mole) of compound II was heated at about 150° for 5 hr. The crude product was crystallized from hexane to give 2.2 g. of the redistribution product.

**$(C_5H_5)_2ClSnMn(CO)_5$.**—A mixture of 4.2 g. (0.01 mole) of the chloro derivative IX and 11.0 g. (0.02 mole) of compound II was heated at about 150° for 0.75 hr. The crude product was crystallized from *n*-hexane to give 13.0 g. of $(C_6H_5)_2ClSnMn(CO)_5$.

**$Cl_2Sn[Mn(CO)_5]_2$ (XI).**—Anhydrous hydrogen chloride was passed through a solution of 2.0 g. (0.003 mole) of $(C_6H_5)_2Sn[Mn(CO)_5]_2$ in about 75 ml. of methylene chloride for 0.5 hr. The solvent was evaporated and the residue was recrystallized from ethanol to give 1.2 g. of white needles identified as XI by elemental analysis.

**$Cl_3SnMn(CO)_4P(C_6H_5)_3$.**—Chlorine was passed through a solution of 2.0 g. (0.0013 mole) of compound VI in 90 ml. of methylene chloride at a moderate rate for 10 min. Evaporation of the solvent left a solid that was redissolved in methylene chloride and filtered. Hot hexane was added, and methylene chloride was distilled until white needles began to crystallize. The product, m.p. 159° (dec.), was shown to be $Cl_3SnMn(CO)_4P(C_6H_5)_3$ by elemental analysis. The yield was 1.1 g. The infrared spectrum showed bands only at 6.75 and 6.97 $\mu$ characteristic of a phenyl–phosphorus bond. Compound VI showed a weak doublet at 6.97 and a singlet at 7.03 $\mu$, the latter characteristic of a phenyl–tin stretching frequency.

**$C_5H_5Fe(CO)_2SnCl_3$ (XIV).**—Two grams (0.0038 mole) of compound V was dissolved in about 90 ml. of methylene chloride. Anhydrous hydrogen chloride was passed through the solution for 10 min. at room temperature after which time the solvent was evaporated. The product, 1.43 g., was recrystallized from a mixture of methylene chloride and carbon tetrachloride to give 1.3 g. of reddish-brown needles which were identified as compound XIV by elemental analysis.

When compound V was treated with excess chlorine in carbon tetrachloride between 0 and 10°, the tin–iron bond was broken to give a black solid which was insoluble in common organic solvents.

**Chlorine and XI.**—Chlorine was bubbled through 25 ml. of methylene chloride containing 0.3 g. (0.0005 mole) of compound XI for 10 min. The cloudy mixture was filtered and the solvent distilled. The residue was fractionally crystallized from carbon tetrachloride to give 0.1 g. (35%) of compound IX, m.p. 168° (dec.) having an infrared spectrum identical with that of an authentic specimen. The remainder of the product consisted of a mixture of compound IX and $Cl_2Mn_2(CO)_8$, the latter being identified by infrared analysis.

**Chlorine and X.**—Two grams (0.003 mole) of $(C_5H_5)_2Sn[Mn(CO)_5]_2$ in 25 ml. of methylene chloride was treated with chlorine for 10 min. Evaporation of the solvent gave a yellow solid consisting of a mixture of compound IX and $ClMn(CO)_5$. The products were partially separated with difficulty by first extracting the yellow solid four times with ether. The solid from the extract was refluxed in carbon tetrachloride to convert $ClMn(CO)_5$ to $Cl_2Mn_2(CO)_8$. Fractional crystallization from carbon tetrachloride gave 0.15 g. of compound IX, m.p. 168° (dec.), identified by elemental analysis, and 0.08 g. of $Cl_2Mn_2(CO)_8$. The infrared spectrum of the latter showed terminal metal–carbonyl stretching frequencies very similar to those described previously. The ether-insoluble material was refluxed in carbon tetrachloride to give 0.7 g. of a product which was shown by its infrared spectrum to consist of a mixture of $Cl_2Mn_2(CO)_8$ and compound IX.

**Hydrogen Chloride and $(C_6H_5)_3PlMn(CO)_5$.**—Anhydrous hydrogen chloride was passed through a methylene chloride solution containing 2.0 g. (0.0032 mole) of $(C_6H_5)_3PbMn(CO)_5$ for 20 min. A white unidentified inorganic lead compound, 0.8 g., was filtered off. From the filtrate was obtained a solid which was recrystallized from carbon tetrachloride to give 0.6 g. (93%) of $Cl_2Mn_2(CO)_8$, m.p. 165° (dec.), identified by infrared analysis.

**Chlorine and $(C_2H_5)_2Pb[Mn(CO)_5]_2$.**—Two grams (0.0031 mole) of $(C_2H_5)_2Pb[Mn(CO)_5]_2$ in 60 ml. of carbon tetrachloride was treated with chlorine for four minutes. Excess chlorine was removed and the product was refluxed in carbon tetrachloride. The solvent was distilled under reduced pressure. The residue, 1.87 g., was washed with water, leaving $Cl_2Mn_2(CO)_8$, m.p. 165° (dec.). Evaporation of the water left a white solid. The infrared spectrum showed this solid to contain both diethyl and triethyllead groupings.

**Acknowledgments.**—The author wishes to thank Dr. J. D. Johnston for helpful discussions. He also wishes to express his appreciation to Dr. R. P. Curry for infrared data and interpretation and to extend thanks to members of the Analytical Group: Messrs. R. A. Ashby, W. J. Easley, S. R. Henderson, M. B. Smith and G. Z. Smith.

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[Contribution from the Department of Biochemistry, Louisiana State University School of Medicine, New Orleans 12, La.]

# The Amminehydroxocopper(II)-diolate Chelation Reaction[1,2]

By Richard E. Reeves and Philip Bragg[3]

Received February 3, 1962

Potentiometric methods have led to the finding of approximate constants ($k_1$ = 250, $k_2$ = 49) for the stepwise addition of two hydroxide ions to amminecopper(II) in ammonia solutions of unit activity. This finding has facilitated a further study of the amminecopper-diol chelation reaction and evidence is presented which indicates that the reactive species are amminemonohydroxocopper(II) and the singly charged diolate anion. Chelation constants were calculated for three cyclic diols, methyl α-D-glucopyranoside, D-mannosan and lactate.

In the conformational analysis of carbohydrate derivatives with the ultimate objective of relating molecular shape to chemical properties, or to factors such as enzyme specificity, emphasis must be placed upon methods which cast light on the shapes of these molecules in aqueous solution. The amminecopper-diolate chelation reaction has received attention in such studies because it proceeds to a stable equilibrium accompanied by the liberation of protons, by extensive changes in ultraviolet absorbancy, and—with certain substances—by dramatic changes in optical activity. Although the reaction has been known for a century, *e.g.*, in the solubilization of cellulose. only recently has the one-to-one combining ratio between copper and diol been firmly established, and a singly charged diolate anion implicated as one of the reacting

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[1] This work was supported in part by a grant from the Corn Industries Research Foundation.

[2] The derivation of equations and data for the calculation of one of the chelation constants has been deposited as Document number 7101 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

[3] Present address: Department of Biochemistry, Faculty of Medicine, University of British Columbia, Vancouver, B. C.

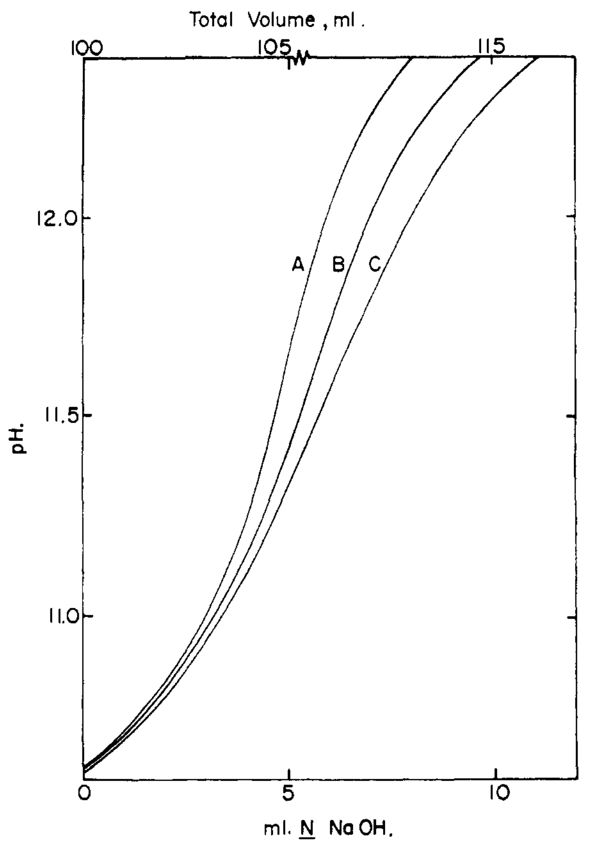

Fig. 1.—Potentiometric titrations: A, 100 ml. of M $NH_3$ containing 5 m$M$ $NH_4NO_3$; B, 100 ml. of 1.042 $M$ $NH_3$ containing 1.0 m$M$ $Cu(NO_3)_2$ and 5 m$M$ $NH_4NO_3$; C, 100 ml. of 1.084 $M$ $NH_3$ containing 2.0 m$M$ $Cu(NO_3)_2$ and 5 m$M$ $NH_4NO_3$.

species.[4] It was anticipated that further progress would result if amminediolatecopper(II) formation constants could be calculated and related to the shapes of the diol-containing molecules in aqueous solution.

A prerequisite to the determination of amminecopper-diolate chelation constants was the extension of information concerning the equilibria among amminecopper(II) species in relatively alkaline media. Bjerrum's[5,6] classical investigations on the amminecopper(II) species established the constants for the stepwise reactions involving the $Cu^{2+}$ ..... $Cu(NH_3)_5{}^{2+}$ species. However, none of these is the reactive species in the diol chelation reaction. At alkalinities greater than about *p*H 10 the amminecopper species exist in equilibrium with significant concentrations of hydroxo species, one of which is the participant in the diol chelation reaction. This report describes findings concerning the equilibria between amminecopper(II) and amminehydroxocopper(II) species, and the application of these findings to the determination of the chelate formation constants of reactive diols.

## Results

**Equilibria Involving Amminehydroxocopper(II) Complexes.**—In view of the difficulties which arose in elucidating the stoichiometry of ammonia in the various equilibria, the expedient was adopted of working with solutions in which the activity of ammonia was essentially unity. In this medium the doubly charged species are principally tetra- and pentaamminecopper(II) having bound, on the average, 4.2 moles of ammonia per copper atom.[6] In formulating the constants for the reactions of these species the stoichiometry of ammonia could be neglected provided the system is kept at unit ammonia activity.

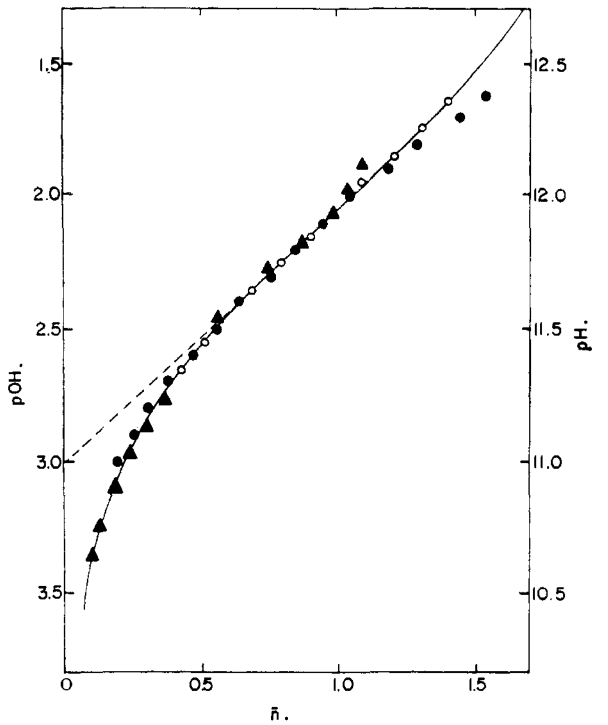

Fig. 2.—The formation curve for the hydroxo complexes of aminecopper(II) in ammonia at unit activity. The experimentally derived points indicated by open circles, solid circles and triangles were derived from titration data at 0.5-, 1.0- and 2.0 × $10^{-2}$ $M$ copper concentration, respectively. The solid curve is the theoretical curve representing $k_1$ = 255, $k_2$ = 49.2.

Figure 1 illustrates a typical potentiometric titration experiment in which normal sodium hydroxide was titrated against solutions containing ammonium nitrate and ammonia with 0, 1 and 2 m$M$ of added cupric nitrate (curves A, B and C, respectively). Subtracting curve A from either B or C gave values for Δ NaOH and Δ$v$ over the investigated *p*H region. The amount of bound hydroxide ion, $OH^-{}_B$, is found with sufficient accuracy by eq. 1.

$$OH^-{}_B = \Delta NaOH - \Delta v[OH^-] \qquad (1)$$

The average number of hydroxide ions bound per copper atom, $\bar{n}$, is given by eq. 2, where $\overline{Cu}$ represents total copper species.

$$\bar{n} = OH^-{}_B/\overline{Cu} \qquad (2)$$

The formation curve for hydroxo complexes of amminecopper(II) in ammonia at unit activity is shown in Fig. 2. This figure includes data derived

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(4) R. E. Reeves and P. Bragg, *J. Org. Chem.*, **26**, 3487 (1961).

(5) J. Bjerrum, *Det Kgl. Danske Videnskabernes Selskab. Mat. fys.*, **11**, 10 (1932).

(6) J. Bjerrum, *ibid.*, **12**, 15 (1933).

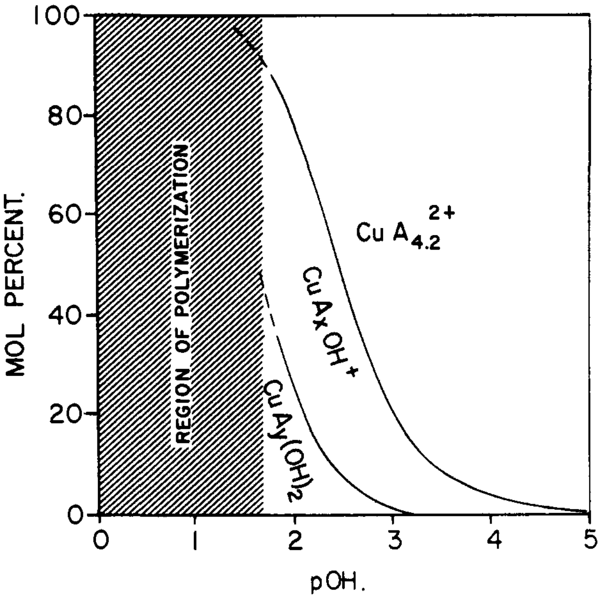

Fig. 3.—The distribution of ammine-, amminemonohydroxo- and amminedihydroxocopper(II) species in ammonia at unit activity as a function of $p$OH.

from several titrations over a four fold range of copper concentrations. Data became erratic and non-reproducible with the highest copper concentration at about $p$H 12, and at the intermediate concentration at about $p$H 12.2, presumably because of polymerization phenomenon.

It may be observed that the experimental points of Fig. 2 follow a single curve up to about $p$H 12.2. The reactions which require consideration in the region below this limit are given in eq. 3-6, where A = $NH_3$

$$CuA_{4.2}{}^{2+} + OH^- \rightleftarrows CuA_xOH^+ + (4.2 - x)A \quad (3)$$

$$k_1 = [CuA_xOH^+]/[CuA_{4.2}{}^{2+}][OH^-] \quad (4)$$

$$CuA_xOH^+ + OH^- \rightleftarrows CuA_y(OH)_2 + (x - y)A \quad (5)$$

$$k_2 = [CuA_y(OH)_2]/[CuA_xOH^+][OH^-] \quad (6)$$

Following Bjerrum's[7] method for the calculation of stepwise formation constants for an N = 2 reaction, the slope of the $\bar{n}$ *versus* $p$H curve at $\bar{n} = 1$ was found to be $-0.95$. Substituting this into the formula for determining the slope of the formation function with respect to ligand concentration gave for $\Delta$, the midpoint slope, the value 0.467. From this the spreading factor, $\bar{X}$, was calculated, by means of the equation $\bar{X} = (1 - \Delta)/\Delta$, to be 1.14. Taking $pK_w$ as 14.00 the so-called "average constant" ($\bar{k}$), equal to the reciprocal of the ligand concentration at $\bar{n} = 1$, was found to be 112. This value is related to the stepwise constants through the spreading factor by the equations: $k_1 = 2\bar{X}(\bar{k})$; and $k_2 = (\bar{k})/2\bar{X}$. Accordingly, the stepwise constants for the binding of two hydroxo groups by amminecopper(II) in ammonia at unit activity were found to be: $k_1 = 255$ and $k_2 = 49.2$. The solid curve of Fig. 2 is the theoretical curve representing these constants. It fits all of the experimentally derived values acceptably in the region below $p$H 12.

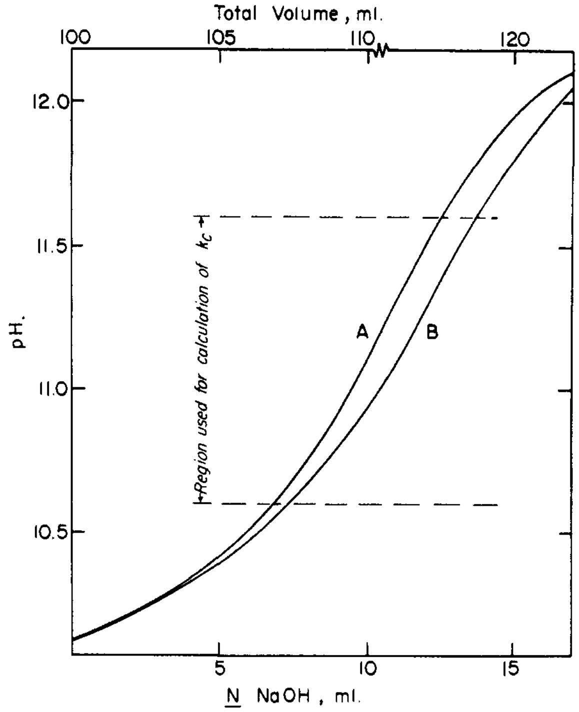

Fig. 4.—Potentiometric titrations of cupric nitrate in $M$ ammonia without and with added erythritol anhydride (A and B, respectively). The solutions were those described in the protocol of Table I.

The calculated distribution of amine-, ammine-monohydroxo- and amminedihydroxocopper(II) species is shown diagramatically in Fig. 3. The maximum concentration of the monohydroxo species occurs at approximately $p$H 11.95 where it reaches 53% of the total copper species. Polymerization is probably due to the increasing concentration of neutral aminedihydroxo species, and the position of the region of polymerization would be dependent upon the copper concentration. The illustrated position of this region sseems to be about correct for $10^{-2}$ $M$ copper.

**The Diolate Chelation Reaction.**—Having a mathematical expression for the amminehydroxocopper(II) system, albeit one applicable under very restricted conditions, the ground was prepared for a further investigation of the diolate chelation reaction.

It was undertaken to test the validity of the hypothesis that the chelation reaction proceeds according to eq. 7 and 8 where $DH_2$ represents the diol.

$$DH_2 \rightleftarrows DH^- + H^+ \quad (7)$$

$$DH^- + CuA_xOH^+ \rightleftarrows CuA_zD + H_2O + (x - z)A \quad (8)$$

At unit ammonia activity the equation for the chelation constant, $k_c$, becomes

$$k_c = [CuA_zD]/[DH^-][CuA_xOH^+] \quad (9)$$

Data were collected from experiments in which sodium hydroxide was titrated against a solution containing cupric nitrate, ammonium nitrate, potas-

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[7] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 298.

sium nitrate and ammonia at unit activity, with and without added diol. Two such titrations are illustrated in Fig. 4 with erythritol anhydride (*cis*-3,4-dihydroxyoxolane) as the added diol. The experimentally derived data necessary for calculating the chelation constant are *p*H, $v$, $\Delta$ NaOH and $\Delta v$, the last two quantities being determined by the subtraction of one curve from the other along the $X$ axis.

Table I records a number of calculated values for the chelation constant of erythritol anhydride at selected *p*H intervals in the region between *p*H 10.6 and 11.6. Table II lists the acid dissociation constants and average chelation constants found for five diol-containing substances, and for lactic acid.

TABLE I[2]

CALCULATED FORMATION CONSTANTS FOR THE ERYTHRITOL ANHYDRIDE CHELATE USING DATA FROM THE POTENTIOMETRIC TITRATIONS OF TWO SOLUTIONS

Solutions A and B contained, initially, 10 $mM$ $NH_4NO_3$, 7.5 m$M$ $KNO_3$, 2.5 m$M$ $Cu(NO_3)_2$ and 110.5 m$M$ $NH_3$ in 100 ml.; solution B contained 1.0 m$M$ erythritol anhydride

| *p*H | m$M$ Chelate | log $kc$ |
|---|---|---|
| 10.6 | 0.089 | 4.22 |
| 10.8 | .242 | 4.34 |
| 11.0 | .345 | 4.22 |
| 11.2 | .500 | 4.19 |
| 11.4 | .640 | 4.30 |
| 11.6 | .657 | 4.08 |
| | log average $k_c$ | 4.24 |

TABLE II

COMPILATION OF VALUES FOR ACID DISSOCIATION CONSTANTS AND CHELATION CONSTANTS FOR VARIOUS SUBSTANCES AT 25°

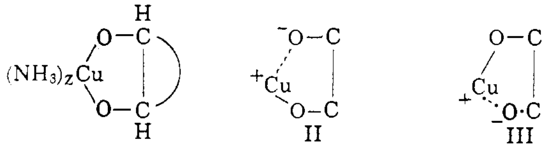
| Substance | $k_a \times 10^{14}$ | log $k_c$ |
|---|---|---|
| Methyl α-D-glucopyranoside | 4.37 | 2.41 |
| *cis*-Cyclohexanediol | 0.56 | 2.81 |
| *cis*-Cyclopentanediol | 3.5 | 3.24 |
| D-Mannosan | 9.7 | 4.41 |
| Erythritol anhydride | 8.0 | 4.24 |
| Lactic acid | [a] | 1.42 |

[a] Non-chelated species taken to be entirely in the $DH^-$ form.

## Discussion

Although most of the present work was done in a *p*H region generally unfavorable for accurate potentiometric measurements, sufficient data were obtained to allow the calculation of constants for the formation of amminemono- and dihydroxocopper(II) complexes in a limited *p*H region. Using these constants to determine the concentration of the monohydroxo species permitted the calculation of diolate chelation constants according to eq. 8 and 9. The finding of relatively constant $k_c$ values for the chelation of erythritol anhydride in the range from 9 to 66% reaction is interpreted as supporting not only the validity of the expressions for the equilibria among amminehydroxocopper species, but also that of the formulation of the chelation reaction. It appears that in the region below *p*H 12 the cuprammonium-diol chelation reaction takes place between a negatively charged diolate anion and an amminemonohydroxocopper(II) species to produce an uncharged chelate. Under conditions considerably more alkaline, a further replacement of ammonia by hydroxide ion might occur giving a negatively charged chelate species.

Although the structure of the amminediolatecopper(II) chelate is not a matter of immediate concern it appears that I satisfies the recognized experimental information. The stability of the chelate and its enhanced ultraviolet absorbance may be the result of resonance among forms I to III.



I, Z = 2 or 3

II

III

The examples of chelation constants reported in Table II serve to illustrate the applicability of the method employed, but the list is not great enough to provide the basis for a considerable extension of conformational information. As might be expected, the constant for the glucoside (*trans*-diol groups) is smaller than that of *cis*-cyclohexanediol. Among the *cis*-diols it is of interest to compare the constants of the cyclopentane with the oxolane (erythritol anhydride). Since the adjacent hydroxyl groups on the former are probably held more closely to the 0° projected angle, there is the implication that some small deviation from this angle favors the chelation reaction, a finding previously suggested by the results of Kwart and Gatos.[8]

The finding that lactic acid has a chelation constant lower than that of any of the reactive diols is probably a reflection of greater oxygen–oxygen distances in the lactate ion since there would seem to be no restriction upon the projected angle between C–O bonds in this molecule.

The reaction constant for the formation of the cuprammonium-D-mannosan complex reported earlier[9] was based upon the incorrect presumption that all of the copper and D-mannosan of the system were in their respective reactive forms. The earlier constant was less than that presently reported ($2.5 \times 10^3$ *vs* $2.6 \times 10^4$).

## Experimental

A stock solution of Baker A.R. cupric nitrate (0.1 $M$, *p*H 4.3) was prepared and analyzed for copper by electrolytic deposition. All of the subsequent solutions and dilutions were made with distilled water which had been passed through a monobed deionizing resin and subsequently heated to boiling under vacuum to remove dissolved $CO_2$. Molar solutions of ammonium nitrate and potassium nitrate was prepared from the A.R. grade salts. Stock ammonia solutions were made by dissolving tank ammonia gas in water. Standardization was done by back titration with alkali after pipetting an aliquot of the ammonia into an excess of acid. Commercially available $CO_2$-free sodium hydroxide concentrates were diluted to normal concentration, checked for the absence of carbonate with barium chloride solution and standardized against potassium acid phthalate.

**Potentiometric Titrations.**—A Beckman model G *p*H meter fitted with external calomel and type E glass electrodes was employed. The titration vessel was a beaker bearing a rubber stopper drilled to take the electrodes, buret, an inlet tube for nitrogen, and to provide an escape port for gas.

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[8] H. Kwart and G. C. Gatos, *J. Am. Chem. Soc.*, **80**, 881 (1958).

[9] R. E. Reeves, *ibid.*, **73**, 957 (1951).

The temperature was kept at 25 ± 1° during the titration, a water-bath surrounding the titration vessel being employed when necessary. Stirring was accomplished by a Teflon coated magnetic stirring bar. The reference solution was 0.05 *M* potassium hydrogen phthalate for which the value *p*H 4.00 was taken. A secondary standard chosen to ensure reproducible operation of the electrodes in the high *p*H range was 0.05 *M* $NH_4NO_3$ in molar ammonia for which the value *p*H 10.63 was repeatedly observed. Deviation from this value for the secondary standard indicated that rejuvenation of the electrodes was required.

Two titrations were required to secure data leading the calculation of $\bar{n}$, the degreee of hydroxo complexing by ammine-copper species. A solution containing ammonia and ammonium nitrate was titrated potentiometrically with NaOH and a second solution containing in addition cupric nitrate was similarly titrated. In order to maintain the desired ammonia activity during the titrations, the following steps were required: first, the free ammonia concentration was initially adjusted to $1 + 4.2 \times C_{Cu}$ secondly, the titration was conducted using normal sodium hydroxide solution; and finally, after the addition of NaOH equivalent to the ammonium nitrate each subsequent addition of alkali was accompanied by the addition of an equal volume of 2 *M* $NH_3$. These conditions resulted in maintaining the ammonia activity essentially unchanged except for the small amount liberated from the amminecopper species upon complexing with hydroxide ions. Where the concentration of copper with respect to ammonia was small this uncertainty became negligible.

A similar technique was employed to obtain data for the calculation of chelation constants except that here both of the titrated solutions contained the cupric nitrate and one contained in addition the diol-containing substance.

In calculating the $k_a$ values for the diols, corrections to allow for the activity of sodium hydroxide were applied.[2]

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

# Metal Carbonyls. IV. Kinetics of the Reaction of Manganese Pentacarbonyl Halides with a Variety of Ligands

BY ROBERT J. ANGELICI AND FRED BASOLO

RECEIVED DECEMBER 20, 1961

The reaction in solution of $Mn(CO)_5X$ with various reactants L was found to yield the monosubstituted derivative $Mn(CO)_4LX$, where X = Cl, Br, I and L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, $C_2H_5NC$, $P(C_6H_5)Cl_2$, $P(OC_4H_9)_3$, $P(OCH_2)_3CCH_3$ and $P(OC_6H_5)_3$. Under similar conditions when L = $P(C_4H_9)_3$, $C_5H_5N$, $C_6H_5NH_2$, *p*-$CH_3C_6H_4NH_2$ and *o*-$CH_3C_6H_4NH_2$, the disubstituted derivative $Mn(CO)_3L_2X$ was obtained. Kinetic studies show that the rates of reaction depend neither on the nature of L nor its concentration. The rates decrease with increasing atomic number of X and also decrease slightly with increasing polarity of the solvent. The reactions are assigned a dissociation mechanism. The infrared absorption wave numbers of the carbonyl groups of the products are reported.

The kinetics and mechanism of carbon monoxide exchange with $Mn(CO)_5X$ were reported recently.[1] It has also been found that $Mn(CO)_5X$ reacts with several reagents in the absence of solvent at 120° to yield disubstituted products of the type $Mn(CO)_3L_2X$.[2] The preparation of a monosubstituted product, $Mn(CO)_4P(C_6H_5)_3I$, was mentioned earlier.[3] The present paper reports the formation of $Mn(CO)_4LX$ by the reaction between $Mn(CO)_5X$ and L in solution at room temperature. Kinetic studies are reported for the reaction

$$Mn(CO)_5X + L \longrightarrow Mn(CO)_4LX + CO \quad (1)$$

## Experimental

**Preparation and Purification of Materials.**—The $Mn_2(CO)_{10}$ was a gift from Dr. T. H. Coffield of the Ethyl Corporation. With it as a starting material, $Mn(CO)_5Cl$[2], $Mn(CO)_5Br$[2] and $Mn(CO)_5I$[4] were prepared as described in the literature and identified by their infrared spectra.

The triphenylphosphine (m.p. 79–80°) and triphenyl phosphite were obtained from the Matheson, Coleman and Bell Co., triphenylarsine, triphenylstibine, aniline and *p*-toluidine from the Eastman Kodak Co., tributylphosphine from the Westvaco Co., and tributylphosphite and phenyldichlorophosphine from the Victor Chemical Works. All were used without further purification. The ethyl isocyanide, *o*-toluidine and *o*-chloroaniline from Eastman Kodak were distilled at 78–80°, 197° and 205–206°, respectively. The preparation and purification of 1-methyl-phospha-3,5,8-trioxabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_3$, was carried out by Mr. Smith Holt as reported.[5] Toluene and chloroform were purified according to Fieser.[5] Carbon tetrachloride, benzene and nitrobenzene were dried over calcium chloride and distilled; nitromethane was washed twice with aqueous sodium hydrogen carbonate, dried over calcium chloride and distilled; acetone was dried over potassium carbonate and distilled. Other solvents used were of reagent grade.

**Determination of Rates.**—The rates were determined by following the disappearance of the higher frequency carbonyl absorption of $Mn(CO)_5X$ as it reacted with L to form $Mn(CO)_4LX$. A Baird-Associates Model 4–55 double beam recording spectrophotometer with NaCl optics was used to follow the reactions as well as to determine the product absorptions in the carbonyl stretching region. A polystyrene standard was used for calibration.

An aluminum foil-wrapped round bottom flask containing a 5 ml. solution of $Mn(CO)_5X$ and a flask containing a 5 ml. solution of the ligand, L, were thermostated in a constant temperature bath. At zero time the ligand solution was poured into the foil-wrapped flask and mixed well. A sample of this solution was withdrawn with an eye-dropper and placed in an infrared cell. The spectrum of this sample was then taken in the carbonyl region using a solvent reference. Figure 1 illustrates a typical series of spectra taken at different times. From the transmittances, linear plots of ln $(A - A_\infty)$ *versus* time were obtained and the first order rate constants were calculated from the slopes of these lines. In these calculations, A is the absorbance, at time *t*, and $A_\infty$, the absorbance at $t = \infty$. The $A_\infty$ used was that measured experimentally and was almost zero in all cases except for $Mn(CO)_5I$ where the reactions did not go to completion. Then $A_\infty = 0$ was assumed and the rate constants were calculated from the initial first order slope before the reverse rate became significant. The maximum deviation of the calculated rate constants was ± 3%, except for the reactions involving ethyl isocyanide where the deviation was ±6.5%. It should be noted that the variations of the absorption intensities with concentrations of manganese

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