# Chelates of Cadmium with Kojic Acid[1]

BY R. L. PECSOK, R. L. MEEKER[2] AND L. D. SHIELDS

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The cadmium kojate complex system has been studied at 25° by polarography, potentiometric titration and zone electrophoresis. The consecutive formation constants k_1 and k_2 have been determined by both polarography ($k_1 = 1.48 \times 10^4$, $k_2 = 2.59 \times 10^3$), and potentiometric titration ($k_1 = 1.50 \times 10^4$, $k_2 = 2.42 \times 10^3$) with good agreement. A third complex, hitherto unreported, is shown to be negatively charged from electrophoresis data, to contain more than two kojates per cadmium from pH titrations and to have a formula of Cd(kojate)$_3^-$ and a log stability constant of 9.43 from polarographic data.

Introduction

Kojic acid is an organic heterocyclic ring compound with the structure[3]
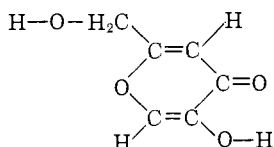
It has one acidic proton on the hydroxyl group adjacent to the carbonyl. The ionization constant has been reported as 4×10^{-10} in a 50% water-dioxane mixture[4] and 1.8×10^{-8} in 0.1 M potassium chloride.[5]

Previous work has shown the existence of two complexes, monokojatocadmium(II) ion (A) and biskojatocadmium(II) (B).

A

B
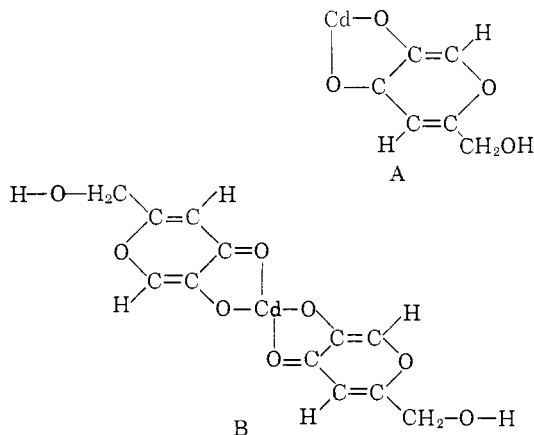
Bryant and Fernelius,[4] using a 50% dioxane-water solution, determined the consecutive formation constants for A and B. They give log k_1 as 6.6 and log k_2 as 4.7. Okáč and Kolařík[5] reported log k_1 as 4.6, determined by potentiometric titration in 0.1 M aqueous potassium chloride. The solid biskojatocadmium(II) compound was isolated by Musante.[6] It was crystallized from

aqueous solution buffered with sodium acetate. He reported the solubility as 8.6×10^{-4} mole per liter.

We have redetermined the first and second formation constants in 1.00 M potassium nitrate by two independent methods. We have also shown the existence and determined the formation constant of a new complex with the empirical formula Cd(kojate)$_3^{-1}$.

Experimental

Reagents and Equipment.—All polarographic investigations were carried out in solutions of 1.00 M constant ionic strength using potassium nitrate, "Baker Analyzed" Reagent, which was polarographically pure.

The kojic acid (donated by Charles Pfizer and Co., Inc., New York) was purified by sublimation at 0.1 mm. pressure. The product was a white crystalline solid with a melting range of 154.0 to 155.0°, yield 80–90%. Challenger, et al.,[7] give the melting point as 154°. No polarographic reduction waves were obtained with freshly prepared solutions up to 0.5 M concentration and up to pH 12. Above about pH 12 an anodic wave appeared at -0.44 v., an anodic–cathodic wave at -0.66 v. and a small cathodic wave at -0.88 v. Less basic solutions gave the same waves after standing. All kojic acid solutions turned yellow on aging. The decomposition was accelerated by base.[8,9]

"Baker Analyzed" Reagent cadmium nitrate was used without further purification. In 1.00 M potassium nitrate it gave a single polarographic wave at -0.582 v.

A Sargent Polarograph, Model XXI, was used. The applied potential was measured accurately with a Gray potentiometer immediately preceding and following the wave. Potentials are reported vs. the saturated calomel electrode. The maximum value of the current oscillations was used for the calculation of half-wave potential. Corrections were made for residual current and iR drop. The polarographic cell was a three compartment H-type.[10] The middle compartment contained saturated potassium chloride to separate the calomel electrode from the d.m.e. compartment. The resistance of the cell and d.m.e. was 125 ohms (at maximum drop size) as measured with a 1000 cycle a.c bridge. The capillary of the d.m.e. had a value of $m = 2.27$ mg. per sec. The reduction reaction of the cadmium complexes was reversible, the log plots having a slope of 0.030 (± 0.002) volt. The reaction was diffusion controlled. In order to suppress maxima, 0.004% gelatin was used throughout.

For the more precise work a Radiometer Model PHM4b was used, standardized with a solution of nitric acid in 1.00 M potassium nitrate, pH 1.191, calculated from the known hydrogen ion concentration. All pH measurements and equilibrium constants are based on data at constant ionic strength. Where less precise measurements were satisfactory, a Leeds and Northrup pH indicator (Cat. No. 7664) was used.

All data were taken at 25.0°.

(1) Abstracted from the Ph.D. thesis of R. L. Meeker, University of California, Los Angeles, April, 1960.

(2) Union Carbide Chemicals Company, South Charleston 3, West Virginia.

(3) H. A. McKinstry, P. F. Eiland and R. Pepinsky, Acta Cryst., 5, 285 (1952).

(4) B. E. Bryant and W. C. Fernelius, J. Am. Chem. Soc., 76, 5351 (1954).

(5) A. Okáč and Z. Kolařík, Collection Czech. Chem. Commun., 24, 266 (1959).

(6) C. Musante, Gazz. chim. ital., 79, 679 (1949).

(7) F. Challenger, T. Klein and T. K. Walker, J. Chem. Soc., 1948 (1929).

(8) C. N. Reilley and R. W. Schmid, Anal. Chem., 30, 947 (1958).

(9) Ibid., 30, 953 (1958).
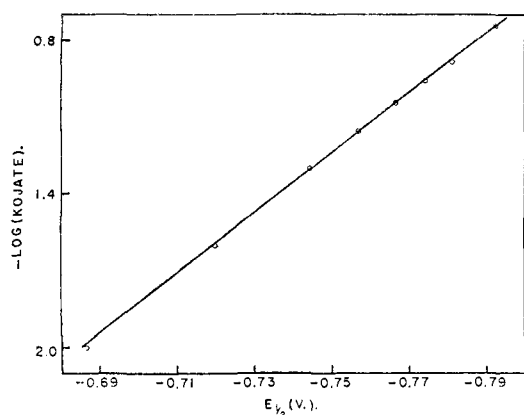
(10) R. L. Pecsok and R. S. Juvet, Jr., ibid., 27, 165 (1955).

Fig. 1.—Half-wave potential of the cadmium kojate complex as a function of log(kojate).

Results and Discussion

Polarography.—In regions of concentration of complexing agent where one metal complex species predominates, the method outlined by Kolthoff and Lingane[11] may be applied, yielding the empirical formula and the over-all formation constant of the complex. We use this method for studying the cadmium kojate complex containing the maximum number of ligands.

When more than one complex exists at the same time, the method of DeFord and Hume[12] may be used to determine consecutive formation constants. This method requires a knowledge of the formula. We use this technique to determine the first and second formation constants.

The general equation for the reduction of a mononuclear complex metal ion at a dropping mercury electrode may be written

$$MX_p^{+(n-pb)} + ne^- + Hg = M(Hg) + pX^{-b} \quad (1)$$
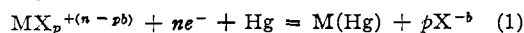
where X is the ligand and M the metal ion. The half-wave potential for the above reaction can be expressed

$$E_{1/2} = \epsilon + (0.0591/n) \log (f_{mx}k_a/K_c f_a k_c) - p(0.0591/n)\log C_x f_x \quad (2)$$

In this work, M is cadmium, so that $n = 2$, and X is the anion of kojic acid, called kojate. For simplicity, kojic acid will be referred to as HKo and kojate ion as Ko^-. In equation 2, ϵ is a constant.[11] The activity coefficients f_x, f_{mx} and f_a are, respectively, those of kojate ion, the cadmium kojate complex and the cadmium metal in the amalgam. Because the measurements are made in solutions of 1.00 M constant ionic strength, we can assume that f_x and f_{mx} are constant. We can also assume that f_a is 1, because the amalgam formed is so dilute. The quantities k_c and k_a are proportional to the square roots of the diffusion coefficients, D, of the complex metal ion and the metal in the amalgam. The quantity K_c is the formation constant for the reaction

$$Cd^{++} + p Ko^- = CdKo_p^{+(2-p)} \quad (3)$$
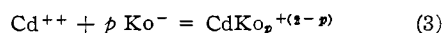
(11) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952.

(12) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

and

$$K_a = [CdKo^{+(2-p)}]/[Cd^{++}][Ko^-]^p \quad (4)$$

Using the above assumptions and definitions, equation 2 may be simplified

$$E_{1/2} = \epsilon_1 - p (0.0296) \log [Ko^-] \quad (5)$$

where ϵ_1 is a constant. A plot of $E_{1/2}$ vs. log $[Ko^-]$ will yield the value of p, the number of ligands bound to each metal ion.

Solutions containing potassium nitrate, 1.0 mM cadmium nitrate, 0.004% gelatin and varying amounts (0.001 to 0.18 M) of kojic acid were prepared. The solutions were adjusted to pH 10.40 and constant ionic strength of 1.00 M. The kojic acid exists primarily as kojate ion at this pH. $E_{1/2}$ is plotted vs. log $[Ko^-]$ in Fig. 1. A straight line is obtained above about 0.01 M kojate, with a slope of 85.7 mv., corresponding to a value of $p = 2.90$. This indicates that 3.0 kojates are bound to one cadmium in the region of kojate concentration above 0.01 M.

The above data were taken at constant pH, which eliminates any effect of hydrogen ion (or hydroxide ion). If data are taken at various pH's, it is possible to determine how many hydroxide ions are involved in the electrode reaction. We can postulate the general reaction

$$MX_p(OH)_a^{+(2-p-a)} + 2e^- + Hg = M(Hg) + pX^- + aOH^- \quad (6)$$
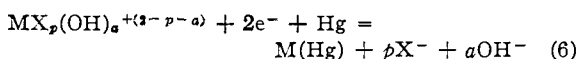
Then the simplified expression for the half-wave potential is

$$E_{1/2} = \epsilon_2 - p (0.0296) \log [Ko^-] - a (0.0296) \log [OH^-] \quad (7)$$

where ϵ_2 is a constant involving activity coefficients, diffusion coefficients and formation constants. Substituting for $[Ko^-]$ its equivalent, $K_a[HKo]/[H^+]$, and for $[OH^-]$ its equivalent, $K_w/[H^+]$, we obtain

$$E_{1/2} = \epsilon_3 - p (0.0296) \log [HKo] + (p + a) \log [H^+] \quad (7a)$$

The free kojic acid [HKo] can be expressed in terms of the known total kojic acid $[HKo]_0$

$$[HKo] = [HKo]_0 - p [CdKo_p] - [Ko^-] \quad (7b)$$

Again substituting for $[Ko^-]$, rearranging and solving equation 7b for [HKo], we have

$$[HKo] = [H^+]\{[HKo]_0 - p [CdKo_p]\}/\{[H^+] + K_a\} \quad (7c)$$

Substitution of [HKo] from equation 7c into the expression for the half-wave potential, equation 7a, gives, with suitable rearrangement

$$E_{1/2} = \epsilon_3 - p (0.0296) \log \{[HKo]_0 - p [CdKo_p]\}[H^+]/ \{[H^+] + K_a\} + (p + a) (0.0296) \log [H^+] \quad (8)$$

where $[KHo]_0$ is the total amount of kojic acid in all forms. Because $[HKo]_0$ is kept constant, and only that region of kojate concentration where p is constant is used, the expression $[HKo]_0 - p[CdKo_p]$ is a constant and can be included in ϵ_4 to give, with rearrangement

$$E_{1/2} = \epsilon_4 + p (0.0296) \log \{[H^+] + K_a\} + a (0.0296) \log [H^+] \quad (9)$$

Using equation 9, a plot of $E_{1/2} - p(0.0296)$ log $\{[H^+] + K_a\}$ vs. log $[H^+]$, will enable us to calculate the value of a.

Solutions containing 0.15 M kojic acid, 1.0 mM cadmium nitrate, 1.00 M potassium nitrate, 0.004% gelatin and varying amounts of sodium hydroxide were prepared. The pH of these solutions ranged from 6.04 to 9.35. The plot of equation 9 gives a straight line of zero slope, therefore $a = 0$. Therefore, the reduction reaction must be

$$CdKo_3{}^{-1} + 2e^- + Hg = Cd(Hg) + 3Ko^- \quad (10)$$
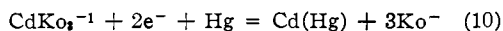
A formation constant, K_3, is defined as

$$K_3 = [CdKo_3{}^-]/[Cd^{++}][Ko^-]^3 \quad (11)$$

Following the derivations and symbology of Kolthoff and Lingane,[11] we have

$$K_3 = (k_s/k_c) \text{ antilog } \{ -(1/0.0296)[(E_{1/2})_s - (E_{1/2})_s + p\ (0.0296) \log [Ko^-]] \} \quad (12)$$

Referring to Fig. 1, a point on the line was used as the best average of the experimental data $(E_{1/2})_s$ was determined by taking polarograms of a number of solutions containing cadmium nitr te, both 0.1 and 1.0 mM, in 1.00 M potassium nit ate. The average value was -0.582 v. The qua tities k_s and k_c are proportional to the diffusion currents at constant metal ion concentration.[11] The diffusion current for the complex was determined in 0.13 M kojic acid, 1.0 mM cadmium nitrate, 0.004% gelatin at 1.00 M constant ionic strength using potassium nitrate as the supporting electrolyte. The pH was 10.40. The diffusion current for the simple metal ion was determined under identical conditions, except that the pH was 2.7. At pH 2.7, the cadmium is not complexed, as shown by the half-wave potential of -0.582 v., which is the same as the value obtained in absence of kojic acid. The diffusion current of the simple metal ion is somewhat smaller in the presence of kojic acid, and this value was used. The ratio of k_s/k_c is found to be 1.342 by the above method, and log K_3 is 9.43.

Firs and Second Formation Constants, Polarographic Method.—DeFord and Hume[12] have shown that the half-wave potential can be expressed

$$(E_{1/2})_c = E_a{}^0 - (0.0591/n) \log (I_m)\sum_j (K_j C_x{}^j f_x{}^j/f_{mx_j}) \quad (13)$$

where K_j is the formation constant for the j'th complex, and other symbols have their usual polarographic meanings. Following their derivation and symbology, we have

$$F_0(X) = \sum_j (K_j C_x{}^j f_x{}^j/f_{mx_j}) =$$
antilog $\{(n/0.0591)[(E_{1/2})_s - (E_{1/2})_c] + \log (I_s/I_0)\} \quad (14)$

where the symbol $F_0(X)$ is introduced for convenience to represent the experimentally measurable quantities on the right side of the equation.

The functions $F_0(X)$, $F_1(X)$ and $F_2(X)$ are defined by DeFord and Hume.[12] For the cadmium kojate system, they are

$$F_0(Ko^-) = K_0 + K_1[Ko^-] + K_2[Ko^-]^2 + K_3[Ko^-]^3 \quad (15)$$

$$F_1(Ko^-) = K_1 + K_2[Ko^-] + K_3[Ko^-]^2 \quad (16)$$

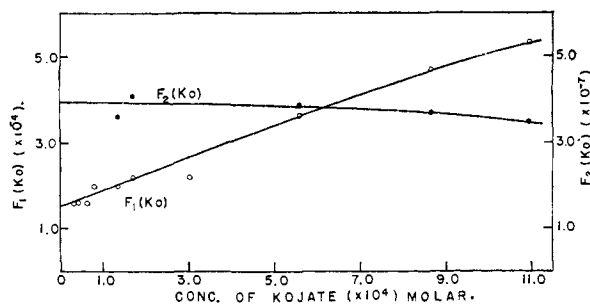$$F_2(Ko^-) = K_2 + K_3[Ko^-] \quad (17)$$

Fig. 2.—$F_1(Ko)$ and $F_2(Ko)$ as a function of kojate concentration.

The function $F_0(Ko)$ can be determined experimentally (equation 14). $F_1(Ko^-)$ can be calculated from $[Ko^-]$ and $F_0(Ko^-)$ and plotted against $[Ko^-]$. The intercept at $[Ko^-] = 0$, as can be seen from equation 16, will give K_1. K_2 may be calculated in a similar manner.

Solutions of 0.125 M kojic acid, 0.1 mM cadmium nitrate, 0.002 M nitric acid and 1.00 M potassium nitrate were prepared and the pH adjusted to various values (2.7 to 5.7), measured with the Radiometer pH Meter. The half-wave potentials were estimated to 0.1 mv., with a precision estimated to be ±0.5 mv. The ratio (I_s/I_c) in equation 14 is equal to the ratio of the respective diffusion currents. The diffusion current for the simple metal ion was determined from a solution which contained 0.125 M kojic acid but with enough excess nitric acid so that essentially no complex was formed. Table I gives the experimental data and the calculated values for the F_j functions.

TABLE I

$F(Ko)$ FUNCTIONS

$-E_{1/2}$, v.	$[Ko^-]$, $\times 10^4$ M	i_d, μamp.	$F_0(Ko)$	$F_1(Ko)$, $\times 10^{-4}$	$F_2(Ko)$, $\times 10^{-7}$
0.5827	0	0.937	1.00	..	..
.5877	0.342	.898	1.54	1.58	..
.5887	.449	.874	1.71	1.58	..
.5906	.644	.863	2.01	1.57	..
.5934	.772	.851	2.54	1.99	..
.5980	1.36	.838	3.68	1.97	3.61
.6010	1.73	.818	4.77	2.18	4.06
.6069	3.05	.810	7.63	2.17	2.26
.6197	5.61	.777	21.5	3.66	3.88
.6279	8.66	.767	41.4	4.67	3.69
.6325	10.97	.764	59.3	5.31	3.49

A plot of $F_1(Ko)$ vs. the kojate concentration is shown in Fig. 2. The value of K_1, $F_1(Ko)$ at $[Ko^-] = 0$, is 1.52 (±0.22) $\times 10^4$. The precision was calculated from the estimated precision of the half-wave potentials. Figure 2 also gives the plot of $F_2(Ko)$ vs. the kojate concentration. The value of K_2, obtained from the plot at $[Ko^-] = 0$, is 3.84 (±1.50) $\times 10^7$. The precision of K_2 was calculated from the precision of K_1. The consecutive formation constants, expressed by the equations

$$k_1 = [CdKo^+]/[Cd^{++}][Ko^-],$$
$$k_2 = [CdKo_2]/[CdKo^+][Ko^-] \quad (18)$$
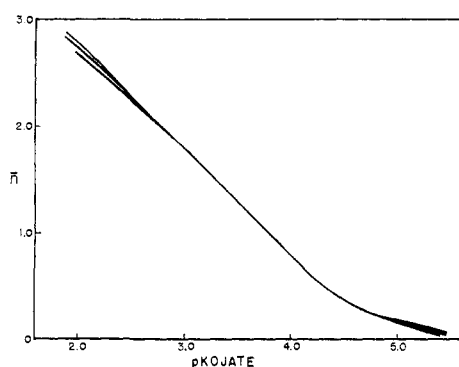
can now be calculated. Thus

Fig. 3.—The formation curve of the cadmium kojate system.

$$k_1 = K_1 = 1.52 \, (\pm 0.22) \times 10^4; \ \log k_1 = 4.18 \quad (19)$$

$$k_2 = K_2/k_1 = 2.6 \, (\pm 1.1) \times 10^3; \ \log k_2 = 3.4 \quad (20)$$

First and Second Formation Constants, Potentiometric Method.—In the Bjerrum method[13] the average number of ligands bound per metal ion, $\bar{n}$, is determined and plotted against the concentration of the ligand to give the formation curve. Formation constants can be calculated from the formation curve.

The complexation reactions for mononuclear complexes can be written as

$$\mathrm{Cd^{++} + HKo = CdKo^+ + H^+} \quad (21)$$

$$\mathrm{CdKo^+ + HKo = CdKo_2 + H^+} \quad (22)$$
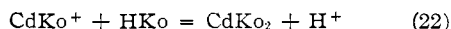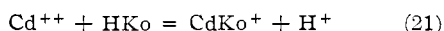
For the above reactions, $\bar{n}$ can be expressed mathematically as

$$\bar{n} = ([\mathrm{CdKo^+}] + 2[\mathrm{CdKo_2}])/\Sigma[\mathrm{Cd}] \quad (23)$$

For simplicity, we have left out any higher forms of the complex in the derivation. If they are included, as the form $\mathrm{Cd}_x\mathrm{Ko}_n{}^{+ \, (2x \, - \, n)}$, the final equation is not changed. For this system, where the reagents are kojic acid, cadmium nitrate, nitric acid and sodium hydroxide, we can write a charge balance equation

$$2[\mathrm{Cd^{++}}] + [\mathrm{H^+}] + [\mathrm{Na^+}] + [\mathrm{CdKo^+}] =$$
$$[\mathrm{Ko^-}] + [\mathrm{OH^-}] + [\mathrm{NO_3^-}] \quad (24)$$

We will ignore the 1.00 M potassium nitrate supporting electrolyte, since it plays no part in the reactions. We can also write two material balance equations

$$\Sigma[\mathrm{Cd}] = [\mathrm{CdKo^+}] + [\mathrm{CdKo_2}] + [\mathrm{Cd^{++}}] \quad (25)$$

$$\Sigma[\mathrm{Ko}] = [\mathrm{HKo}] + [\mathrm{Ko^-}] + [\mathrm{CdKo^+}] + 2[\mathrm{CdKo_2}] \quad (26)$$

We can solve the above equations for total bound ligand in terms of known quantities and obtain an expression for $\bar{n}$

$$\bar{n} = \{([\mathrm{H^+}] + K_\mathrm{a})/[\mathrm{H^+}]\Sigma[\mathrm{Cd}]\} \{2\Sigma[\mathrm{Cd}] + [\mathrm{Na^+}] + [\mathrm{H^+}] - [\mathrm{OH^-}] - [\mathrm{NO_3^-}] - \frac{K_\mathrm{a}\Sigma[\mathrm{Ko}]}{[\mathrm{H^+}] + K_\mathrm{a}}\} \quad (27)$$

This equation, similar to the equations developed by Martell and Calvin,[14] can be related to experimental quantities as follows. If we substitute in the right side of equation 27 the millimoles (mmoles)

(13) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(14) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, Inc., Englewood Cliffs, New Jersey, 1952.

of materials present and the total volume of the solution, V, we obtain the final equation for $\bar{n}$

$$\bar{n} = \frac{[\mathrm{H^+}] + K_\mathrm{a}}{\text{mmoles Cd} \times [\mathrm{H^+}]} \{\text{mmoles NaOH} - \text{mmoles HNO}_3$$
$$+ V([\mathrm{H^+}] - K_\mathrm{w}/[\mathrm{H^+}]) - K_\mathrm{a}/([\mathrm{H^+}] + K_\mathrm{a}) \text{ mmoles HKo}\} \quad (28)$$

All the quantities in equation 28 can be calculated or measured experimentally.

The ionization constant of kojic acid, K_a, was determined by titration with sodium hydroxide. Values of K_a were calculated from experimental values of the hydrogen ion concentration near the half-equivalence point in the usual manner. The ionization constant of kojic acid in 1.00 M potassium nitrate was 1.928 (± 0.022) $\times$ 10^{-8}, pK_a was 7.715 (± 0.005).

For the determination of $\bar{n}$ and the formation curves, solutions containing 1.00 M potassium nitrate, 0.2 M kojic acid, 1.5 mM cadmium nitrate and 0.001 M nitric acid were titrated with 0.5 M sodium hydroxide. The pH measurements were made with the Radiometer pH Meter. The electrode system was found to have a drift of about $+3$ mv. per hour during the first hour of immersion in a new solution. This corresponds to about -0.05 pH unit per hour. Because the titration required about ten minutes to complete, the pH readings near the end of the titration were probably low by about 0.01 pH unit. For the calculation of $\bar{n}$ and pKo we used the FORTRAN automatic coding system and the IBM 709 computer located at the Western Data Processing Center (Graduate School of Business Administration, U.C.L.A.). Three typical formation curves obtained are shown in Fig. 3. It can be seen that the curves begin to diverge above $\bar{n}$ about 2.2. At this point and beyond, the value of $\bar{n}$ becomes increasingly sensitive to pH (and similarly to K_a) because the term $K_\mathrm{a}/([\mathrm{H^+}] + K_\mathrm{a}) \times$ mmoles kojic acid in equation 28 is becoming a predominant quantity. It can also be seen that the curves are rising above $\bar{n} = 2.5$ and appear to be approaching $\bar{n} = 3.0$.

The method used for the calculation of the formation constants involves the slope of the formation curve at $\bar{n} = 1.0$. Bjerrum[13] defines a "spreading factor," $x = \frac{1}{2}(k_1/k_2)^{1/2}$, related to the slope, D, of the formation curve at $\bar{n} = 1$ by the expression $D = -2.303/(1 + x)$. By combining the two equations we can obtain a single expression involving the slope and the formation constants

$$(k_1/k_2)^{1/2} = -2(2.303/D + 1) \quad (29)$$

He also derives an equation for the formation constants in terms of the concentration of the complexing agent at $\bar{n} = 1$. With kojate as the ligand

$$k_1 k_2 [\mathrm{Ko^-}]^2 = 1 \quad (30)$$

We can then combine equations 29 and 30 to get k_1 and k_2 in terms of the slope and the concentration of the complexing agent

$$k_1 = 2[-(2.303/D) - 1][\mathrm{Ko^-}] \quad (31)$$

$$k_2 = 1/[\mathrm{Ko^-}]2[-(2.303/D) - 1] \quad (32)$$

Values were calculated for the three titrations and the average deviation is reported.

$$k_1 = 1.50 \, (\pm 0.08) \times 10^4; \ \log k_1 = 4.18 \quad (33)$$

$$k_2 = 2.42 \, (\pm 0.07) \times 10^3; \ \log k_2 = 3.38 \quad (34)$$

Zone Electrophoresis.—In order to confirm the existence of a negatively charged complex, zone electrophoresis was used. This technique involves moistening a suitable strip of paper with the solution to be investigated and applying a d.c. voltage to the ends of the strip.

The electrophoresis studies were carried out with varying ratios and concentrations of kojate and cadmium nitrate. In all cases, the solutions were adjusted to pH 10.5 with sodium hydroxide. For maximum efficiency, it is desirable to keep the ionic strength as low as possible, so no attempt was made to maintain constant ionic strength.

A 10 × 2.5 cm. strip of Whatman Glass Chromatography paper GF-B was cut into three pieces. The two end pieces were moistened with the kojate solution. The center piece was moistened with a cadmium solution containing the same concentration of kojate as the end pieces. The three pieces were placed in adjoining positions on a glass plate. Platinum electrodes were laid across the ends of the strip and the assembly covered with another glass plate. A regulated d.c. voltage was applied for several minutes. Hydrogen sulfide was used as a developer.

With a solution of 5.05 mM cadmium nitrate and 0.26 M kojate, under applied voltages of 200 v. for eight minutes or 250 v. for five minutes the cadmium zones moved about 2 cm. toward the positive electrode. The movement was irregular, the original rectangular shape being distorted. The results are shown in Fig. 4, B and C. A control paper, A, shows the movement of the zone with no potential applied. The two vertical lines near the center of each drawing indicate the boundaries between the three pieces of the strip. The shaded areas indicate the final position of the cadmium. The dashed lines show the position of the electrodes. D and E show the results when the solution con-
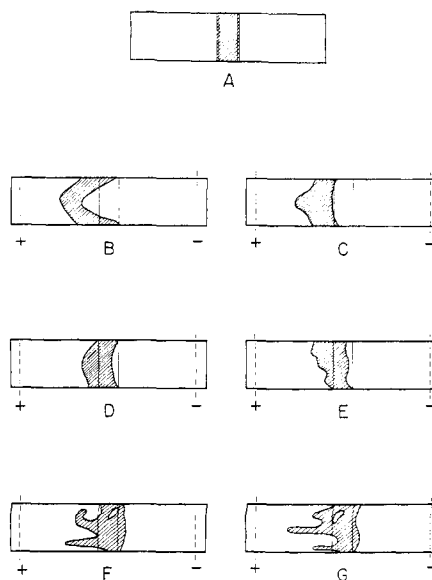

Fig. 4.—Zone electrophoresis of the cadmium kojate system.

tained 0.050 M kojate and 5.05 mM cadmium nitrate. In D, 220 v. were applied; in E, 250 v., for twenty minutes. Definite movement toward the positive electrode still occurred, although the movement was much less than in B and C, which contained five times as much kojate. Solutions containing 0.015 M kojate and 5.05 mM cadmium were run. The results are given in F and G (450 and 300 v. for fifteen minutes). In these cases, there was movement toward both the positive and negative electrodes. The zones were also very irregular on the positive side, with long streamers. This probably is due to local concentration gradients in the kojate caused by its movement.

Molecular Complexes and Their Spectra. XIII. Complexes of Iodine with Amides, Diethyl Sulfide and Diethyl Disulfide

By Hiroshi Tsubomura[1] and Robert P. Lang

Spectrophotometric studies of solutions of iodine with acetamide, N,N-dimethylformamide, diethyl sulfide and diethyl disulfide have given results that are consistent with an interpretation of 1:1 charge transfer complex formation in all cases. The thermodynamic and spectral characteristics of these complexes have been determined. A discussion on the nature of the bonding responsible for the formation of these complexes is given. In addition a discussion on the general features of the spectra of iodine–donor complexes is presented.

Introduction

Although extensive studies have been made on molecular complexes between iodine and organic compounds, there still remain some compounds whose interactions with iodine have not been carefully studied. Among them, amides, sulfides and disulfides seem to be of particular interest. The present paper gives the results of a spectrophoto-

metric investigation of iodine complexes formed from some of these compounds and also with di-t-butyl peroxide.

Amides are known to form complexes with metal ions,[2] the hydrogen ion[3] and electron-deficient molecules such as BCl_3.[4] There is evi-

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(1) On leave of absence from the University of Tokyo, 1958–1960. Institute for Solid State Physics, the University of Tokyo, Meguroku, Tokyo, Japan.