[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Polarographic Study of the Hydrazine Complexes of Zinc

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The polarographic behavior of zinc ion in hydrazine media at various *p*H values has been investigated. The reduction processes are reversible, and at *p*H 9 or below the half-wave potentials are dependent only on hydrazine concentration. Zinc ion adds successively four molecules of hydrazine to form the species $[Zn(N_2H_4)]^{++}$, $[Zn(N_2H_4)_2]^{++}$, $[Zn(N_2H_4)_3]^{++}$ and $[Zn(N_2H_4)_4]^{++}$. The over-all formation constants are 2.5×10^3, 5.0×10^3, 6.0×10^3 and 7.6×10^3, respectively. Above *p*H 9 the half-wave potentials are dependent upon both *p*H and hydrazine concentration, and zinc hydroxide is an equilibrium with soluble hydroxo-hydrazine complexes.

There are several references to hydrazine complexes of zinc in the early chemical literature. The list includes dihydrazine zinc chloride,[1-3] dihydrazine sulfate,[1,2] dihydrazine zinc iodide,[2,3] dihydrazine zinc oxalate,[2] dihydrazine zinc cyanide[4] and dihydrazine zinc thiocyanate.[5,6] Trihydrazine zinc complexes are reported to be formed when the anion is nitrate[2] or thiosulfate,[7] and an indefinite number of hydrazine molecules was assigned to the complexes formed from zinc chlorate and perchlorate.[8]

The general properties of the hydrazine complexes of the di- and trivalent metals are described by Audrieth and Ogg.[9] They report that hydrazine complexes may be prepared by addition of anhydrous hydrazine to a solid salt, by replacement of the ammonia in a metal ammine, or by addition of hydrazine hydrate to a solution containing the metal ion. Although the number of coördinated hydrazine molecules is usually half the coördination number of the metal, Audrieth and Ogg[10] also describe some mixed complex species containing hydroxo and hydrazine bridges.

Schwarzenbach and Zobist[11] have investigated zinc–hydrazine complexes by means of *p*H measurements. Their study was limited to the *p*H range from *p*H 6 to *p*H 7, zinc ion concentrations from 3 to 5 m*M*, and about 2.5-fold excess of hydrazine. Under these conditions zinc tetrafluoroborate adds successively four molecules of hydrazine. The logarithms of the successive formation constants are 2.4, 1.8, 1.3 and about 0.8. These investigators encountered precipitation at higher *p*H values. They believe that the precipitate contained hydroxyl and hydrazine groups in addition to zinc and tetrafluoroborate ions.

It is the purpose of this investigation to determine the nature of the zinc–hydrazine complexes which exist in solution from polarographic data. The half-wave potential of zinc ion was measured as a function of hydrazine concentration and *p*H.

Experimental

Reagent grade zinc oxide and sodium hydroxide and chemically pure sodium perchlorate and perchloric acid were used. Stock solutions of zinc perchlorate were prepared by dissolving weighed samples of zinc oxide in a minimum amount of perchloric acid and diluting to the proper volume. Hydrazine hydrate (100%) was standardized by titration with standard potassium iodate solution by the Andrews method and was used without further purification. Frequent restandardizations indicated that no decomposition of the hydrazine hydrate took place during the time of the investigation.

A series of solutions containing 0.5 m*M* zinc perchlorate of varying hydrazine concentration at a given *p*H was prepared by the addition of perchloric acid and adjustment, if necessary, with sodium hydroxide. The concentrations of hydrazine and of hydrazonium ion were calculated from the first dissociation constant of hydrazine

$$N_2H_4 + H_2O \rightleftharpoons N_2H_4^+ + OH^-, K_1 = 8.5 \times 10^{-7}$$

Sodium perchlorate was added to adjust the ionic strength to unity.

Gelatin (0.003%) was found to be a satisfactory maximum suppressor. Air was removed from the solutions to be studied polarographically by passing hydrogen through them for 15 minutes.

The Sargent Recording Polarograph, Model XXI, was used to determine all current-voltage data. A conventional "H" cell with its two arms separated by a sintered glass plug was employed with the the solution in question in both sides. A saturated sodium chloride–agar salt bridge led from the cell to an intermediate potassium chloride solution, which was connected in the conventional manner to an external saturated calomel reference electrode. This arrangement was necessary to avoid precipitation of potassium perchlorate in the salt bridge. The minimal resistance of the "H" cell containing 1.0 *M* sodium perchlorate with the dropping electrode was measured with a 1000-cycle conductance bridge and was found to be 700 ohms. The capillary had the following characteristics: h = 100 cm., m = 1.58 mg. sec.$^{-1}$, t = 5.14 sec., and $m^{2/3}t^{1/6}$ = 1.78 mg.$^{2/3}$ sec.$^{-1/2}$ at the electrocapillary maximum in 1.0 *M* sodium perchlorate. The temperature of the cell was maintained at 25 ± 0.05°, but the thermostat circuit was disconnected during determinations to ensure stable operation of the polarograph. The *p*H measurements were made with a line-operated Beckman *p*H meter, Model H. Due to the precipitation of potassium perchlorate at the tip of the calomel electrode, accurate *p*H measurements could be made only immediately after the immersion of the electrodes.

The polarograph was set for an initial voltage of −0.900 v. and a voltage span of 0.5 v. using an external Rubicon potentiometer. Current measurements were made using the maximum currents. It has been verified by Hume, DeFord and Cave[12] that the half-wave potential is the same regardless of whether the maximum or average currents are used. Half-wave potentials were obtained by plotting the logarithm of $(i_d - i)/i$ against voltage. The potentials thus determined were reproducible to within 2 millivolts.

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Results and Discussion

The experimentally determined half-wave potentials over the range of 0.1–3.0 M hydrazine at an ionic strength of 1.0 are plotted against logarithm of hydrazine concentration in Fig. 1. All of the reduction processes are reversible since, for any given polarogram, the slope of a plot of logarithm of $(i_d - i)/i$ against voltage equals 0.030. The plot at pH 8 or pH 9 indicates that zinc adds four molecules of hydrazine consecutively. The evaluation of the formation constants of the species is possible by the method of Hume and co-workers.[12] They have defined $F_j(X)$ values as follows

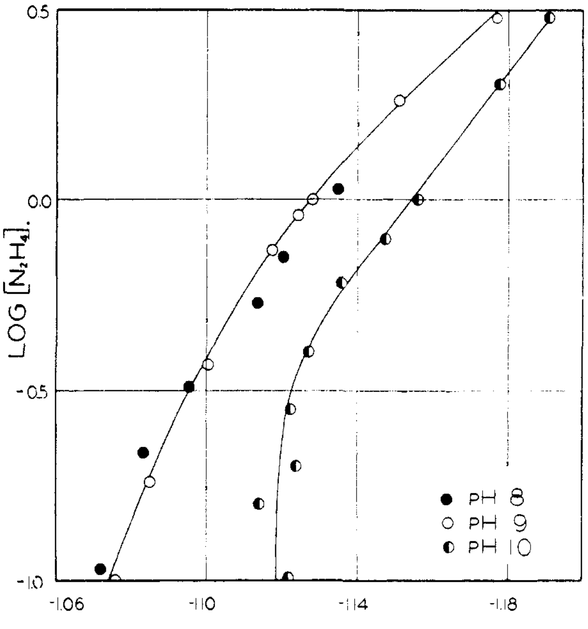

Fig. 1.—Plot of logarithm of hydrazine concentration against half-wave potential.

$$F_0(X) = \text{antilog}\left\{0.435\,\frac{nF}{RT}\,[(E_{1/2})_s - (E_{1/2})_c] + \log\frac{I_s}{I_c}\right\}$$

$$F_1(X) = \frac{[F_0(X) - (K_0/f_s)]}{C_xf_x}$$

$$F_2(X) = \frac{[F_1(X) - (K_1/f_{MX})]}{C_xf_x}, \text{ etc.}$$

where I_s/I_c is the ratio of the diffusion current constant of the aquated zinc ion to the apparent (measurable) diffusion current constant of the complexes, K_0 is the formation constant of the zero complex (unity), f_s is the activity coefficient of the aquated metal ion, C_x is the concentration of complexing agent, f_x is the activity coefficient of the complexing agent, K_1 is the formation constant of the complex containing one ligand, and f_{MX} is the activity coefficient of this complex.

If $F_j(X)$ is plotted against C_x and is extrapolated to $C_x = 0$, the intercept is equal to K_j, the over-all formation constant of the complex having j ligands of type X.

Convenient values of concentration of hydrazine and the corresponding values of half-wave potentials at pH 9 taken from the plot in Fig. 1 were used to calculate values of $F_j(X)$. The value of $(E_{1/2})_s$, the half-wave potential of zinc ion in 1.00 M sodium perchlorate, was taken as −1.000 v. In Fig. 2 $F_0(X)$, $F_1(X)$ and $F_2(X)$ are plotted against hydrazine concentration. The values of K_1 and K_2 are 2.5 × 10³ and 5 × 10³, respectively. In Fig. 3 straight lines are obtained for $F_3(X)$ and $F_4(X)$, the latter being horizontal. The values of $F_3(X)$ and $F_4(X)$ are neglected at low hydrazine concentrations because the error is greatest here. When each of these lines is extrapolated to zero hydrazine concentration, the intercepts, K_3 and K_4, equal 6.0 × 10³ and 7.6 × 10³, respectively. The probable error of each formation constant is estimated to be ±500.

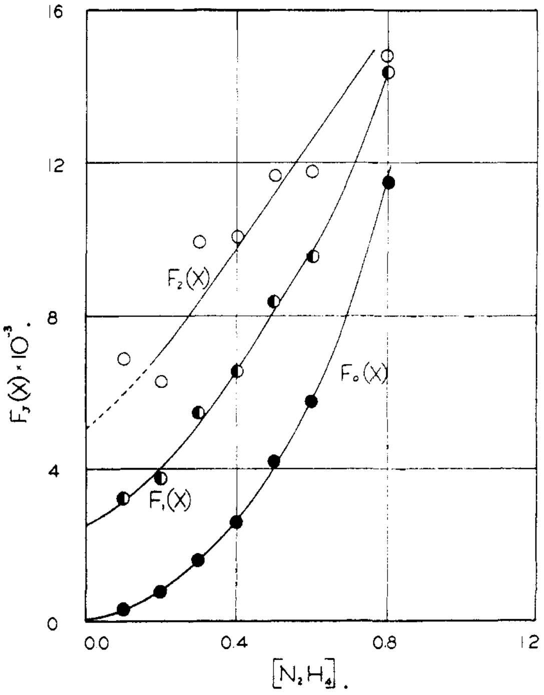

Fig. 2.—Values of $F_0(X)$, $F_1(X)$ and $F_2(X)$ for zinc in hydrazine medium.

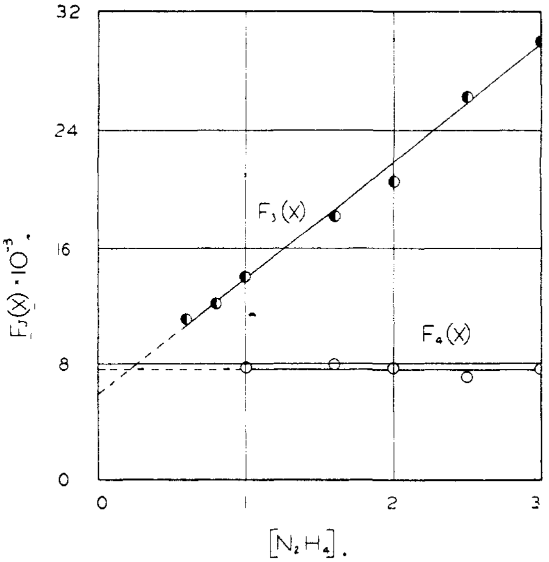

Fig. 3.—Values of $F_3(X)$ and $F_4(X)$ for zinc in hydrazine medium.

At *p*H 10 there appeared a solid phase which was shown by analysis to contain no nitrogen. This white, flocculent precipitate was undoubtedly zinc hydroxide. The diffusion current values at this *p*H increase with increasing hydrazine concentration until complete dissolution of the precipitate is indicated by the limiting value of the diffusion current. Thus at hydrazine concentrations of 0.1, 0.2, 0.4, 0.8, 1.0 and 2.0 the diffusion current values were, respectively, 0.20, 0.60, 1.20, 2.44, 2.94 and 3.12 microamperes.

Since, for the same concentration of free hydrazine, the half-wave potentials at *p*H 10 are more negative than those at *p*H 9, it is believed that hydroxo-hydrazine species exist in solution in equilibrium with zinc hydroxide. The limiting slope of the plot of $E_{1/2}$ *versus* log $[N_2H_4]$ (*p*H 10) has a value of about 0.08, indicating that there are probably two or three hydrazine molecules coördinated to the central zinc ion. In addition, the half-wave potential data indicate that at least one hydroxyl group is also coördinated. The existence of the cationic complexes, $[Zn(N_2H_4)_3(OH)]^+$ or $[Zn(N_2H_4)_2(H_2O)(OH)]^+$, appears more probable than that of the neutral species, $[Zn(N_2H_4)_2(OH)_2]$, since the latter would probably be insoluble. As the concentration of excess free hydrazine is decreased, water gradually replaces the remaining hydrazine molecules. The replacement of the last hydrazine molecule is accompanied by the addition of another hydroxyl group, and ultimately all of the zinc is precipitated as the hydroxide.

The logarithms of the successive formation constants (as distinguished from over-all formation constants) by the polarographic technique are approximately 3.4, 0.3, 0.1 and 0.1, whereas 2.8, 1.8, 1.3 and 0.8 were obtained by Schwarzenbach and Zobist[11] from *p*H measurements. These two sets of data are not easily compared, and each is probably valid only for the system from which it was derived. Our values for K_1, K_2, K_3 and K_4 were obtained under conditions quite different from those used by Schwarzenbach and Zobist.[11] The most striking difference is that the polarographic technique involves from 20–600-fold excess free hydrazine, whereas the method of *p*H measurements involves only 2.5-fold excess, under which condition the percentage of lower complexes is greatest. Both methods neglect activity coefficients, and both involve unknown liquid junction potentials which are specific for each system.

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Polarographic Study of Several *cis* and *trans* Coördination Compounds of Cobalt[1]

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Polarographic reductions were made on several pairs of *cis* and *trans* coördination compounds of cobalt. In the presence of supporting electrolyte, the *cis* isomer was found to exhibit a more positive half-wave potential than the corresponding *trans* isomer for compounds containing negative groups on two of the coördination positions and neutral groups on the other four. For compounds with only one or no negative groups, the *cis* isomers showed no trend toward more positive half-wave potentials. Two distinct polarographic waves for the reduction step Co(III) to Co(II) were noted for several compounds. A postulate is proposed for this phenomenon. Three of the *cis–trans* pairs were also reduced polarographically in the absence of supporting electrolyte, and the limiting currents were compared.

Methods for distinguishing between *cis* and *trans* isomers of inorganic coördination compounds in solution are limited. Recently, Basolo[3] has used the spectrophotometer to study differences in absorption spectra of *cis* and *trans* isomers of certain coördination compounds in solution. A recent paper from this Laboratory[4] reported a polarographic study of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride which showed that the half-wave potential for the *cis* isomer is considerably more positive than that for the *trans*. This suggested that the polarograph might be adapted to a general study of other *cis* and *trans* inorganic coördination compounds. The object of this investigation is to study several groups of *cis* and *trans* isomers of cobalt coördination compounds polarographically to determine whether consistent differences exist between isomeric pairs.

Experimental

Apparatus.—A Sargent Model XXI Polarograph was used with a cell of the type described by Lingane and Kolthoff.[5] Nitrogen, purified of oxygen by means of a vanadyl sulfate column,[6] was bubbled through the cell solution prior to each electrolysis. The potentials of the dropping mercury electrode during electrolysis were measured against an external saturated calomel electrode by means of a standard potentiometer circuit. Cell temperature was maintained at 25.0 ± 0.1° by means of a water thermostat. Reversibility of the electrode reactions was tested by determining the slopes of the plots of log $i/(i_d - i)$ *versus* potential. Half-wave potentials were taken from the logarithmic plots. Each solution for electrolysis was made fresh from the dry cobalt complex before use.

Preparation of Compounds. 1. ***cis*- and *trans*-Dinitrotetramminecobalt (III) Chloride.**—These salts had previously

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(1) Abstracted from the Ph.D. Thesis of David P. Sheetz, July, 1952, University of Nebraska. Presented at the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 16, 1953.

(2) Eastman Kodak Fellow, 1951–1952.

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