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Thermodynamics of Metal Cyanide Coordination. V. Log K, $\Delta H°$, and $\Delta S°$ Values for the Hg^{2+}–CN^- System[1a,b]

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Equilibrium constants have been determined for the stepwise formation of $Hg(CN)_4^{2-}$ from Hg^{2+} and CN^- at 10, 25, and 40°. Corresponding $\Delta H°$ values have been determined calorimetrically at 25°, and $\Delta S°$ values were calculated from these and the measured $\Delta G°$ values. The thermodynamic quantities for $Hg(CN)_2$ formation in the gaseous phase and in aqueous solution are compared and discussed. Trends in the $\Delta H°$ and $\Delta S°$ values are discussed and compared with earlier results for the Hg^{2+}–Cl^-, –Br^-, and –I^- systems.

Introduction

In a previous paper[2] of a series designed to provide thermodynamic data for the reaction of X^- (X = Cl, Br, and I) with type B metal ions, the thermodynamic quantities for Hg^{2+}–X^- interactions were reported. From these $\Delta G°$, $\Delta H°$, and $\Delta S°$ values conclusions were drawn regarding the relative contributions of $\Delta H°$ and $\Delta S°$ in determining the magnitude of $\Delta G°$, the relative stabilities of the aqueous and gaseous ions, and the degree of solvent ordering by the several aqueous complex ions. Because of its similarity to the Hg^{2+}–X^- systems studied previously, it was decided to obtain similar data for the Hg^{2+}–CN^- system. Also, a knowledge of the thermodynamic quantities for stepwise formation of $Hg(CN)_4^{2-}$ from Hg^{2+} and CN^- should improve our understanding of the factors which cause the consecutive formation constants of $Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$ to be much smaller in aqueous solution than are those of $HgCN^+$ and $Hg(CN)_2$.

No calorimetric ΔH data or consecutive formation constants (K_i) corrected to ionic strength, μ, = 0 have been reported for the Hg^{2+}–CN^- system. Previously reported equilibrium constant values have been summarized[3–5]; however, none was obtained under the conditions of μ and temperature used in the present study, and it is not possible from reported data to determine quantitatively the variation of any of the consecutive concentration formation constants, Q_i, with temperature or ionic strength.

In the present study are reported thermodynamic log K_i values for the stepwise formation of $Hg(CN)_4^{2-}$ from Hg^{2+} and CN^- at 10, 25, and 40° together with corresponding $\Delta S_i°$ and calorimetric $\Delta H_i°$ values valid at 25°.

Experimental

Materials.—Reagent grade NaCN (Baker Analyzed), $HClO_4$ (Baker and Adamson), NaOH (Baker Analyzed), $Hg(CN)_2$ (Mallinckrodt), HgO (Baker and Adamson), and triple distilled mercury (Wasatch Chemical Co.) were used in the preparation of solutions for the determinations. Standard $Hg(ClO_4)_2$ solutions were obtained by dissolving HgO in excess perchloric acid. A solution of $Hg_2(ClO_4)_2$ was prepared by equilibrating HgO for several days with excess liquid Hg in excess perchloric acid. The excess acid in this solution was determined by titration with standard NaOH. All water used in the preparation of the solutions was recently boiled distilled water. Fresh NaCN solutions were prepared and standardized weekly against $AgNO_3$. Solutions of $Na_2Hg(CN)_4$ were prepared for subsequent titration either by mixing known amounts of $Hg(ClO_4)_2$, NaCN, and NaOH solutions or by mixing known amounts of $Hg(CN)_2$ and NaCN solutions and diluting to volume. All cyanide-containing solutions were stored at 5° to minimize decomposition.

Equilibrium Constant Determinations.[6]—The aqueous Hg^{2+}–CN^- system is characterized by two very stable ($HgCN^+$ and $Hg(CN)_2$) and two much less stable ($Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$) species. For this reason, the equilibrium constant determinations fall naturally into two parts.

Values for K_3 and K_4 were determined by pH titration of $Na_2Hg(CN)_4$ solutions with $HClO_4$. The pH readings were taken using a Leeds and Northrup pH meter (Catalog No. 7401) equipped with Beckman glass and saturated calomel electrodes. A heliopot and microdial were used with the pH meter giving a tenfold sensitivity increase. The pH meter was calibrated against buffer solutions prepared using standard pH samples obtained from the National Bureau of Standards.

Determination of the K_1 and K_2 values required the measurement of the product K_1K_2 (β_2^0) and the ratio K_1/K_2. The β_2^0 values were determined using a combined pH titration–potentiometric procedure involving a mercury electrode. The e.m.f. measurements were made with a Leeds and Northrup Type K-2 potentiometer. The potentiometer was standardized in the usual manner. In these determinations solutions of $Na_2Hg(CN)_4$ were titrated with $HClO_4$. Values for K_1/K_2 were determined by potentiometric titrations of $Hg(ClO_4)_2$ and $Hg_2(ClO_4)_2$ solutions with NaCN using a platinum electrode. A saturated calomel electrode was used as the reference electrode in all the titrations. The experimental procedure for determination of β_2^0 and K_1/K_2 was identical with that used by Anderegg[7] except that (a) the Hg(l)–Hg^{2+} and Hg^{2+}–Hg_2^{2+} half-cell potentials

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[1] (a) Supported by U. S. Atomic Energy Commission Contract AT(04-3)-299. Presented at the 19th Annual Northwest Regional American Chemical Society Meeting, Spokane, Wash., June 15–16, 1964. (b) Part IV: R. M. Izatt, J. J. Christensen, J. W. Hansen, and G. D. Watt, *Inorg. Chem.*, **4**, 718 (1965). (c) To whom inquiries should be directed.

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[3] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Special Publication No. 7, The Chemical Society, London, 1957, p. 36.

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[6] Material supplementary to this paper in the form of pH titration, potentiometric titration, and thermometric titration data has been deposited as Document No. 8488 with the A.D.I. 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 $3.75 for photoprints or $2.00 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[7] G. Anderegg, *Helv. Chim. Acta*, **40**, 1022 (1957).

and the Q_i values derived from them were obtained as a function of μ in order to permit extrapolation to $\mu = 0$, and (b) the total CN^- to total Hg^{2+} ratio was maintained higher than 0.75 in the K_1/K_2 determinations to minimize errors due to polynuclear species formation.[8] Values for Q_3 and Q_4 were determined at $\mu = 0.005$ and 0.009, β_2 (Q_1Q_2) values at $\mu = 0.003$, 0.02, and 0.06, and Q_1/Q_2 values at $\mu = 0.05$.

Heat Determinations.—Solutions of mercuric perchlorate containing sufficient perchloric acid to repress mercuric ion hydrolysis were titrated with sodium cyanide by a thermometric titration procedure.[9,10] Because of the relative magnitudes of the equilibrium constants of the cyanide-containing species, the resulting thermometric titration curves showed three distinct reaction regions. As NaCN titrant was added to the acidic Hg^{2+} solution $HgCN^+$ and $Hg(CN)_2$ were formed first since their formation constant values are much larger than are those of any other possible species. A sharp end point indicating stoichiometric formation of $Hg(CN)_2(aq)$ was observed followed by a marked slope change of the curve. A second sharp end point with continued addition of NaCN was identified with the stoichiometric disappearance of the original excess H^+ indicating formation of HCN (pK = 9.2) in this region. The final region on the curve is that corresponding to the formation of $Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$. Four determinations were made at each of two μ values (approximately 0.01 and 0.02 M). No apparent trend of ΔH with μ was observed, and all eight values were averaged to give a $\Delta H°$ value.

Volatilization of HCN in the equilibrium constant and heat determinations was minimized by titrating all solutions in a closed vessel under a standing nitrogen atmosphere. The volume of air above the solution was kept as small as possible in each case.

Calculations.—The method used to calculate consecutive heats of formation from the thermometric titration data has been described.[2,9,10]

Values for β_2, Q_1/Q_2, Q_3, and Q_1 were calculated from the experimental data in a manner similar to that used by Anderegg.[7]

A Debye–Hückel expression of the form

$$\log \gamma = \frac{-AZ^2\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + CZ^2\mu \qquad (1)$$

where the several quantities have their usual significance,[11] was used to convert the ion product of water,[11] the dissociation constant of HCN,[10] and pH to the corresponding concentration quantities at the desired μ value. Equation 1 was also used to convert the calculated concentration constants to thermodynamic constants. In the conversion of pH to [H^+], the values $B\mathring{a} = 1$ and $C = 0.1$ were used,[12] and in all other cases $\mathring{a} = 4$ Å. and $C = 1.1$ were used as these gave thermodynamic constants which were independent of μ.

Since the determination of Q_1/Q_2 at low μ values was prevented by Hg^{2+} hydrolysis, the log γ values calculated in the determination of β_2^0 were used to correct Q_1/Q_2 to K_1/K_2. The value used for the heat of dissociation of HCN was taken from the literature.[10]

Calculations were aided by the use of IBM 650 and 7040 computers.

Results

In Table I are given log Q_3, log Q_4, log β_2, and log Q_1/Q_2 values at each ionic strength and temperature studied.

TABLE I

LOG OF EQUILIBRIUM QUOTIENT VALUES (Q_3, Q_4, β_2, AND Q_1/Q_2) AT EACH μ VALUE AND TEMPERATURE STUDIED[a]

t, °C.	$\mu \times 10^3$	Log equilibrium quotient
	$Hg(CN)_2(aq) + CN^- = Hg(CN)_3^-$ (Q_3)	
10	4	3.82 ± 0.02
	9	3.79 ± 0.02
25	4	3.57 ± 0.01
	9	3.55 ± 0.02
40	5	3.37 ± 0.02
	9	3.37 ± 0.02
	$Hg(CN)_3^- + CN^- = Hg(CN)_4^{2-}$ (Q_4)	
10	4	2.76 ± 0.03
	9	2.73 ± 0.04
25	4	2.57 ± 0.02
	9	2.58 ± 0.01
40	5	2.37 ± 0.02
	9	2.33 ± 0.02
	$Hg^{2+} + 2CN^- = Hg(CN)_2(aq)$ (β_2)	
10	14	34.43 ± 0.03
	25	34.46 ± 0.04
	59	34.38 ± 0.10
25	3	32.62 ± 0.10
	23	32.44 ± 0.08
	63	32.45 ± 0.13
40	4	31.12 ± 0.03
	22	31.11 ± 0.06
	60	31.09 ± 0.05
	$Hg^{2+} + Hg(CN)_2(aq) = 2HgCN^+$ (Q_1/Q_2)	
10	55	1.15 ± 0.04
25	55	1.15 ± 0.04
40	55	1.14 ± 0.04

[a] Estimated uncertainties are given as the standard deviation in each case.

In Table II are given the log K_i, $\Delta H_i°$, and calculated $\Delta S_i°$ values determined in the present study for the Hg^{2+}–CN^- system.

TABLE II

LOG K_i, $\Delta H_i°$ (KCAL./MOLE), AND $\Delta S_i°$ (E.U.) VALUES VALID AT $\mu = 0$ AND THE INDICATED TEMPERATURE FOR Hg^{2+}–CN^- INTERACTION IN AQUEOUS SOLUTION[a]

i	t, °C.	log K_i	$\Delta H_i°$, kcal./mole	$\Delta S_i°$, e.u.
1	10	17.97 ± 0.05		
	25	17.00 ± 0.08	−23.0 ± 0.6	0.7
	40	16.26 ± 0.07		
2	10	16.74 ± 0.05		
	25	15.75 ± 0.08	−25.5 ± 0.5	−13.4
	40	15.02 ± 0.07		
3	10	3.81 ± 0.03		
	25	3.56 ± 0.02	−7.6 ± 0.2	−9.0
	40	3.37 ± 0.02		
4	10	2.81 ± 0.05		
	25	2.66 ± 0.01	−7.2 ± 0.2	−12.1
	40	2.42 ± 0.03		

[a] The standard deviations for the log K_i values and the estimated uncertainties of the $\Delta H_i°$ values are given in each case. The i value in each case is related to that in the reaction $Hg(CN)_{i-1}^{3-i} + CN^- = Hg(CN)_i^{2-i}$.

Discussion

Previous equilibrium constant studies[3-5] were not carried out under the same experimental conditions of temperature and μ as those used in the present study; therefore, no comparisons with them are attempted.

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In most cases, however, good qualitative agreement with previous results is observed, with the β_2 values in the present study being slightly lower than those of earlier workers.

The data in Table II show each of the consecutive equilibrium constants to decrease with increasing temperature; however, K_1/K_2 does not vary with temperature. Plots of log K_i *vs.* $1/T$ give $\Delta H_i°$ values at 25° of −22, −23, −6, and −5 kcal./mole for stepwise formation from Hg^{2+} and CN^- of $HgCN^+$, $Hg(CN)_2$, $Hg(CN)_3^-$, and $Hg(CN)_4^{2-}$, respectively. These values are in good agreement with the calorimetric results reported in Table II. However, because of the loss of significant figures involved in taking the derivative of the log K_i *vs.* $1/T$ curve, the calorimetrically determined values are the more accurate.

Mercury(II) chemistry is characterized by the strong interaction of two unidenate ligands with Hg^{2+}. In the Hg^{2+}–CN^- system this characteristic behavior is primarily an enthalpy effect as can be seen (Table II) by the large magnitude of $\Delta H_2°$ compared to that of $\Delta H_3°$ while corresponding $T\Delta S_i°$ values (kcal./mole) remain essentially unchanged.

In Table III are given $\Delta G_i°$, $\Delta H_i°$, and $T\Delta S_i°$ values in kcal./mole for the stepwise formation of HgX_2(aq) (X = Cl, Br, I, CN) from Hg^{2+} and X^- in aqueous solution at 25°.

Table III

$\Delta G_i°$, $\Delta H_i°$, and $T\Delta S_i°$ Values (kcal./mole) for Several Hg^{2+}–X^- Systems[a]

Reaction	X[b]	$\Delta G_i°$	$\Delta H_i°$	$T\Delta S_i°$
1	Cl	−9.2	−5.5	3.7
	Br	−12.3	−10.2	2.1
	I	−17.6	−18.0	−0.4
	CN	−23.2	−23.0	0.2
2	Cl	−8.8	−7.2	1.6
	Br	−11.3	−11.0	0.3
	I	−15.0	−16.2	−1.2
	CN	−21.5	−25.5	−4.0

[a] Temperature 25°; the indicated reactions refer to (1) $Hg^{2+} + X^- = HgX^+$ and (2) $HgX^+ + X^- = HgX_2$(aq). [b] Data for Cl^-, Br^-, I^- taken from ref. 2, data for CN^- taken from Table II.

The data in Table III show that the importance of the $\Delta H°$ term relative to that of the $T\Delta S°$ term in determining the magnitude of the $\Delta G°$ values increases in the order Cl, Br, I, CN.

The increasing order of stability of the HgX_2 species in aqueous solution was shown earlier[2] to be a result of the decreasing magnitudes of the heats of hydration of X^- in the order Cl, Br, I. This stability order was reversed when the corresponding gaseous reactions were considered. Similar calculations in the case of $Hg(CN)_2$(g) have been made using literature data.[2,13–16] These calculations give $\Delta H°$ values for the reaction $Hg^{2+}(g) + 2X^-(g) = HgX_2(g)$ of −608, −601, −596, and −628 kcal./mole for X = Cl, Br, I, and CN, respectively. The corresponding $\Delta H°$ values for the reactions in the aqueous phase are −13, −21, −34, and −49 kcal./mole, respectively. These results show $\Delta H°$ to be largest in both the aqueous and gaseous phases for the formation of the $Hg(CN)_2$ species. The heats of hydration of CN^-(g) and $Hg(CN)_2$(g) differ by only 3 and 7 kcal./mole, respectively, from the corresponding values for Br^-(g) and $Hg(Br)_2$(g). Thus, it is evident that the high $\Delta H°$ value for $Hg(CN)_2$(aq) formation cannot be accounted for by heat of hydration effects alone, but is probably a result of some unknown combination of π bonding and/or larger than expected Hg^{2+}–CN^- electrostatic interaction.

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