effects of this order of magnitude.[8] The Np^{+4} (aq.) ion presumably is formed by further reaction of the dismutation products of the activated complex with hydrogen ions.

LEMONT, ILLINOIS

[8] *Cf.* V. Gold and D. P. N. Satchell, *Quart. Rev.*, **9**, 51 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Polarographic Study of Mercuric Cyanide and the Stability of Cyanomercuriate Ions[1]

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The reduction of mercury cyanide and the oxidation of mercury in hydrogen cyanide were shown to be polarographically irreversible in acid solutions, becoming reversible in basic solutions. In basic solutions the cyanide released by the reduction can complex mercuric cyanide at or around the surface of the drop. The species being reduced are $Hg(CN)_2$, $Hg(CN)_3^-$ and $Hg(CN)_4^{--}$. The logarithms of the over-all formation constants of these species are 33.9, 38.1 and 40.6, at an ionic strength of 2.0 and a temperature of 30°.

Introduction

The reduction of mercuric cyanide at the dropping mercury electrode was first extensively studied by Tomeš[2] who found in the range *p*H 6.0 to 9.5 a reversible wave corresponding to the over-all electrode reaction

$$Hg(CN)_2 + 2H^+ + 2e^- \longrightarrow Hg + 2HCN$$

In basic media the reaction became

$$Hg(CN)_2 + 2e^- \longrightarrow Hg + 2CN^-$$

The half-wave potentials in the *p*H range above 9.5 were observed to deviate from predicted values, and this was attributed to complexation of mercuric cyanide by cyanide ions liberated in the electrode reaction. Tomeš offered no experimental evidence for the formation of higher complexes, and the deviations were in the opposite direction from that expected to be caused by such an effect. It has been the purpose of the present investigation to study the polarographic behavior of mercuric cyanide over a much wider range of *p*H values and determine the nature and effect of possible complex formation.

Since the completion of this study,[1] Tanaka and Murayama[3] have reported an extensive study of the anodic wave of mercury in cyanide medium which corroborates our findings regarding the formation of higher cyanide complexes of mercury at the drop and leads to values for the formation constants which are in substantial agreement with those determined from our cathodic waves of mercuric cyanide. About the same time, Anderegg[4] published the results of a potentiometric determination of mercuric cyanide stability constants.

Theory

Tomeš derived for the equation of the wave, the expression

$$E_{de} = E_{1/2} + 0.030 \log \frac{i_d}{2} + 0.03 \log \frac{(i_d - i)}{i^2} \quad (1)$$

and pointed out that $E_{1/2}$ was not independent of concentration. In place of $E_{1/2}$ it is more convenient to use the concentration-independent potential on the wave, which we shall call E_f and which leads to

$$E_{de} = E_f + 0.030 \log \left(\frac{i_d - i}{i^2}\right) \quad (2)$$

for the equation of the wave. It is shown readily that

$$E_f = E' + 0.060 \log \frac{K_A + C^0_H + f_H + f_{CN}^-}{K_A} \quad (3)$$

in which

$$E' = E_0 + 0.030 \log \frac{d_1{}^2}{d_n K_2 f^2_{CN}{}^-} \quad (4)$$

where K_A is the ionization constant of hydrogen cyanide, $C^0{}_{H^+}$ is the concentration of hydrogen ion at the electrode surface, f_{H^+} and f_{CN^-} are the activity coefficients of hydrogen and cyanide ions, E_0 is the standard potential of the mercury–mercuric ion couple, d_1 and d_n are the diffusion coefficients of cyanide and mercuric cyanide, respectively, and K_2 the formation constant of mercuric cyanide. It is seen that E_{de} is equal to E_f when $(i_d - i)/i^2$ is equal to unity and that E_f is independent of mercuric cyanide concentration. It should be noted, however, that the relative position of E_f on the wave shifts with concentration. If all measurements are done at a fixed, high ionic strength, activity coefficients may be assumed to be constant. The equation of the wave predicts a plot of E_f *vs.* *p*H to be linear with a slope of 60 mv. per *p*H as long as $C^0{}_{H^+} f_{H^+} f_{CN^-} >> K_A$. For values of $C^0{}_{H^+} f_{H^+} f_{CN^-} << K_A$, E_f should be independent of *p*H.

Experimental

Reagents. Mercuric Cyanide.—C.P. Baker Analyzed was used without further purification. A 0.1 *M* stock solution was made. Airco Prepurified Nitrogen was further purified by successively scrubbing with chromous chloride, sodium hydroxide and water. For all other chemicals, analytical grade reagents were used.

Apparatus.—The polarographic cell consisted of a 100-ml. beaker fitted with a rubber stopper which was bored for nitrogen inlet and outlet tubes, the dropping mercury electrode (D.M.E.), a fritted-glass-disc salt bridge and an inlet for covering the solution with a blanket of nitrogen. The D.M.E. was constructed from marine barometer tubing with an adjustable leveling bulb to maintain a constant head of pressure on the capillary.

The capillary characteristics were determined using a 0.1 *M* potassium chloride solution in the cell with dropping

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[1] Taken in part from the Doctoral Dissertation of Leonard Newman, Massachusetts Institute of Technology, 1956.

[2] J. Tomeš, *Collection Czech. Chem. Commun.*, **9**, 81 (1937).

[3] N. Tanaka and T. Murayama, *Z. physik. Chem. N. F.*, **11**, 366 (1957).

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

electrode short-circuited to the saturated calomel reference electrode. The drop time of the capillary used was 4.00 sec. and the mercury flow 1.567 mg./sec., giving $m^{2/3}t^{1/6}$ equal to 1.70. A home-made automatic polarograph similar in design and characteristics to the Sargent Model XXI was used. The current scales were calibrated using precision resistors which had been carefully checked.

A Rubicon potentiometer, Catalogue No. 8702 (Rubicon Co., Philadelphia, Pennsylvania), was used to obtain accurate initial and final potentials. The Beckman Model G *p*H meter was equipped with general-purpose glass electrodes for the *p*H range 1 to 8 and with Beckman type E electrodes for the *p*H range 8 to 12. The conductivity bridge utilized to determine the resistance of the cells was an Industrial Instruments, Model RC-1B (Industrial Instruments, Inc., Jersey City, New Jersey).

Techniques and Conditions.—For all polarographic experiments, the ionic strength was maintained at 2.0 *M* with sodium nitrate and the solutions were made 0.004% in gelatin. The reference electrode was the conventional saturated calomel, connected to the cell by a saturated potassium nitrate agar bridge. The cell and reference electrode were thermostated at 30.0 ± 0.1° and the water-bath grounded to prevent stray pickups. The solutions were freed of dissolved oxygen by passing nitrogen through them for 15 minutes. During the running of a polarogram, nitrogen was passed over the solutions. Unless otherwise noted the drop time at the diffusion current of the polarogram was between 4 and 5 seconds, currents being measured on the peaks of the pen excursions. Residual currents were taken for each solution. The blanks contained everything except the electro-active material. The *p*H for each solution was measured before and after each polarogram. These values always agreed to within 0.02 *p*H unit. The potential span was determined by measuring the potential across the cell before and after each polarogram. The scanning rate was assumed to be constant and the potential at any point could be calculated. Potentials were corrected for *IR* drop across the cell.

Results

Acid Region: *p*H 1 to 5.5.—Table I is a summary of the polarographic data obtained. Equation 2 predicts that the slope (*S*) should be 30 mv., while the experimental values vary between 35 and 65 mv. When the value of *S* approaches 65 mv. the plots of E_{de} *vs.* $\log[(i_d - i)/i^2]$ are no longer straight lines. In these cases the reported slopes are only rough approximations taken from points near the foot of the wave. From Fig. 1 it is obvious that in this *p*H range, the $\Delta E_f/\Delta p$H values come nowhere close to conforming with the theoretical value of 60 mv. Indeed, there appears to be no regularity to the change in E_f with *p*H. In comparing experiments 8 with 9 and 23 through 25, it is evident that the value of E_f is dependent upon the concentration of mercuric cyanide. The value of E_f is also dependent upon the buffer used (*e.g.* compare experiment 9 with 15).

The marked deviation of E_f from the theoretical behavior in solutions of low *p*H would suggest either complex formation between mercuric cyanide and acid or irreversibility of the electrode process. The appearance of some of the waves and the deviations in slope suggested irreversibility and this possibility was examined first. Anodic waves of mercury in acidic cyanide media were run, and the E_f values instead of coinciding with those of cathodic mercuric cyanide waves at the same *p*H, differed by as much as 250 mv (experiment 12 *vs.* experiment 30 in Table I). The E_f values of anodic waves were observed to be concentration dependent (experiments 31 and 32). As a final test, the dependence of E_f upon drop time was determined at *p*H 4.6 in an acetate buffer. The observed 10 mv. change in E_f with fivefold variation in drop time is further indication of irreversible behavior.[5] The reaction appears to be diffusion controlled, however, as a normal temperature coefficient, for uncharged molecules, of 2.0% per degree was obtained using the method described by Meites,[6] and the limiting current was linear with $h^{1/2}$ (corrected for back pressure) over the whole range from 25 to 120 cm. head of mercury.

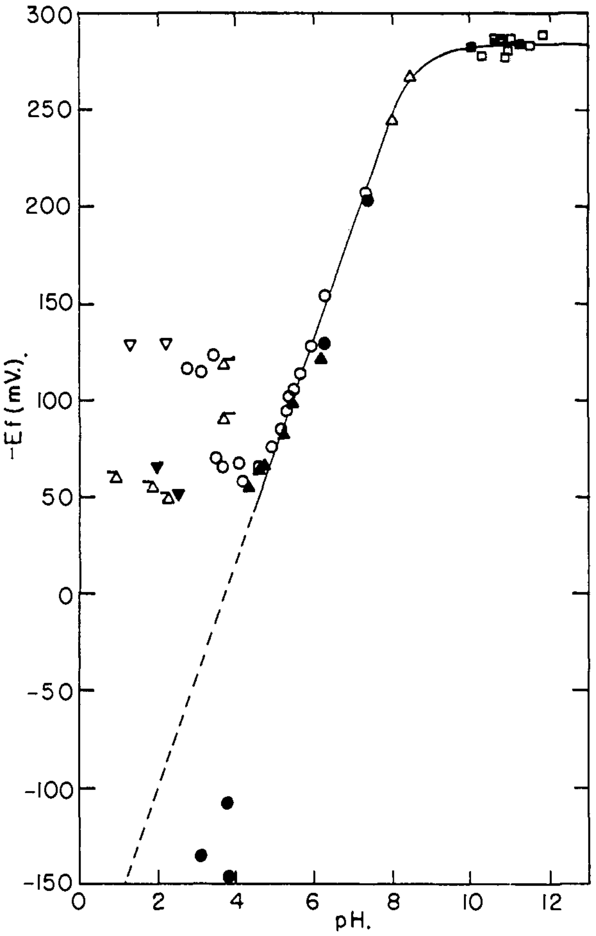

Fig. 1.—E_f as a function of *p*H. The buffers used for mercuric cyanide solutions, 0.2 to 1.0 m*M*, were: Δ̈, acetic acid/nitric acid; ∇, nitric acid; ▼, sulfuric acid; Δ́, potassium acid phthalate; O, acetic acid/sodium acetate; ▲, monohydrogen phosphate/dihydrogen phosphate; Δ, boric acid/sodium hydroxide; □, sodium hydroxide. Anodic waves of 0.2 to 1.0 m*M* sodium cyanide solutions were run in acetate buffers, ●; and sodium hydroxide, □.

Although the evidence for polarographic irreversibility was clear-cut, it did not rule out the possibility that acid-complex formation might also be present. Accordingly, experiments were designed to detect, if possible the addition of either hydrogen ions or hydrogen cyanide molecules to mercuric cyanide. It was found that titration curves were obtained which were identical within ±0.02 *p*H unit when 2 *M* nitric acid was added to 2 *M* sodium nitrate solutions in the presence and absence

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[5] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, p. 81.

[6] L. Meites, "Polarographic Techniques," Interscience Publishers, New York, N. Y., 1955, p. 55.

TABLE I

POLAROGRAMS IN THE ACID REGION

No.	pH	$Hg(CN)_2$ × 10^4, (M)	Buffer (M) HOAc	Buffer (M) HNO_3	S (mv.)	$-E_f$ (mv.)
1	0.95	2.25	1.0	0.1	42	60
2	1.86	2.25	1.0	.01	45	56
3	2.25	2.25	1.0	.001	46	49
			H_2SO_4			
4	1.25	2.25	...	0.04	58	130
5	1.96	15.0	0.005	...	56	66
6	2.15	2.25	...	0.004	55	130
7	2.54	15.0	0.001	...	57	52
			KHPhth			
8	3.65	1.13	0.05	...	65	120
9	3.65	2.25	0.05	...	65	94
			HOAc	NaOAc		
10	2.48	2.25	1.6	0.020	51	102
11	2.76	2.25	0.80	.020	41	117
12	3.10	2.25	.40	.020	47	115
13	3.40	2.25	.20	.020	50	124
14	3.49	2.25	.20	.020	47	70
15	3.65	2.25	.18	.030	43	65
16	4.01	2.25	.18	.040	44	68
17	4.18	2.25	.16	.060	42	58
18	4.40	10.0	.10	.10	47	89
19	4.40	10.0	.010	.010	45	87
20	4.52	2.25	.12	.10	40	66
21	4.85	2.25	.080	.14	35	76
22	5.12	2.25	.060	.16	34	85
23	5.28	2.25	.040	.18	34	95
24	5.28	5.00	.040	.18	35	102
25	5.28	10.0	.040	.18	36	106
			KH_2PO_4	Na_2HPO_4		
26	4.32	2.25	1.0	0.010	45	56
27	4.53	2.25	1.0	.020	43	64
28	4.62	2.25	1.0	.030	40	65
29	5.10	2.25	0.25	.040	37	84
		NaCN × 10^4, (M)	HOAc	NaOAc		
30	3.10	1.8	0.40	0.020	38	−135
31	3.70	2.5	.20	.040	48	−108
32	3.70	10	.20	.040	68	−147

of 0.2 M mercuric cyanide. This would rule out the possibility of mercuric cyanide–hydrogen ion complexes of any appreciable stability, but would not necessarily exclude the possibility of mercuric cyanide–hydrogen cyanide adducts. Experiments were therefore performed to determine the effect of mercuric cyanide on the vapor pressure of hydrogen cyanide in acid solutions. Nitrogen was passed through pH 1.5 solutions of 0.01 M hydrogen cyanide in 0.02 M mercuric cyanide under carefully controlled conditions. The evolved hydrogen cyanide, caught in an alkaline scrubber solution, was determined polarographically. Within experimental error, no difference in volatility could be detected between the mercuric cyanide solutions and similar solutions containing none.

Neutral Region: *p*H 5.5 to 9.5.—In a plot of $E_{1/2}$ *vs.* pH, Tomeš observed an agreement with theory between pH values 6 and 9.5. The data of Tomeš cover this pH range adequately. A few points were taken to verify our ability to reproduce the theoretical relationship between E_f and pH. A strict numerical comparison of the data of Tomeš with those of this investigation is not possible due to differences in reference cell, ionic strength and capillary characteristics and due to the fact that Tomeš calculated the concentration dependent $E_{1/2}$ values instead of the concentration independent E_f.

At a given pH, E_f should be independent of the concentration of the reducible species. In experiments 3 to 8 of Table II this was observed to be true. It can be seen that S approaches the theoretical value of 30 mv. (see also Fig. 1). Over the pH range $\Delta E_f/\Delta p$H follows the theoretical value of −60 mv.

E_f should be independent of the buffer used; however it appears from Fig. 1 that E_f in an acetate buffer differs from that in a phosphate. It was thought that complexes might have been formed with the buffer. If this were true, the degree of complexation, and therefore E_f, should be dependent upon the buffer concentration. Experiments 18 and 19 of Table I demonstrate that E_f is independent of buffer concentration.

TABLE II

POLAROGRAMS IN THE NEUTRAL REGION

No.	pH	$Hg(CN)_2$ × 10^4, (M)	Buffer (M) HOAc	Buffer (M) NaOAc	S (mv.)	$-E_f$ (mv.)
1	5.46	2.25	0.030	0.18	33	106
2	5.61	2.25	.020	.18	33	114
3	5.94	2.25	.020	.20	33	129
4	5.94	5.00	.020	.20	33	128
5	6.25	2.25	.020	1.0	32	154
6	6.25	10.0	.020	1.0	33	153
7	7.25	2.25	.002	1.0	32	208
8	7.25	10.0	.002	1.0	33	208
			KH_2PO_4	Na_2HPO_4		
9	5.45	2.25	0.25	0.040	36	99
10	6.10	2.25	.13	.080	30	122
			H_3BO_3	NaOH		
11	7.90	2.25	0.050	0.010	31	245
12	8.40	2.25	.050	.020	33	268
		NaCN × 10^4, (M)	HOAc	NaOAc		
13	6.25	10.0	0.020	1.0	30	130
14	7.25	2.3	.002	1.0	31	202

To examine further the possibility of complexes with the buffer, another potentiometric titration of mercuric cyanide was run, this time using sodium acetate as the titrant. The values of pH of the blank and sample agreed so closely that it can be assumed that complex formation cannot be taking place in significant amounts.

If $Hg(CN)_3^-$ and $Hg(CN)_4^{--}$ ions were being formed in this pH region, S would be significantly greater than 30 mv. Therefore, these complexes can be ruled out as principal contributors to the electrode process in this pH region. It was thought necessary to ascertain whether the waves were polarographically reversible over this pH range. Anodic waves of hydrogen cyanide were run and E_f and S calculated on the assumption that mercury is oxidized in the presence of hydrogen cyanide to mercuric cyanide. In comparing experiments 6 and 13 of Table II, it can be seen that there is a 23 mv. separation in the values of E_f at pH 6.25. However, in experiments 7 and 14, at pH 7.25, this separation is reduced to only 6 mv. Since the separation in E_f decreases as the pH increases, the amount of irreversibility must be decreasing. The extent of irreversibility probably is affected by the buffer used, which accounts for the differences in E_f observed for phosphate and acetate buffers. The slight residual irreversibility in this region is not sufficient to affect the theoretical variation of E_f with acidity.

Basic Region: pH 9.5 to 12.—As theory predicts, E_f becomes independent of pH at values greater than 10.5 (Fig. 1). In Table III, experiments 6 to 12, it can be seen that E_f becomes 28 mv. more negative over a 40-fold decrease in mercuric cyanide concentration. It can also be seen that S is too large in the more concentrated solutions but that it approaches the theoretical 30 mv. as the concentration is decreased. These phenomena can be explained if cyanide ions freed by the electrode reaction form complex ions with mercuric cyanide molecules as they diffuse to the surface of the drop.

TABLE III

POLAROGRAMS IN THE BASIC REGION

No.	pH	$Hg(CN)_2 \times 10^4$, (M)	S (mv.)	$-E_f$ (mv.) $Hg(CN)_2$	$-E_f$ (mv.) $Hg(CN)_3^-$	$-E_f$ (mv.) $Hg(CN)_4^{-}$	$d_n \times 10^{-3}$, (μa/M)
1	9.92	10.0	49	283	..	..	8.2
2	10.20	10.0	50	279	..	..	8.3
3	10.56	10.0	50	287	..	..	8.2
4	10.56	1.00	33	291	..	..	8.3
5	10.70	10.0	50	287	..	..	8.2
6	10.83	20.0	62	263	257	234	8.2
7	10.84	15.0	55	269	265	245	8.1
8	10.86	10.0	52	276	272	260*	8.2
9	10.85	5.00	49	282	286	277	8.1
10	10.83	2.00	38	286	300*	292	8.1
11	10.88	1.00	35	292	302	312	8.1
12	10.88	0.50	32	291*	304	319	8.2
13	11.42	10.0	49	285	..	..	8.2
14	11.72	10.0	48	289	..	..	8.3
					NaCN (M)		$d_1 \times 10^{-3}$, (μa./M)
15	10.60	..	52	286	0.001	..	7.1
16	10.70	..	52	286	.001	..	7.3
17	11.18	..	49	284	.001	..	7.2
18	11.27	10.0	36	594	.10	..	..
19	11.70	2.0	31	592	.10	..	..

* E_f for the species as explained in the text.

For relatively high concentrations of mercuric cyanide, the large amounts of cyanide released might result in considerable complex formation with a corresponding change in slope on the upper part of the wave. But for low mercuric cyanide concentrations, and especially at the foot of the wave where the extent of reduction is slight, the probability of a mercuric cyanide molecule encountering a free cyanide ion at the drop surface would be greatly diminished and the slope should approach 30 mv.

If this hypothesis is true, then the reduction takes place by more than one mechanism. Plots of $E_{d.e}$ *vs.* log $(i_d - i)/i^n$ for $n = 2$, 3 or 4 should be linear over that portion of the polarogram where $Hg(CN)_2$, $Hg(CN)_3^-$ or $Hg(CN)_4^{--}$ is the predominating species. The linear portions should each have a slope of 30 mv.

The log plots in Fig. 2 show a typical example. In this case it can be seen that for $n = 2$, the slope is greater than 30 mv. There is fairly good agreement for $n = 3$, but deviations at the beginning of the polarogram for $n = 4$. This type of result indicates the possibility of interpreting the polarograms on the basis that 2, 3 or 4 cyanides complex the mercury. The values of E_f obtained on this basis are summarized in Table III, experiments 6 to 12.

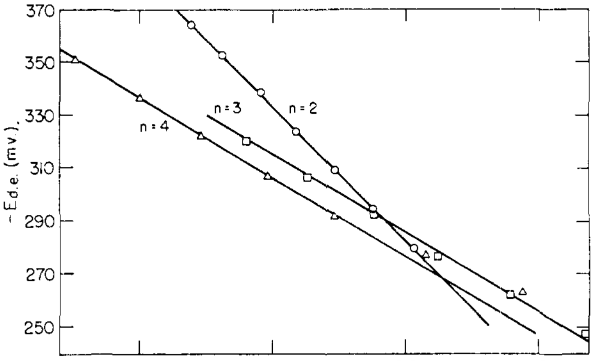

Fig. 2.—Interpretation of a polarogram of 0.5 mM mercuric cyanide in terms of $Hg(CN)_2$, $Hg(CN)_3^-$ and $Hg(CN)_4^{--}$ reduction.

On a mercuric cyanide interpretation, E_f and S were determined from the line best fitting all the points. The values of E_f for $Hg(CN)_3^-$ and $Hg(CN)_4^{--}$ were obtained from a line, with a slope of 30 mv., placed through as many points as possible. The values of E_f marked with an asterisk were obtained from the polarograms where the chosen value of n gave the best correlation.

The asterisk-marked values can be considered the values of E_f for the reduction of $Hg(CN)_2$, $Hg(CN)_3^-$ and $Hg(CN)_4^{--}$. As might be expected, the E_f for the more complexed $Hg(CN)_3^-$ is more negative than the E_f for mercuric cyanide. However, the E_f for the tetracyano mercuriate is less negative. It can be shown that the reason this occurs is that the polarographic diffusion constant, d_1, appears in E_f as a second, third and fourth power for the corresponding complexes. The effect introduced by the changes in the power of d, can be great enough to offset the differences in the formation constants.

In order to show that the E_f for each species is valid, the over-all formation constants were calculated and found to compare well with those in the literature.

In the basic region where $K_a >> D^0{}_{H^+} + f_H + f_{CN^-}$, we have, analogous to the sum of equations 3 and 4

$$E_f + E_0 + 0.030 \log \frac{d_1{}^n}{d_n K_n f^n{}_{CN^-}} \qquad (5)$$

where n is the cyanide–mercuric ratio of the particular complex. From Table III it can be seen that d_n is independent of whether the reduction depends upon $Hg(CN)_2$, $Hg(CN)_3^-$ or $Hg(CN)_4^{--}$.

The average values of d_n and d_1 calculated from $i_d{}^{cathodic}/C^0{}_{Hg(CN)_2}$ and $i_{d\,anodic}/C^0{}_{CN^-}$ are 8.2×10^3 and 7.1×10^3, respectively. With E_0 for the mercuric–mercury couple equal to 612 mv. *vs.*

TABLE IV

SUMMARY OF FORMATION CONSTANTS FOR THE CYANIDE-MERCURIC SYSTEM

Worker	Log K_2	Log K_3	Log K_4	Log k_3	Log k_4	Log (K_4/K_2)	μ	Method
This work	33.9	38.1	40.6	4.2	2.5	6.7	2.0	Polar.
Brigando and Job[7]	..	..	..	3.9	2.9	6.8	0.01 to 0.02	Poten. at 2°
Sherrill[13]	..	..	41.4	..	..	..	0.05 to 0.2	Poten.
Charlot and Gauguin[12]	..	..	40.5	..	..	..	....	...
Gauguin[14]	21.7	..	27.7	..	..	6.0	0	Cond.
Tanaka and Murayama[3]	35.3	39.0	41.5	3.7	2.5	6.2	0.2	Polar.
Anderegg[4]	34.7	38.5	41.5	3.8	3.0	6.8	0.1	Poten.

saturated calomel electrode and the E_f values -291, -300 and -260 mv. for $Hg(CN)_2$, $Hg(CN)_3^-$ and $Hg(CN)_4^{--}$, the over-all formation constants K_2, K_3 and K_4 can be calculated from equation 5 where

$$K_2 = \frac{[Hg(CN)_2]}{[Hg^{++}][CN^-]^2}$$

and

$$K_3 = \frac{[Hg(CN)_3]^-}{[Hg^{++}][CN^-]^3}$$

and

$$K_4 = \frac{[Hg(CN)_4^=]}{[Hg^{++}][CN^-]^4}$$

if we assume that the activity coefficient of CN^- is not only constant due to the high and constant ionic strength, but is also equal to one.

The stepwise formation constants k_3 and k_4 can be calculated from K_3/K_2 and K_4/K_3. A summary of the logarithms of the formation constants calculated in our study and those reported in the literature are included in Table IV.

Brigando and Job,[7] in a potentiometric study at 2° and $\mu = 0.01$ to 0.02, reported formation constants of

$$3 \times 10^{-6} = \frac{[Hg(CN)_3^-][H^+]}{[Hg(CN)_2][HCN]}$$

and

$$10^{-12} = \frac{[Hg(CN)_4^=][H^+]^2}{[Hg(CN)_2][HCN]^2}$$

The value of K_3 and K_4 and K_4/K_2 can be calculated from the ionization constant of hydrogen cyanide. The value of this quantity is not known accurately: various experimental determinations in the literature have given values of 7.2×10^{-10},[4,8] 13×10^{-10},[9] and 260×10^{-10}.[10] Latimer[11] gives the value 4×10^{-10}, calculated indirectly from thermodynamic data, as the most probable one, and we have used this value to derive the additional constants from the data of Brigando and Job. Considering the differences in temperature and ionic strength, the agreement between their constants and ours is quite good. The value of K_4 which we have obtained also agrees well with the value reported in the text by Charlot and Gauguin,[12] but only fairly well with the potentiometric value reported by Sherrill.[13] The differences in ionic strength might account for some of this discrepancy; however, since Sherrill did not consider the formation of $Hg(CN)_3^-$, his value for K_4 should be too high.

The values of K_2 and K_4 as obtained from conductivity measurements, and reported by Gauguin,[14] are obviously too low; however, the value of K_4/K_2 falls in line with the one calculated in this study and with the one calculated from the study of Brigando and Job. It appears that we are the first to have determined values for K_2 and K_3 independent of values reported for K_4 and/or K_A.

The main difference between the values of our constants and those of Tanaka and Murayama arise from the assumptions made in calculating K_2. Tanaka and Murayama assume that f_{CN^-} can be calculated from Kielland's[15] data at ionic strength of 0.2, that glass electrode measurement of *p*H at $\mu = 0.2$ gives the activity of hydrogen ion directly and that K_A is 4.0×10^{-10}. For our calculation of K_2 we assume only that the f_{CN^-} at $\mu = 2.0$ is equal to one. Whereas our values of K_3 and K_4 are calculated directly from the experimental data, Tanaka and Murayama utilized Sherrill's[13] data for K_4 and their value of K_2 in the calculation of K_3. The results of Anderegg, calculated by application of the Bjerrum average ligand number technique to potentiometric data obtained with the glass and mercury electrodes are in good agreement with ours and those of Tanaka and Murayama, especially, in view of the differences in experimental approach.

To further demonstrate that the value obtained in this study for the E_f of $Hg(CN)_4^{--}$ is valid, polarograms were run on mercuric cyanide with a large excess of cyanide in basic solution. It can be assumed that all the mercuric cyanide is complexed as $Hg(CN)_4^{--}$. For a mixed anodic-cathodic wave

$$E_{de} = E_f + 0.030 \log \frac{(i_{dc} - i)}{(i - i_{da})^4} \qquad (6)$$

where i_{dc} and i_{da} represent the anodic and cathodic diffusion currents. When cyanide is a lot greater than mercuric cyanide, the I_{da} becomes a lot greater than *i;* and the denominator becomes a constant. Therefore

$$E_{de} = E_{f,\,CN^-} + 0.030 \log (i_{dc} - i) \qquad (7)$$

where in basic solution

$$E_{f,\,CN} = E_0 - 0.030 \log d_4 K_4 (CN^-)^4 f^4_{CN^-} \quad (8)$$

Equation 7 predicts that a plot of E_{de} *vs.* log $(i_{dc} - i)$ should have a slope S equal to 30 mv. Experiment 19 of Table III shows that the proper slope for the postulated $Hg(CN)_4^{--}$ is attained.

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From $E_{f,\,CN^-} = -592$ mv., $E_0 = 612$ mv., $d_4 = 8.2 \times 10^3$, µa./M, cyanide = 0.1 M and $f_{CN^-} = 1.0$, K_4 was calculated from equation 8 as $10^{40.1}$. This can be considered good agreement with the $K_4 = 10^{40.6}$, obtained when mercuric cyanide was assumed to be complexed as $Hg(CN)_4^{--}$ at the surface of the drop.

It was thought necessary to test the polarograms for polarographic reversibility since the arguments above are based upon this condition. In order to do this, anodic waves of cyanide were obtained in basic solutions. As can be seen in Table III, the analyses of the anodic waves were the same as analogous cathodic waves. The system can therefore be said to be polarographically reversible.

Another usually important criterion for reversibility is the attainment of a single continuous polarogram for a mixed anodic and cathodic wave. It can be shown that with the type of electrode phenomena that we have observed this behavior is not to be expected.

In an equimolar solution of cyanide and mercuric cyanide most of the cyanide is complexed by the mercuric cyanide. The cathodic portion of the polarogram should start with a dependency on the reduction of $Hg(CN)_3^-$, with the reduction of $Hg(CN)_4^{--}$ taking over quite early. On the other hand, since the activity of the mercuric ion is decreased by the presence of mercuric cyanide, the anodic portion should start with a dependency upon $Hg(CN)_3^-$, with the reduction of mercuric cyanide taking over quite early.

The cathodic portion would be mainly dependent upon the reduction of $Hg(CN)_4^{--}$ and the anodic portion upon the oxidation of mercury to mercuric cyanide. One should not expect to obtain a straight line over the anodic and cathodic portions from any plot of E_{de} *vs.* log $(i_d - i)/i^n$. When this experiment was tried, the polarogram looked like a single continuous wave, but, as expected, no log plot gave a straight line with the proper slope over the anodic–cathodic portion.

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CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Lower Hydrides of Phosphorus. II. The Decomposition of Biphosphine in Liquid Ammonia[1,2]

BY EVAN H. STREET, JR., DAVID M. GARDNER AND E. CHARLES EVERS

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Biphosphine decomposes in liquid ammonia to lose phosphine, leaving a black residue of variable composition containing phosphorus, hydrogen and solvent. Products are obtained whose P/H ratio varies from 3.05 to 4.81 and whose NH_3/H ratio varies from 0.09 to 0.92. Similar substances are formed on treating phosphorus with ethylamine. The constitution of these substances is discussed in relation to solid hydrides obtained when biphosphine is decomposed *in vacuo* and in the presence of moisture.

In our previous communication,[3] we described the decomposition of biphosphine at room temperature under anhydrous conditions. Decomposition *in vacuo* proceeded with the elimination of phosphine, forming orange-yellow solids whose ultimate compositions appear to lie in the neighborhood of $P_{2.25}H$, (P_9H_4). With moisture present the products contained larger proportions of hydrogen; materials obtained in a variety of ways have reported compositions averaging around P_2H.[3-5] These preparations left small amounts of non-volatile residue on strong heating *in vacuo*.

Another class of hydrides has been prepared by treating solid hydrides[6,7] or white phosphorus[6] with a variety of amine solvents. Stock[4a] found that phosphine was eliminated and reddish colored solutions were formed when P_2H was treated with liquid ammonia. The substance $P_{4.5}H$, (P_9H_2), which was reportedly obtained by the thermal decomposition of P_2H under the proper conditions,[4a] likewise dissolved, but without the evolution of phosphine. In all cases black substances were obtained by evaporating the solvent, whose compositions averaged around $P_{4.5}H$ and which contained up to one molecule of ammonia. A small amount of non-volatile residue remained on strong heating *in vacuo*. This appeared to be P_3N_5.[6a] Products obtained by the direct action of liquid ammonia on phosphorus were similar. Although comprehensive quantitative data have been reported only in the case of products obtained from ammonia, it seems likely that other nitrogen bases also yield similar products.

In view of the thermal instability of biphosphine

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[1] Taken in part from a Thesis by Evan H. Street, Jr., presented in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

[2] This research was supported in part by the Office of Naval Research under Contracts Nonr-598(00) and N8onr-74200. Reproduction in whole or in part is permitted for any purpose of the United States Government. Presented before the Inorganic Division of The American Chemical Society, 132nd National Meeting, New York, September, 1957.

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