AgClO_4}\ \text{in}\\ \text{aqueous solution}\end{array}\Big|\,\mathrm{AgCl{-}Ag}$$

The emf (millivolts) of cell 3 at 25° may be written as

$$E = E^\circ - 59.15 \log h - 59.15 \log f_H - E_j(h,B) \qquad (4)^{12}$$

where E° is a constant and f_H represents the activity coefficient of hydrogen ion. The standard state is defined so that f_H, as well as the activity coefficients of the other reacting species, tends toward unity as the composition of the solution approaches 3 M $LiClO_4$ in 0.2 mole fraction of aqueous dioxane. Since Z never exceeds 0.0013, the composition of a test solution of constant B changes only slightly upon hydrolysis. Therefore, as long as B is maintained constant, the activity coefficients of the reacting species may reasonably be assumed to be constant.

$E_j(h,B)$ is the liquid-junction potential at the junction: test solution|3 M $LiClO_4$ in 0.2 mole fraction of aqueous dioxane. At constant B, $E_j(h,B)$ can be assumed to be a function of h only. At $B = 0$ it was found in a cell of similar design that $E_j(h,0) = -8.3h$ mV.[8] In the present study $E_j(h,B)$ was assumed to be equal to $E_j(h,0)$ in the systems of low and constant B studied.

Evaluation of the Composition of Products and the Equilibrium Constants of Hydrolytic Reactions

Values of Z and $-\log h$ for each value of B are represented graphically in Figure 1.

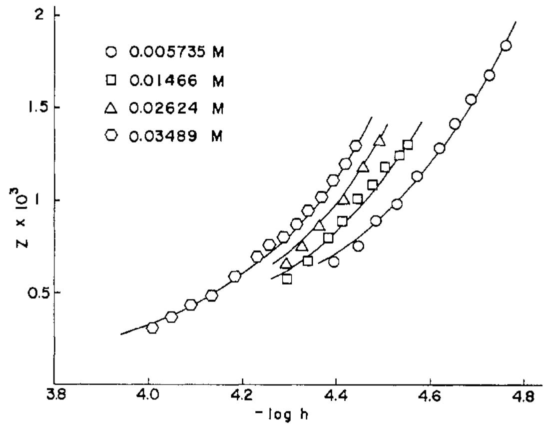

Figure 1.—Z as a function of $-\log h$. Curves were calculated with $^*\beta_{1,1} = 2.52 \times 10^{-8}$ and $^*\beta_{2,2} = 1.11 \times 10^{-11}$.

The concentration of hydrogen ion set free by hydrolysis, BZ, is given by the general formula

$$BZ = \sum_p \sum_q p[\mathrm{Cu}_q(\mathrm{OH})_p{}^{(2q-p)+}] = \sum_p \sum_q p^*\beta_{p,q}h^{-p}b^q \qquad (5)$$

In cases where the maximum value of Z is very low, we may, without introducing any appreciable error, simplify the preliminary calculations by employing the approximation

$$[\mathrm{Cu}^{2+}] = b \approx B \qquad (6)$$

Applying approximation 6 to eq 5 and rearranging, we may derive

$$Zh = \sum_p pK_p h^{-(p-1)} \qquad (7)$$

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[10] G. Biedermann and S. Hietanen, *Acta. Chem. Scand.*, **14**, 711 (1960); G. Biedermann and L. Ciavatta, *ibid.*, **16**, 2221 (1962); G. Biedermann and L. Ciavatta, *Arkiv Kemi*, **22**, 253 (1964).

[11] F. J. Welcher, "Organic Analytical Reagents," Vol. III, 2nd. ed, D. Van Nostrand Co., Inc., New York, N. Y., p 262 (1947).

[12] $+E_j(h,B)$ in eq 5 of ref 8 and in the same equation in ref 16 should read $-E_j(h,B)$.

where

$$K_p = \sum_q {}^*\beta_{p,q}B^{q-1} \qquad (8)$$

Plots of Zh against h^{-1} gave a set of straight lines with a common intercept. This result showed that the intercept $K_1 = \Sigma_q {}^*\beta_{1,q}B^{q-1}$ is independent of B, thus establishing that $q = 1$ and $p \leqslant 2$. The slope of the line is $2K_2 = 2({}^*\beta_{2,1} + {}^*\beta_{2,2}B + {}^*\beta_{2,3}B^2 + \ldots)$ at each B. A plot of these K_2 values against B gave a straight line passing through the origin. This result excludes, then, $Cu_q(OH)_2{}^{2(q-1)+}$ species other than $Cu_2(OH)_2{}^{2+}$.

Thus the species formed by the hydrolysis of copper(II) ion are $CuOH^+$ and $Cu_2(OH)_2{}^{2+}$. Equation 5 may then be written as

$$BZ = {}^*\beta_{1,1}h^{-1}b + 2{}^*\beta_{2,2}h^{-2}b^2 \qquad (9)$$

Now

$$B = b + {}^*\beta_{1,1}h^{-1}b + 2{}^*\beta_{2,2}h^{-2}b^2 \qquad (10)$$

Therefore

$$b = B(1 - Z) \qquad (11)$$

Inserting eq 11 into eq 9, we obtain

$$BZ = {}^*\beta_{1,1}h^{-1}B(1 - Z) + 2{}^*\beta_{2,2}h^{-2}B^2(1 - Z)^2 \qquad (12)$$

If we set $BZ \equiv y$, ${}^*\beta_{1,1}h^{-1}B(1 - Z) \equiv x$, and $2{}^*\beta_{2,2}/{}^*\beta_{1,1}{}^2 \equiv u$, eq 12 may be compared with the normalized function

$$y = x + ux^2 \qquad (13)$$

A plot of BZ against $\log B + \log (1 - Z) - \log h$, which will be independent of B, can be fit to a plot of y against $\log x$ at a particular value of u. Figure 2 shows a satisfactory agreement of the plot of the data with the normalized curve at $u = 3 \times 10^4$. From the position of best fit of curves we obtained $\log {}^*\beta_{1,1} = -7.58$ and $\log {}^*\beta_{2,2} = -10.98$.

The comparison of eq 12 with another normalized function, $y = vw + w^2$, gave $\log {}^*\beta_{1,1} = -7.57$ and $\log {}^*\beta_{2,2} = -11.00$.

Finally, the data have been treated by a generalized least-squares method with the help of an electronic computer, HITAC 5020E, in order to make the error-square sum ($U = \Sigma(Z - Z_{\text{calcd}})^2$) a minimum with respect to variation of the equilibrium constants, ${}^*\beta_{p,q}$. Z_{calcd} denotes the values $Z_{\text{calcd}} = \Sigma_p\Sigma_q p{}^*\beta_{p,q}h^{-p}b^q/B$ for a particular set of the constants, ${}^*\beta_{p,q}$.

Calculations of Z_{calcd} with a set of ${}^*\beta_{1,1}$ and ${}^*\beta_{2,2}$, varying these constants as parameters, resulted in a satisfactory agreement with the experimental data. Another set of constants, ${}^*\beta_{1,1}$, ${}^*\beta_{1,2}$, and ${}^*\beta_{2,2}$, which had been proposed by Pedersen in aqueous solutions,[2] gave rise to a slightly larger error-square sum, and the assumption of the presence of only $Cu_2(OH)_2{}^{2+}$ gave an apparently worse agreement with the experimental results. No evidence was found for the formation of any higher complexes than $Cu_2(OH)_2{}^{2+}$ in the present work.

The final values of the constants obtained by the computer calculation, taking into account the values and their uncertainties estimated by the "curve-fitting" method, are $\log {}^*\beta_{1,1} = -7.60 \pm 0.02$ and $\log {}^*\beta_{2,2} = -10.95 \pm 0.05$. These are listed in Table I together with values reported by previous studies in aqueous solution.

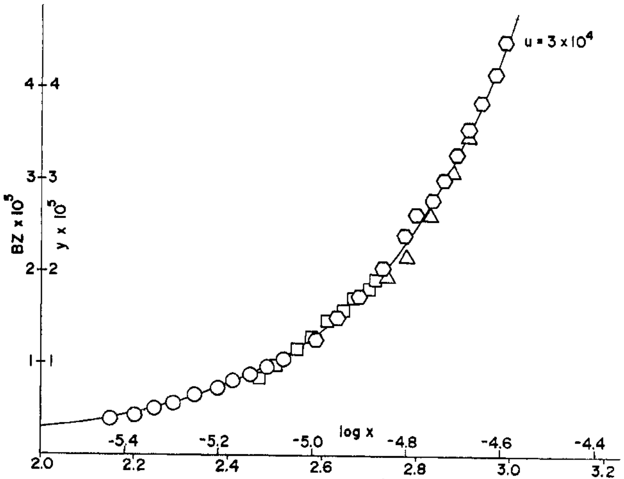

Figure 2.—Z or y as a function of $\log B + \log (1 - Z) - \log h$ or $\log x$. Symbols used are the same as those in Figure 1.

TABLE I

THE EQUILIBRIUM CONSTANTS OF THE HYDROLYTIC REACTION OF COPPER(II) ION

Ref	Temp, °C	Log ${}^*\beta_{1,1}$	Log ${}^*\beta_{1,2}$	Log ${}^*\beta_{2,2}$	Log ${}^*\beta_{4,3}$
Hagisawa[1]	25			−10.86	
Pedersen[2]	18	−7.97	−6.82	−10.89	
Pedersen[2] (Berecki-Biedermann[3])[a]	18	−8.0		−10.95	
Berecki-Biedermann[3]	25			−10.6	
Perrin[4]	20			−10.53	−21.17
Owen, Gurry[14] (Fuget[14])[b]	25	−7.73[c]			
Achenza[13]	25	−7.34			
Present work	25	−7.60		−10.95	

[a] Data obtained by Pedersen were recalculated by Berecki-Biedermann. [b] Data obtained by Owen and Gurry were recalculated by Fuget. [c] A correction is made for the value in ref 14 using $\log K_w = -14.00$.

Discussion

It may be seen from Table I that the formation constant of the $Cu_2(OH)_2{}^{2+}$ complex does not appreciably change from an aqueous solvent to a 0.2 mole fraction dioxane–water solvent. The value of ${}^*\beta_{1,1}$ found in the present work falls between −7.34[13] and −7.73,[14] which are two extremes reported in aqueous solutions at 25°.[15] Therefore, it may be concluded that ${}^*\beta_{1,1}$ changes only to a very small extent with wide variation in the solvent composition. A similar phenomenon was found in the study of hydrolysis of beryllium ion[8,16,17] and thus seems to be common in

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[13] F. Achenza, *Ann. Chim.* (Rome), **48**, 565 (1958).

[14] B. B. Owen and R. W. Gurry, *J. Am. Chem. Soc.*, **60**, 3074 (1938); C. R. Fuget, Thesis, The Pennsylvania State University, 1956.

[15] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

[16] H. Ohtaki and H. Kato, *Inorg. Chem.*, **6**, 1935 (1967).

[17] H. Ohtaki and H. Kato, Proceedings of the 10th International Conference on Coordination Chemistry, Tokyo and Nikko, Sept 12–16, 1967, p 48.

the hydrolysis reaction of metal ions, but the phenomenon is different from that in the dissociation reactions of acetic acid and other carboxylic acids and phenols[18] and ammonium ion and anilinium and their homologs.[18-20] The dissociation constants of carboxylic acids and phenols decrease almost invariably on addition of a miscible organic solvent, and the solvent effect is qualitatively interpreted in terms of the decrease of the dielectric constant of the solvent and the decrease of the concentration of water which solvates the proton released in the dissociation.[21] The dissociation constants of ammonium ion and its related compounds,[18-20] on the other hand, increase on addition of methanol or other organic solvents and then sharply decrease. The hydrolytic reaction of metal ions differs from these two dissociation reactions and the dissociation constant, that is, the formation constant of a complex, is relatively unaffected by the addition of dioxane. A study of the medium effect on activity coefficients of ions and on variation of water activity might give some interpretation of the solvent effect on the equilibrium constants of metal hydrolysis, on which a study is in progress in our laboratory.

Acknowledgment.—The author wishes to thank Professor Motoharu Tanaka for his continued interest in this work. The work has been supported in part by the Tokai Educational and Scientific Study Promotion Association (Tokai Gakujutsu Shōrei-Kai).

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(19) M. Paabo, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, **70**, 247 (1966).

(20) G. Douhéret, *Bull. Soc. Chim. France*, 1412 (1967).

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Organometallic Compounds with Metal–Metal Bonds. XIII. Reactions of Iron Pentacarbonyl with Halides and Organometallic Halides of Germanium(IV) and Tin(IV)[1]

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Received January 22, 1968

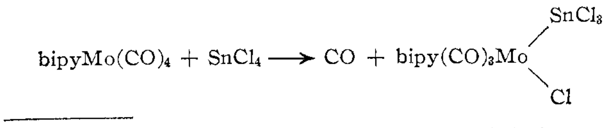
Iron pentacarbonyl has been found to undergo an oxidative elimination reaction with tetrahalides of germanium and tin (MX_4). Under mild conditions, the initial product is *cis*-octahedral $(OC)_4XFeMX_3$ (I). Heating of I or reaction of $Fe(CO)_5$ with MX_4 under more vigorous conditions affords octahedral $(OC)_4Fe(MX_3)_2$ (II). In reactions with GeX_4, only *trans*-II is formed for X = Br or I, while for X = Cl, a mixture of *cis*- and *trans*-II results. Reaction with SnX_4 (X = Cl, Br) affords only *cis*-II, although *trans*-$(OC)_4Fe(SnCl_3)_2$ was formed in an unusual reaction with $C_6H_5SnCl_3$. The *trans* forms of both $(OC)_4Fe(GeCl_3)_2$ and $(OC)_4Fe(SnCl_3)_2$ isomerized to *cis* in solution. Reaction of GeX_4 with $Fe(CO)_5$ under still more vigorous conditions or of II (M = Ge) with $Fe(CO)_5$ affords the cyclic derivatives $[(OC)_4FeGeX_2]_2$ (III). Reaction of $LFe(CO)_4$ or $L_2Fe(CO)_3$ (L = triphenylphosphine) with SnX_4 (X = Cl, I) yields $L(OC)_3XFeSnX_3$. Carbonyl stretching frequencies of all compounds are reported and qualitatively discussed.

Introduction

A number of metal carbonyls and their derivatives undergo a reaction with halogens in which one of the carbonyl groups is expelled and replaced by two univalent ligands, as illustrated by the example[2]

$$\text{bipyMo(CO)}_4 + I_2 \longrightarrow CO + \text{bipy(CO)}_3\text{MoI}_2$$

The useful term "oxidative elimination" has been applied to processes of this kind.[3] We have recently reported the results of a study of formally similar reactions involving tetrahalides and organometallic halides of germanium and tin,[1,4] of which the following is typical



$$\text{bipyMo(CO)}_4 + \text{SnCl}_4 \longrightarrow CO + \text{bipy(CO)}_3\text{Mo}\begin{matrix}\text{SnCl}_3\\ \text{Cl}\end{matrix}$$

It has long been known that iron pentacarbonyl reacts with halogens to form the tetracarbonyl dihalides $(OC)_4FeX_2$.[5] In view of the foregoing, it might be expected that an analogous reaction with tetrahalides of the fourth main group would be possible. Indeed, Hieber and Wirsching[6] in 1940 investigated the reaction of iron pentacarbonyl with tin tetrachloride, obtaining a compound of composition $Fe(CO)_4 \cdot SnCl_4$. A correct structural formulation was difficult at that early date, as 17 years were to pass before the concept of strong covalent bonding between transition metals was established.[7] The established position of $SnCl_3^-$ as a ligand[8] would now suggest that the Hieber–Wirsching compound be formulated as

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(1) Presented in part at the 50th Canadian Chemical Conference and Exhibition, Toronto, June 4–7, 1967. Part XII: R. Kummer and W. A. G. Graham, submitted for publication in *Inorg. Chem.*

(2) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962); bipy = 2,2′-bipyridyl.

(3) J. Lewis and S. B. Wild, *ibid.*, *A*, 69 (1966).

(4) R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 310 (1968).

(5) W. Hieber and G. Bader, *Ber.*, **61**, 1717 (1928).

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