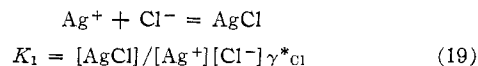


Figure 5.—Dependence of $D[\text{MNO}_3]/[\text{TNO}_3]$ and α_2 on chloride mole fraction.

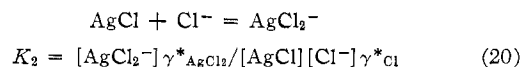
correspond to the mole fraction scale and they are related to the molality scale through the relation

$$\gamma(\text{molality}) = \gamma(\text{mole fraction})x_{\text{NO}_3}$$

The stability constants K_1 and K_2 defined by



and



were calculated from α_2 using the curve-fitting methods described by Rossotti and Rossotti.¹⁴ The values obtained are given in Table III.

Values of K_1 and K_2 have been determined by electromotive force measurements⁶ and by solubility measurements.¹⁵ These values are in good agreement with those given in Table III, except K_2 obtained by the emf method, which seems to be questionable. The significance of the two equilibrium constants in respect to a quasi-lattice model of molten salt is discussed elsewhere.¹⁵

Acknowledgment.—The authors are grateful to Professor C. D. Coryell for valuable comments. The assistance of Mrs. M. Sie in the experimental part of the work is gratefully acknowledged. This work has been supported by the U. S. Atomic Energy Commission, Contract No. AT-(30-1)-305.

(14) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(15) J. Méndez, I. J. Gal, and J. W. Irvine, Jr., to be submitted for publication.

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Monocyanochromium(III) Ion: Kinetics of the Spontaneous Aquation and of the Chromium(II)- and Mercury(II)-Catalyzed Reactions¹

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The kinetics of loss of cyanide ion from the complex $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$ has been studied as a function of hydrogen ion concentration and temperature in solutions of unit ionic strength, in which the supporting electrolyte was either sodium or lithium perchlorate. Small differences in the two sets of results were found, which were attributed to medium effects arising from a nonconstant activity coefficient of hydrogen ion in solutions of constant ionic strength but varying composition. At 55.0° and $\mu = 1.00 M$ (lithium perchlorate medium) the aquation rate is given by the equation $-d \ln [\text{CrCN}^{2+}]/dt = 5.8 \times 10^{-7} \cdot [\text{H}^+]^{-1} + 9.7 \times 10^{-4} + 8.0 \times 10^{-3}[\text{H}^+] \text{ sec}^{-1}$. The catalysis by chromium(II) is consistent with an expression $k[\text{CrCN}^{2+}] \cdot [\text{Cr}^{2+}]/[\text{H}^+]$ with $k = 2.8 \pm 0.3 \times 10^{-3} \text{ sec}^{-1}$ at 55.0° and $\mu = 1.00 M$. Mercury(II) and CrCN^{2+} associate quite strongly; the association quotient of $\text{Cr}(\text{CN})\text{Hg}^{4+}$ is $\geq 10^6 M^{-1}$. Aquation in the presence of mercury(II) is described by the relation $d[\text{Cr}^{3+}]/dt = k_{\text{Hg}}[\text{Cr}(\text{CN})\text{Hg}^{4+}]$, with $k_{\text{Hg}} = 6.6 \pm 0.9 \times 10^{-3} \text{ sec}^{-1}$. The mechanisms of the three reactions are discussed from the standpoint of the net activation processes and the compositions and likely geometries of the transition states involved. Evidence is advanced for the proposal that the reaction of CrCN^{2+} and Hg^{2+} is accompanied by internal ligand isomerization and that the cation complex is $\text{Cr}-\text{NC}-\text{Hg}^{4+}$.

Introduction

The pentaquomonocyanochromium(III) cation, $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$, has been produced from the reduction

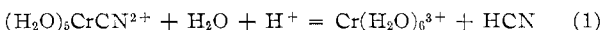
of monocyanocobalt(III) complexes by chromium(II) ion in acidic solutions.^{2,3} The same complex results from the stepwise decomposition of $\text{Cr}(\text{CN})_6^{3-}$ in acidic

(1) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; Contribution No. 2232. Based in part on the Ph.D. thesis of J. P. B., Iowa State University, May 1967.

(2) J. H. Espenson and J. P. Birk, *J. Am. Chem. Soc.*, **87**, 3280 (1965).
(3) J. P. Birk and J. H. Espenson, *ibid.*, **90**, 1153 (1968).

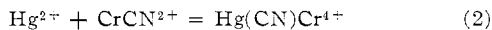
solution^{4,5} and from the partial aquation of $\text{Cr}(\text{CN})_2^+$ and $\text{Cr}(\text{CN})_3$ upon catalysis by chromium(II).⁶

Considerable attention in recent years has been paid to the question of the mechanism of ligand substitution on Cr(III) complexes, especially the rate of aquation of monosubstituted complexes of the general formula $(\text{H}_2\text{O})_5\text{CrX}^{2+}$.⁷⁻¹⁷ One of the reactions whose kinetics we report on in this work is the aquation of CrCN^{2+} (eq 1). Among the questions to be raised is the distribution of protons in the activated complex and the number of parallel and competitive pathways for aquation.



Recent results have shown that a pathway for aquation of monosubstituted Cr(III) complexes involving catalysis by Cr(II)¹⁸⁻²⁰ can operate under some conditions. This reaction, which presumably results from an electron-transfer pathway, has been studied for CrCN^{2+} . This second process did not constitute a major pathway under any circumstances encountered here, but under suitable conditions its contribution to the overall rate was measurable.

The third problem we have considered in this work deals with the aquation reaction in the presence of mercury(II) ion. In perchlorate solution the two cations $\text{Hg}_{\text{aq}}^{2+}$ and $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$ associate so strongly that even at the lowest concentrations studied, equilibrium lay well toward the right (eq 2). The kinetics



of decomposition of CrCN^{2+} was studied in the presence of mercury(II), as a function of $[\text{Hg}^{2+}]$. The question of the structure of the mercury-chromium dinuclear complex was also considered.

Experimental Section

Materials.—Solutions of cyanochromium(III) ion were prepared by both of the reactions cited above. The details of the preparative procedures have appeared in a previous publication.⁶

Lithium and sodium perchlorates were prepared from the carbonates and were recrystallized twice. Mercury(II) perchlorate was prepared as described previously.^{20,21} Laboratory distilled

water was redistilled from alkaline permanganate in a tin-lined Barnstead still.

Rate Measurements.—The extent of aquation was followed spectrophotometrically using a Cary Model 14 instrument. Absorbance measurements were made continuously or intermittently, depending on the rate of the reaction. Reaction solutions, complete but for the complex, were contained in cylindrical quartz spectrophotometer cells. The cells and their contents were brought to temperature by immersion in a constant-temperature bath for at least 30 min. The cell was generally immersed in the constant-temperature bath throughout the run; details of this thermostating arrangement have been published.²²

Some of the experiments at 35–55° were so slow that continuous readings were inconvenient. In some such reactions a quenching procedure was employed. Solutions were made up, excluding CrCN^{2+} , in 100-ml volumetric flasks wrapped in aluminum foil to exclude light. The solution was brought to temperature and CrCN^{2+} was then added. At appropriate intervals aliquots of 7–8 ml were withdrawn using a rapid-draining pipet and delivered into test tubes immersed in a Dry Ice–ethanol bath. The frozen samples were stored at –78°. After the samples were quickly melted and brought to room temperature, the absorbances were measured at an appropriate wavelength. This technique was generally less precise than those described above.

In many aquation studies, the amount of acid added with the CrCN^{2+} solution was known only roughly. The precise value of the hydrogen ion concentration in the run was determined by direct titration of each spent reaction solution with sodium hydroxide. The chromium(III) content was usually sufficiently low to cause no interference with the titration and was also sufficiently low that $[\text{H}^+]$ changed negligibly during the experiment as CN^- was released.

At the higher starting concentrations of CrCN^{2+} ($\geq 0.005 M$) the absorbance change was monitored at its maximum at 5250 Å ($\epsilon_{\text{CrCN}} 25.2 M^{-1} \text{ cm}^{-1}$, $\epsilon_{\text{Cr}^{3+}} 7.3$). Most runs were studied at lower concentrations, and the reaction was followed at shorter wave lengths ($2400 < \lambda < 2100 \text{ Å}$), where CrCN^{2+} absorbs quite intensely ($190 \leq \epsilon \leq 2000$).

Results

Spontaneous Aquation.—The product of aquation of $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$ in perchloric acid solutions was verified as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, as assumed in eq 1, by its visible-uv spectrum. The identity of the product was further verified by its elution characteristics on a column of Dowex 50 W cation-exchange resin. The aquation rate was measured at $\mu = 1.00 M$; in two sets of experiments ionic strength was maintained either with sodium or lithium perchlorate.

At a particular constant hydrogen ion concentration the reaction obeyed a first-order rate law (eq 3). This

$$-d[\text{CrCN}^{2+}]/dt = k_{\text{aq}}[\text{CrCN}^{2+}] \quad (3)$$

relation was verified by linearity of a plot of $\log(D - D_\infty)$ vs. time (D = absorbance) or from linearity of a plot according to the method of Guggenheim.²³ The relation was further verified by lack of variation of k_{aq} values in series of runs with different initial concentrations of the cyano complex. The value of k_{aq} in each run was evaluated by a least-squares treatment using a program²⁴ for the IBM 360 computer.

We presumed that the mechanism consisted of two

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(5) (a) W. B. Schaap, R. Krishnamurthy, D. K. Wakefield, and J. R. Perumareddi, Proceedings of the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, 1966, p 351; (b) D. K. Wakefield and W. B. Schaap, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p 96-L.

(6) J. P. Birk and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2266 (1968).

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(12) J. H. Espenson and D. E. Binau, *ibid.*, **5**, 1365 (1966).

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(18) A. Adin and A. G. Sykes, *J. Chem. Soc. A*, 1518 (1966).

(19) A. Adin, J. Doyle, and A. G. Sykes, *ibid.*, 1504 (1967).

(20) D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, **88**, 3450 (1966); *Inorg. Chem.*, **6**, 2138 (1967).

(21) J. H. Espenson and J. P. Birk, *ibid.*, **4**, 527 (1965).

(22) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

(23) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

(24) We are grateful to Drs. T. W. Newton and R. H. Moore for supplying this program, based on a report from Los Alamos Scientific Laboratory, LA 2367 + addenda.

or more parallel pathways by analogy with other complexes of similar composition. This would correspond to a dependence of k_{aq} upon $[H^+]$ as shown below

$$k_{aq} = \sum_i k_i [H^+]^i \quad (4)$$

Consider first the data obtained in solutions where $NaClO_4$ was added to maintain ionic strength. These solutions covered the range $0.02 \leq [H^+] \leq 1.0 M$ and were carried out at 10° intervals between 35 and 75° . The expected increase in order with respect to $[H^+]$ upon increase in hydrogen ion concentration was noted. This result is depicted in Figure 1 which presents a log-log plot of k_{aq} vs. $[H^+]$. The data are consistent with a rate equation consisting of two numerator terms (eq 5). The data are given in their original form in Table I which lists k_{aq} , $[H^+]$, and T .

$$k_{aq} = k_0 + k_1 [H^+] \quad (NaClO_4; 0.02 \leq [H^+] \leq 1.0 M) \quad (5)$$

Similar experiments were carried out in solutions in which $LiClO_4$ was used to maintain ionic strength. These runs were confined to 45.0 , 55.0 , and 65.0° . The original data are presented in Table II, and appear to be consistent with the same relation (eq 5) as in $NaClO_4$ solution, at $[H^+] \geq 0.02 M$. The values of the rate parameters k_0 and k_1 are changed somewhat, however. Figure 2 depicts a plot of k_{aq} vs. $[H^+]$ in $LiClO_4$ solution, illustrating the agreement of the data to eq 5 at $[H^+] \geq 0.02 M$. The precision of the data made it impossible to detect a small degree of curvature in such plots, although were it possible to obtain such precise data, a more complicated relation might then be demanded.

The runs at 55.0° in $LiClO_4$ solution were extended to very low $[H^+]$, down to $8 \times 10^{-4} M$. Under these conditions the value of k_{aq} increased with decreasing $[H^+]$, as shown in Figure 3. This observation suggests that over this broader range of hydrogen ion concentration an additional term becomes important. The data are consistent with the three-parameter relation given in eq 6. Data at low $[H^+]$ were obtained only at 55.0° . These runs were considered along with all of the runs at 55.0° and were fit to eq 6 using the least-squares computer program.²⁴ The values so computed were: $10^7 k_{-1} = 5.8 \pm 1.1 M \text{ sec}^{-1}$, $10^3 k_0 = 0.972 \pm 0.052 \text{ sec}^{-1}$, and $10^3 k_1 = 7.99 \pm 0.28 M^{-1} \text{ sec}^{-1}$.²⁵ This path was unimportant under the conditions studied at other temperatures and in the $NaClO_4$ media, where no experiments were carried out with $[H^+] \leq 0.01 M$.

The temperature dependence of the rate constants k_0 and k_1 was used to derive the activation parameters for each rate constant. Both independent variables were considered simultaneously, assuming the functional dependence upon $[H^+]$ given by eq 5 for $[H^+] \geq$

(25) The values of k_0 and k_1 computed according to eq 6 using data at only 55.0° can be compared to the results of the computation of a simultaneous fit of $[H^+]$ and temperature. When data at $[H^+] \geq 0.01 M$ and all temperatures were used, we computed that $10^3 k_0 = 1.001 \text{ sec}^{-1}$ and $10^3 k_1 = 7.88 M^{-1} \text{ sec}^{-1}$ at 55.0° and $\mu = 1.00 M$ ($LiClO_4$).

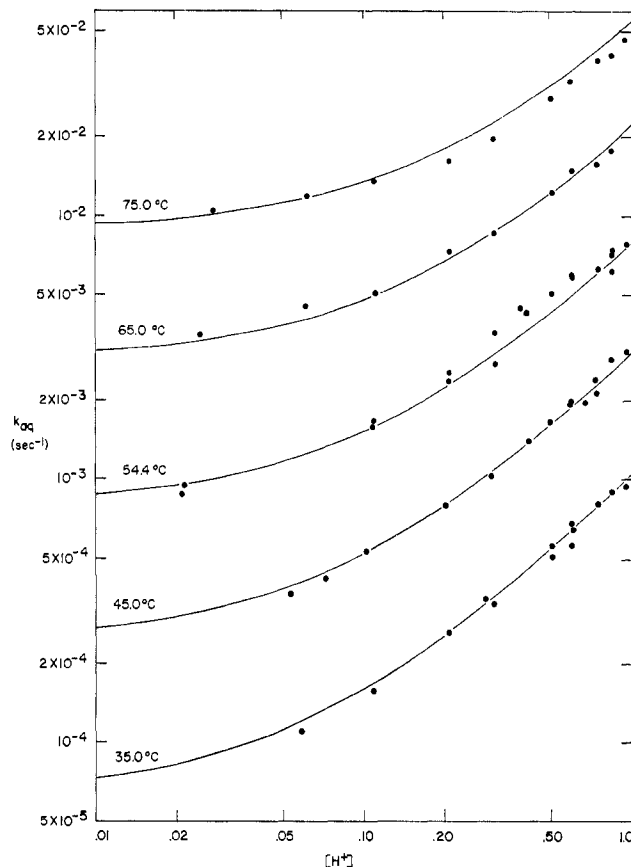


Figure 1.—Plot of k_{aq} vs. $[H^+]$ (each on a logarithmic scale) for the aquation of $CrCN^{2+}$ in sodium perchlorate media with $\mu = 1.00 M$. The lines represent the best fit of the hydrogen ion and temperature dependences.

TABLE I
RATE CONSTANTS ($10^3 k_{aq}$, SEC^{-1}) FOR AQUATION OF
CYANOCHROMIUM(III) ION IN $NaClO_4$
MEDIUM AND AT $\mu = 1.00 M$

$[H^+]$	obsd	calcd	$[H^+]$	obsd	calcd	$[H^+]$	obsd	calcd
0.110	34.2*	0.150	0.601	1.94	1.85	0.857	7.05	6.55
0.210	0.259	0.239	0.602	1.92	1.85	0.969	7.66	7.30
0.310	0.333	0.331	0.750	2.10	2.24	0.025	3.51	3.31
0.510	0.497	0.502	0.750	2.37	2.24	0.0618	4.52	3.96
0.606	0.552	0.593	0.852	2.82	2.51	0.113	5.05	4.88
	35.0*		0.967	3.03	2.82	0.213	7.25	6.66
0.0589	0.107	0.117		54.4*		0.311	8.52	8.41
0.110	0.156	0.165	0.0212	0.880	0.939	0.510	12.1	12.1
0.211	0.264	0.261	0.0216	0.943	0.941	0.607	14.6	13.7
0.289	0.349	0.334	0.110	1.58	1.53	0.757	15.4	16.4
0.508	0.550	0.541	0.111	1.66	1.54	0.857	17.5	18.1
0.607	0.668	0.628	0.211	2.51	2.21	0.970	19.4	20.2
0.611	0.634	0.638	0.212	2.34	2.22		75.0*	
0.759	0.788	0.778	0.311	3.56	2.85	0.0280	10.5	10.1
0.857	0.882	0.871	0.314	2.69	2.90	0.0624	11.8	11.6
0.973	0.912	0.981	0.314	2.95	2.90	0.112	13.4	13.7
	45.0*		0.391	4.42	3.42	0.212	16.2	17.9
0.0539	0.365	0.382	0.411	4.26	3.56	0.311	19.3	22.1
0.0735	0.369	0.435	0.511	5.01	4.27	0.509	27.6	30.6
0.104	0.530	0.517	0.607	5.83	4.87	0.606	32.0	34.7
0.204	0.79	0.784	0.609	5.91	4.88	0.759	38.0	41.2
0.304	1.02	1.05	0.759	6.20	5.89	0.857	39.8	45.4
0.419	1.38	1.36	0.857	7.31	6.55	0.968	45.7	50.1
0.502	1.64	1.58	0.857	6.04	6.55			

$0.02 M$, and upon temperature given by the Eyring relation ($\kappa = 1$). Since the results in solutions containing Na^+ and Li^+ were somewhat different, the two sets of data were considered separately. Values of the activation parameters in each medium are summarized in Table III.

Aquation Catalyzed by Chromium(II).—Cyanochromium(III) aquation was found to be catalyzed by chromium(II), although the effect was not a large one.

TABLE II
RATE CONSTANTS (10^3k , SEC^{-1}) FOR AQUATION OF
CYANOCHROMIUM(III) ION IN LiClO_4
MEDIUM AND AT $\mu = 1.00 M$

$[\text{H}^+]$	obsd	calcd	$[\text{H}^+]$	obsd	calcd	$[\text{H}^+]$	obsd	calcd
0.0503	45.0 ^a		0.00254	1.11	1.22	0.992	7.30	8.82
0.0967	0.429	0.422	0.00435	1.21	1.14	0.996	8.76	8.85
0.204	0.512	0.577	0.00462	1.15	1.14	0.996	8.35	8.85
0.286	0.953	0.939	0.00815	1.13	1.11		65.0 ^a	
0.405	1.50	1.21	0.0101	0.973	1.08	0.0099	3.87	3.84
0.405	1.78	1.61	0.0518	1.48	1.41	0.0491	4.35	4.53
0.595	2.27	2.25	0.0978	1.92	1.77	0.098	5.36	5.39
0.793	2.78	2.91	0.201	2.93	2.59	0.204	6.89	7.24
0.898	3.38	3.27	0.299	3.79	3.36	0.296	9.79	8.86
0.993	3.89	3.59	0.395	4.52	4.12	0.393	11.7	10.6
0.995	3.28	3.60	0.401	4.56	4.16	0.593	13.4	14.1
	55.0 ^a		5.01	4.94	0.794	0.794	16.8	17.6
0.00078	1.91	1.73	0.702	6.69	6.53	0.889	18.9	19.3
0.00097	1.54	1.58	0.799	7.33	7.30	0.992	21.0	21.1
0.00165	1.33	1.34	0.890	8.22	8.02			

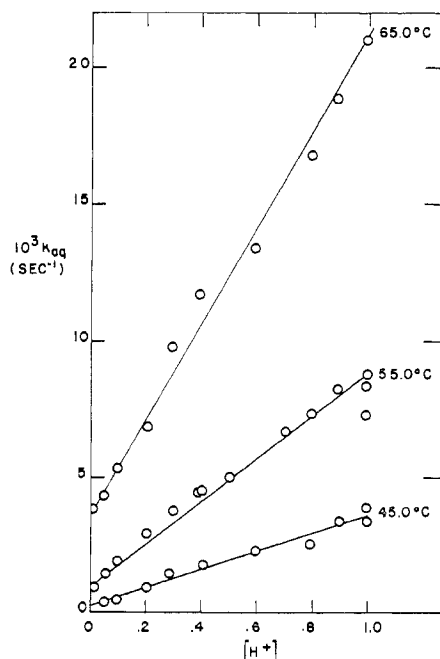


Figure 2.—Plot of k_{aq} vs. $[\text{H}^+]$ for the aquation of CrCN^{2+} in LiClO_4 media with $\mu = 1.00 M$. Only runs with $[\text{H}^+] \geq 0.02 M$ are shown and the lines drawn represent the best fit of the hydrogen ion and temperature dependences.

By analogy with other studies^{18-20,26,27} we assumed on a trial basis that the rate equation would have the form

$$-d[\text{CrCN}^{2+}]/dt = k_{\text{II}}[\text{CrCN}^{2+}][\text{Cr}^{2+}][\text{H}^+]^{-1} \quad (7)$$

Experiments were carried out at 55.0° and $\mu = 1.00 M$, maintained with lithium perchlorate. These runs covered the concentration ranges $0.003 \leq [\text{CrCN}^{2+}]_0 \leq 0.009 M$, $0.017 \leq [\text{Cr}^{2+}] \leq 0.043 M$, and $0.01 \leq [\text{H}^+] \leq 0.048 M$. The results of the rate runs are summarized in Table IV. The value of k_{II} , defined by eq 8, was calculated from the difference of the

$$k_{\text{aq}} = k_{-1}[\text{H}^+]^{-1} + k_0 + k_1[\text{H}^+] + k_{\text{II}}[\text{Cr}^{2+}][\text{H}^+]^{-1} \quad (8)$$

measured rate constant and the spontaneous value computed from the known values of k_{-1} , k_0 , and k_1 under these conditions. The value of k_{II} so obtained was $2.8 \pm 0.3 \times 10^{-3} \text{ sec}^{-1}$ at 55.0° and $\mu = 1.00 M$ (lithium perchlorate). The precision of the measurements was not high, however, and the data that could be obtained were limited partly by the high absorb-

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(27) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

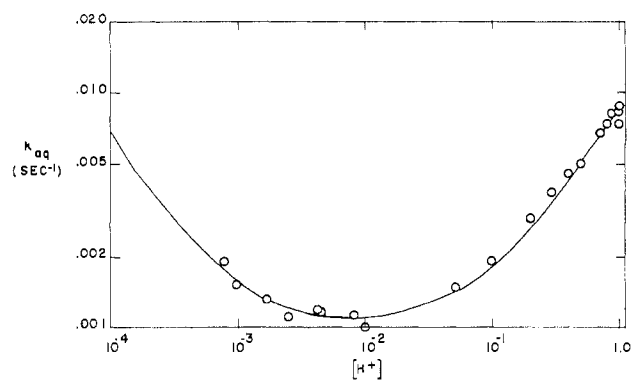


Figure 3.—Logarithmic plot of k_{aq} vs. $[\text{H}^+]$ illustrating the three reaction paths for aquation that become important over a wide range of $[\text{H}^+]$ according to eq 6 (55.0° , LiClO_4 medium with $\mu = 1.00 M$).

TABLE III
ACTIVATION PARAMETERS^a FOR SPONTANEOUS
AQUATION OF CYANOCHROMIUM ION AT $\mu = 1.00 M$

	Supporting electrolyte	
	LiClO_4	NaClO_4
ΔH_0^\ddagger , kcal mole ⁻¹	27.9 ± 1.4	25.6 ± 1.0
ΔS_0^\ddagger , eu	12.7 ± 4.2	5.4 ± 3.1
ΔH_1^\ddagger , kcal mole ⁻¹	17.05 ± 0.73	19.76 ± 0.48
ΔS_1^\ddagger , eu	-16.4 ± 2.2	-8.3 ± 1.5

^a Weighting for the computation of the activation parameters was $1/k^2$.

TABLE IV
RATE CONSTANTS FOR AQUATION OF
CYANOCHROMIUM(III) ION CATALYZED BY CHROMIUM(II) AT 55.0°
AND $\mu = 1.00 M$ (LITHIUM PERCHLORATE)

$[\text{CrCN}^{2+}]_0$, M	$[\text{Cr}^{2+}]$, M	$[\text{H}^+]$, M	$10^3 k_{\text{aq}}$, sec^{-1} , obsd	$10^3 k_{\text{spont}}$, sec^{-1} , calcd ^a	$10^3 k_{\text{II}}$, ^b sec^{-1}
0.00304	0.0168	0.0096	5.93	1.11	2.75
0.00608	0.0168	0.0098	5.23	1.07	2.4
0.00304	0.0168	0.0159	3.06	1.14	(1.8) ^c
0.00304	0.0429	0.0293	5.66	1.23	3.0
0.00304	0.0324	0.0332	3.42	1.26	2.2
0.00914	0.0429	0.0358	5.23	1.28	3.3
0.00608	0.0429	0.0419	4.06	1.32	2.7
0.00304	0.0429	0.0480	4.06	1.37	3.0

^a Calculated from eq 6 using the known values of k_{-1} , k_0 , and k_1 under these conditions. ^b Calculated by the expression $(k_{\text{aq,obsd}} - k_{\text{spont,calcd}})[\text{H}^+]/[\text{Cr}^{2+}]$. ^c Rejected from average; exceeds 3 times the average deviation from the mean.

ance of Cr^{2+} in the uv region, preventing experiments at higher $[\text{Cr}^{2+}]$. The necessity of having a known value of $[\text{H}^+]$ and of maintaining constant $[\text{H}^+]$ in each run prevented our obtaining data at lower $[\text{H}^+]$. The simplest one-parameter expression that accounts for this rate term is given by the last term in eq 11; values of k_{II} so computed revealed no noticeable trend with $[\text{Cr}^{2+}]$ or $[\text{H}^+]$, indicating its probable correctness. At least, it is the only single-parameter term that accounts for the data.

Aquation in the Presence of Mercury(II).—Several lines of evidence were used to establish that aquomercury(II) and pentaquocyanochromium(III) ions associate to a very large extent in perchloric acid solution. The evidence consists of the spectra of such solu-

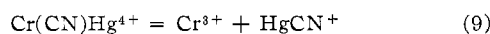
tions, the characteristics of the complex toward elution from a cation-exchange resin, and the kinetics of formation of Cr^{3+} in a solution of CrCN^{2+} to which Hg^{2+} has been added. We propose that the association of the two cations can be represented by the equilibrium given in eq 2.

A series of solutions was prepared, each with $[\text{CrCN}^{2+}] = 0.02 M$, and a varying concentration of Hg^{2+} was added to each. Spectral shifts were observed until $C_{\text{Hg}}/C_{\text{CrCN}}$ was equal to 1.0, but the spectra remained invariant for ratios exceeding unity. The species so formed had an absorption spectrum with maxima at 5650 Å ($\epsilon 17.9 M^{-1} \text{cm}^{-1}$) and 4010 Å ($\epsilon 22.6$), which can be compared with those of CrCN^{2+} , 5250 Å ($\epsilon 25.2$) and 3930 Å ($\epsilon 20.0$), and those of Cr^{3+} , 5740 Å ($\epsilon 13.3$) and 4080 Å ($\epsilon 15.8$).

A lower limit was set on the association stability quotient for this cation-cation complex by the following experiments. A solution was prepared with an equal starting concentration of each material, 0.017 *F* CrCN^{2+} and 0.017 *F* Hg^{2+} . This solution was quantitatively diluted by a series of successively greater factors, with temperature and ionic strength held constant (25°, $\mu = 1.00 M$). The spectrum of the original solution was measured in a cell of optical path 1.00 cm, and the diluted solutions were measured in cells of progressively longer path lengths, so that identical spectra would be obtained had no shift in equilibrium in reaction 2 accompanied the dilution. For solutions as dilute as 0.0033 *F* CrCN^{2+} and 0.0033 *F* Hg^{2+} the spectra remained identical within experimental error. We estimated that, in the least concentrated solution, equilibrium lay $\geq 95\%$ toward the complex; we thus computed that the association quotient $Q_{\text{Hg}} = [\text{Cr}(\text{CN})\text{Hg}^{4+}]/[\text{CrCN}^{2+}][\text{Hg}^{2+}]$ was $\geq 10^5 M^{-1}$.

The complex was readily taken up by Dowex 50 W-X8 cation-exchange resin but was not spread out by 3 *F* perchloric acid. Since the tripositive ion Cr^{3+} was readily eluted from the column by such treatment, a higher net ionic charge was indicated, consistent with the postulated 4+ ion.

The net reaction for aquation in the presence of mercury(II) is given by eq 9, which emphasizes the thermodynamic stability of the monocyano mercury(II) cation even at high concentrations of hydrogen ion.²⁸



The product of the reaction was identified as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ by its absorption spectrum in the reaction solution at the end of a run and by ion-exchange chromatography of the same solution.

The kinetic studies of reaction 9 were carried out in the presence of a large excess of mercury(II). Starting formal concentrations covered the following conditions: 0.001 *F* CrCN^{2+} , 0.013–0.097 *F* Hg^{2+} , 0.04–0.48 *M* H^+ . The reaction was studied at 5250 Å and was found to follow pseudo-first-order kinetics as given by eq 10,

$$+d[\text{Cr}^{3+}]/dt = k_{\text{Hg}}C_{\text{CrCN}} \quad (10)$$

(28) The first association quotient of Hg^{2+} and CN^- is $10^{18} M^{-1}$ at 20° and $\mu = 0.1 M$ (NaNO_3): G. Anderegg, *Helv. Chim. Acta*, **40**, 1022 (1957).

in which C_{CrCN} , the formal concentration of CrCN^{2+} , is essentially $[\text{Cr}(\text{CN})\text{Hg}^{4+}]$ since mercury(II) is in excess. The rate constants were evaluated from the slopes of Guggenheim plots.²³ Values of k_{Hg} are summarized in Table V as a function of $[\text{Hg}^{2+}]$ and of $[\text{H}^+]$. Within experimental error the rate constant k_{Hg} is independent of $[\text{Hg}^{2+}]$ and of $[\text{H}^+]$. The average value at 55.0° and $\mu = 1.00 M$ (LiClO_4) is $k_{\text{Hg}} = (6.6 \pm 0.9) \times 10^{-3} \text{sec}^{-1}$. It should be emphasized that this reaction does not supplement the spontaneous rate (as was the case with Cr^{2+}) but suppresses it. The presence of excess Hg^{2+} lowers the concentration of CrCN^{2+} to a point where the contribution of the spontaneous path is negligible. The calculated values of k_{aq} in Table V are provided for purposes of comparison only: they are not contributing to the rate either as an appreciable part of k_{Hg} or as a supplement to it.

TABLE V

AQUATION OF CYANOCHROMIUM(III) ION^a IN THE PRESENCE OF MERCURY(II) AT 55.0° AND $\mu = 1.00 M$ (LiClO_4), WHERE ClO_4^- IS THE ONLY ANION

$[\text{Hg}^{2+}]$, <i>F</i>	$[\text{H}^+]$, <i>M</i>	$10^3 k_{\text{Hg}}$, ^b sec^{-1} , obsd	$10^3 k_{\text{aq}}$, ^c sec^{-1} , calcd for no Hg^{2+}
0.0126	0.040	6.9	1.31
0.0252	0.041	7.7	1.31
0.0504	0.042	8.7	1.32
0.0504	0.122	7.4	1.94
0.0504	0.242	4.8	2.91
0.0504	0.482	5.7, 5.9	4.82
0.0967	0.043	6.3	1.33

^a $[\text{CrCN}^{2+}]_0 = 0.001 F$. ^b Defined by eq 10. ^c Calculated from the known rate parameters according to eq 6. This column represents what the rate constant would be were no $\text{Hg}(\text{II})$ present.

Interpretation and Discussion

Spontaneous Aquation.—The dependence of the rate of aquation of cyanochromium(III) ion upon $[\text{H}^+]$ requires three rate terms to describe the variation of k_{aq} over the range $8 \times 10^{-4} \leq [\text{H}^+] \leq 1.0 M$. We shall assume that each such term constitutes evidence for a reaction pathway, although this interpretation is unambiguous only if medium effects are not important. On such a basis the reaction mechanism is comprised of three parallel and independent pathways each of which involves a different number of protons.

In a purely formal way the transition states along the presumed pathways have the compositions $\{(\text{H}_2\text{O})_n\text{CrCN}(\text{OH})_{m-2-m}\}^\ddagger$ with $m = -1, 0$, and $+1$. The chief difficulty with this interpretation is the assumption embodied in it that activity coefficients remain constant with varying hydrogen ion concentration provided ionic strength is held constant. Our data in NaClO_4 and LiClO_4 clearly disprove such an assumption. The values we obtained for the observed pseudo-first-order rate constant were not the same, at given values of $[\text{H}^+]$ and temperature, but depended on whether Li^+ or Na^+ was used to maintain unit ionic

strength. Similar variations have been observed in earlier work.^{12,29,30}

Measurements³¹ of activity coefficients of HCl in mixed electrolyte solutions HCl-MCl of constant ionic strength established that Li⁺ was the cation least likely to cause a violation of the "constant ionic strength" principle. Were such variations important in HClO₄-LiClO₄ solutions, a correction of the form suggested by Harned's rule³² could be applied.²⁹ The observed rate of aquation at [H⁺] ≥ 0.02 M would then take the form

$$k_{\text{aq}} = k_0 + k_1[\text{H}^+] = k_0 + k_1^0[\text{H}^+]e^{\beta[\text{H}^+]} \quad (11)$$

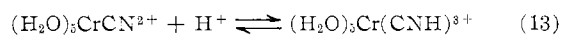
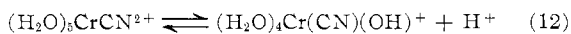
Such electrolyte effects are generally very difficult to distinguish from reaction pathways. The precision of our data did not justify inclusion of a third parameter. The extent to which the Li⁺ and Na⁺ solutions differ undoubtedly reflects the importance of effects such as these. Whatever the contribution of such effects, the conclusion we reach on the basis of presently available data is that these effects are likely to be much less in Li⁺ solution.

The three reaction rate terms will provisionally be interpreted as reaction pathways. The importance of each pathway under a specified set of conditions will be reflected by the relative magnitude of the corresponding rate term only to the extent such medium effects have been properly held constant by constant ionic strength. Since the Li⁺ data represent the best reaction medium, it is useful to note how changes in [H⁺] affect the rate contributions. The summary in Table VI lists the contribution of each rate term at 55.0°.

TABLE VI

[H ⁺], M	% contribution		
	{(H ₂ O) ₄ Cr(CN)(OH) ⁺ }≠	{(H ₂ O) ₅ Cr(CN) ²⁺ }≠	{(H ₂ O) ₅ Cr(CNH ³⁺) ³⁺ }≠
0.001	37.2	62.3	0.5
0.010	5.2	87.6	7.2
0.10	0.3	54.7	45.0
1.00	0.06	10.8	89.2

The mechanism can be represented as the aquation of the species (H₂O)₄Cr(CN)(OH)⁺, (H₂O)₅Cr(CN)²⁺, and (H₂O)₅Cr(CNH³⁺)³⁺ in which labile protolytic equilibria convert the second species to the first and last. Let the equilibrium quotients for reactions 12 and 13 be



represented as Q_a and Q_H , respectively. The over-all rate equation takes the form of (14) in the general case where the equilibrium quotients may have arbitrary values

$$\frac{d[\text{Cr}^{3+}]}{dt} = \frac{C_{\text{CrCN}}}{Q_a[\text{H}^+]^{-1} + 1 + Q_H[\text{H}^+]} \times \{k_{\text{OH}}Q_a[\text{H}^+]^{-1} + k_0 + k_HQ_H[\text{H}^+]\} \quad (14)$$

(29) (a) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963); (b) *Inorg. Chem.*, **4**, 1166 (1965).

(30) (a) G. Gordon and P. H. Tewari, *J. Phys. Chem.*, **70**, 200 (1966); (b) D. H. Huchital and H. Taube, *J. Am. Chem. Soc.*, **87**, 5371 (1965).

(31) H. S. Harned, *ibid.*, **48**, 326 (1926).

(32) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. Ltd., London, 1955, Chapter 15.

where the rate constants k_{OH} , k_0 , and k_H represent the true first-order rate constants of the three species in question. Under the limiting behavior where the species (H₂O)₅CrCN²⁺ predominates over the entire range of [H⁺] under consideration (*i.e.*, $8 \times 10^{-4} \leq [\text{H}^+] \leq 1.0 M$), this equation simplifies to eq 15 and

$$\frac{d[\text{Cr}^{3+}]}{dt} = C_{\text{CrCN}}\{k_{\text{OH}}Q_a/[\text{H}^+] + k_0 + k_HQ_H[\text{H}^+]\} \quad (15)$$

agrees with the experimental rate law, eq 11, with $k_{-1} = k_{\text{OH}}Q_a$ and $k_1 = k_HQ_H$.

The aquation of cyanochromium(III) ion has also been studied by Wakefield and Schaap,^{5b} who worked at [H⁺] ≥ 0.1 M and $\mu = 2.00 M$ maintained with sodium perchlorate. Their data were interpreted in terms of an additional equilibrium parameter, Q_H (eq 13). One interpretation of the different results is that our approximation $1 \gg Q_H[\text{H}^+]$ may not be valid at the higher ionic strength.³³ Alternatively, the third parameter may reflect contributions from a medium effect²⁹⁻³² that have been interpreted in terms of a genuine kinetic rate term. The data of Wakefield and Schaap^{5b} were obtained in solutions of relatively high ionic strength in which sodium and not lithium perchlorate was used as the supporting electrolyte. Were a Harned-type correction term³² introduced, it seems likely this alternative would be as suitable as invoking a value for Q_H that appears unreasonably high considering the known association constants of anionic cyanide complexes and hydrogen ion.^{34,35}

It is possible to make some meaningful comparisons of the two sets of kinetic results. The data of Wakefield and Schaap extrapolate to $k_0 = 4.0 \pm 0.4 \times 10^{-5} \text{ sec}^{-1}$ (35.0°, $\mu = 2.0 M$, NaClO₄) which can be compared with our results $k_0 = 5.3 \times 10^{-5} \text{ sec}^{-1}$ (35.0°, $\mu = 1.00 M$, NaClO₄) and $k_0 = 6.2 \times 10^{-5} \text{ sec}^{-1}$ (35.0° extrapolated from higher temperatures, $\mu = 1.00 M$, LiClO₄). The medium effects on k_0 are expected to be quite small (corresponding values of 10^4k_1 are 18.9, 9.8, and 13.5 M⁻¹ sec⁻¹), since but one ionic species appears in the rate expression. The values of k_0 appear to agree as well as one can hope within the limit of this assumption.

The assumption that two labile equilibria (eq 12 and 13) are involved is not an essential feature of our mechanism. For example, the rate term $k_1[\text{CrCN}^{2+}][\text{H}^+]$ could equally well be described as the rate-determining attack of a proton on the complex, a concerted process involving proton attack and complex dissociation, or the dissociation of the protonated species CrCNH³⁺. One notes that only with basic ligands (*e.g.*, azide,¹³ fluoride,⁵ hypophosphite,¹² sulfate,¹⁵ and cyanide) does one obtain a term first order in [H⁺]. The most

(33) Note that an increase in Q_H is expected with increasing μ considering the charge types of the ions involved. They give $Q_H = 0.25 M^{-1}$ at 35.0° and $\mu = 2.00 M$ (NaClO₄).^{5b} If a lower value, $Q_H \sim 0.1 M^{-1}$, held under our conditions, this would amount at most to a 10% deviation from eq 6 at the highest hydrogen ion concentration. Curvature in plots of k_{aq} vs. [H⁺] (Figure 2) was not observed, however. We have used a two-parameter relation (eq 6) rather than a three-parameter relation. At the relatively high values of [H⁺] employed by Wakefield and Schaap,^{5b} the contribution of the inverse [H⁺] term would be negligible.

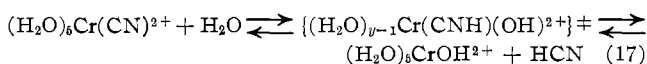
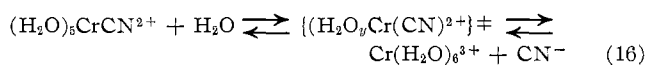
(34) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 955 (1935).

(35) J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).

reasonable interpretation of such a term is that it is energetically profitable to add a proton to the anion position in the transition state because the anion can then be released in the free acid form. The conclusion that the transition state $\{(\text{H}_2\text{O})_2\text{CrX}^{3+}\}^\ddagger$ decomposes to $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and HX introduces a complication for cyanide ion that does not exist for the other ions: the immediate stabilization of cyanide ion would probably be through the isomeric acid HNC .

The precision of our kinetic data would not permit detection of *ca.* 5% of a species CrCNH^{3+} and/or CrNCH^{3+} . The earlier studies on the isocyano complex showed³ that the isocyano complex is appreciably protonated and suggested⁶ further that $\leq 6\%$ of the isocyano complex exists in equilibrium with CrCN^{2+} . (The limitations⁶ inherent in that evaluation allowed us to place only an upper limit on its stability.) In view of the existence of Cr-NC-Hg^{4+} , the involvement of small amounts of a protonated species is reasonable, and it appears likely that the more stable of the protonated species is CrNCH^{3+} and not CrCNH^{3+} .

A duality of interpretation is possible for the rate term $k_0[\text{CrCN}^{2+}]$. The question arises concerning which of the alternative elementary reactions (eq 16 and 17) best represents the reaction mechanism. Both

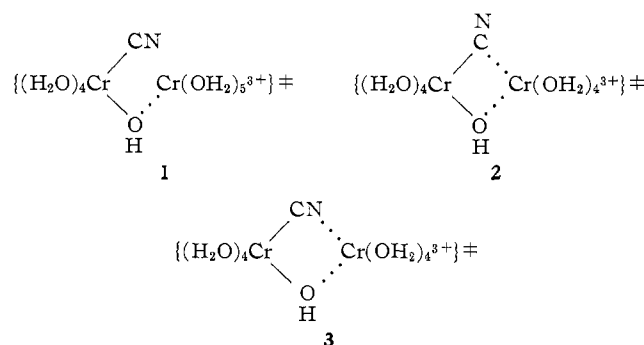


possibilities exist because the acid-base equilibria for chromium(III) and cyanide are labile. An approach to this question was suggested by Swaddle and King,^{8,13} applied to the fluoride and azide complexes, and later extended more generally to polyatomic anions by Swaddle.¹⁴ Following this approach the value of ΔS_0^\ddagger would be expected to be a linear function of the molar entropy of the anion X^- if the free anion were involved as in eq 16. The line was fixed by monatomic anions that are not appreciably basic (Cl^- , Br^- , I^-) and later extended to polyatomic, nonbasic anions (NO_3^- , $-\text{NCS}^-$). A correction was made for the rotational entropy that is present in the free ion but not in the complex. By this procedure the basic anions—both monatomic (F^-) and polyatomic (N_3^-)—were found to have abnormally positive values of ΔS^\ddagger .

According to this correlation, were eq 16 the correct representation, ΔS_0^\ddagger would be expected to be *ca.* -5 eu once the value of the molar entropy³⁶ of cyanide ion, 28.2 eu, is corrected for the rotational entropy of cyanide ion ($S_{\text{rot}} = 11.2$ eu). As in the case of CrF^{2+} and CrN_3^{2+} , the value of ΔS_0^\ddagger for CrCN^{2+} is abnormally high, suggesting that the transition state incorporates the arrangement of protons shown in eq 17.

Chromium(II)-Catalyzed Aquation.—The form of the rate equation for aquation of CrCN^{2+} catalyzed by Cr^{2+} is largely if not entirely consistent with a transition state of composition $\{\text{Cr}(\text{CN})(\text{OH})\text{Cr}^{3+}\}^\ddagger$. This tran-

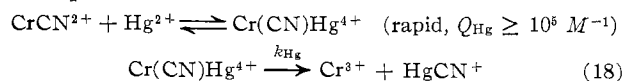
sition state has the same composition as that for the cyanide-exchange reaction of the same compounds.⁶ The products of the two reactions are different, however, and the transition states are isomeric and non-identical. The structures to be considered are given below. Structure 1 is the proposed singly bridged configuration postulated for the aquation process. Structure 2 is the proposed transition state for cyanide



exchange, although it is not the only such alternative. Structure 3 cannot be the transition state for cyanide exchange since the linkage isomerization reaction does not involve a transition state of this composition.^{3,6} Structures 2 and 3 involve cyanide bridging, and thus neither constitutes a pathway for net aquation; a transition state bridged by OH^- appears most probable. The rate constants corresponding to structures 1 and 2 suggest that the latter is more stable by ~ 2 kcal mole⁻¹.

Sykes and coworkers¹⁹ have obtained values for a number of related reactions. If we assume ΔH^\ddagger for the rate constant k_{II} in eq 8 is ~ 21 kcal mole⁻¹, its value at 25°, $\sim 1 \times 10^{-4}$ sec⁻¹, can be interpreted in terms of the nonbridging-ligand effect in this reaction on the following basis. The trends noted¹⁹ suggest that the strong-field cyanide ion, if *trans* to the bridging OH^- in structure 1, would lead to a much lower rate than observed. One should note that with CN^- and OH^- *cis* to one another, the rate would presumably be dictated by the *trans*- H_2O ; the value noted is consistent with the value¹⁹ for H_2O . We conclude that some details of the configuration of structure 1 can be established by this indirect and admittedly tenuous procedure.

Mechanism of Aquation in the Presence of $\text{Hg}(\text{II})$.—The rate law describing the formation of Cr^{3+} from the cation complex was independent of mercury(III). The sequence of reactions



leads to the rate expression

$$\frac{d[\text{Cr}^{3+}]}{dt} = \frac{k_{\text{Hg}} Q_{\text{Hg}} [\text{Hg}^{2+}] C_{\text{CrCN}}}{1 + Q_{\text{Hg}} [\text{Hg}^{2+}]} \quad (19)$$

with $C_{\text{CrCN}} = [\text{CrCN}^{2+}] + [\text{Cr}(\text{CN})\text{Hg}^{4+}]$. Under all the conditions studied here $1 \ll Q_{\text{Hg}}[\text{Hg}^{2+}]$ and $[\text{CrCN}^{2+}] \ll [\text{Cr}(\text{CN})\text{Hg}^{4+}]$, so that the final expression simplifies to

$$d[\text{Cr}^{3+}]/dt = k_{\text{Hg}} C_{\text{CrCN}}$$

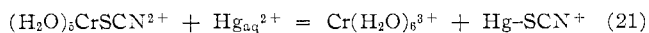
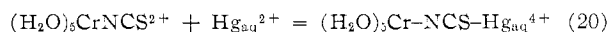
(36) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., p 129.

It is interesting to note that even though the transition state associated with the postulated mechanism has the composition $\{\text{Cr}(\text{CN})\text{Hg}^{4+}\}^\ddagger$, the rate was found to be independent of $[\text{Hg}^{2+}]$. This situation arises because the laboratory rate expression is based on variations for formal concentrations rather than concentrations of predominant species. In the present situation $C_{\text{CrCN}} \cong [\text{Cr}(\text{CN})\text{Hg}^{4+}]$ so that the rate expression, eq 10, when written in terms of the predominant species, does correctly reflect the composition of the transition state.

This system can be contrasted to the Hg^{2+} "catalysis" of the aquation of CrCl_2^{2+} ,²¹ where the rate varied as the first power of $[\text{Hg}^{2+}]$. In that case no evidence was obtained for a cation association complex.

Structure of the Cation-Cation Complex.—The association of two cations as in eq 2 is a very unusual type of reaction, especially an association as stable as the one encountered here. Chromium(III) and neptunyl(VI) ions are known to associate in a rather weak but kinetically stable complex.³⁷ Mercury(II) is known to form rather stable complexes with $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$,³⁸ and the ion CrNCSHg^{4+} is formed in the reaction of $(\text{H}_2\text{O})_5\text{CrNCS}^{2+}$ with Hg^{2+} .³⁹ Other M-thiocyanate and M-azide association reactions with Hg^{2+} have been reported.^{40,41}

The reaction of CrNCS^{2+} and Hg^{2+} (eq 20) stands in contrast to that occurring between CrSCN^{2+} and Hg^{2+} (eq 21). Since mercury(II), a soft acid, will co-



(37) J. C. Sullivan, *J. Am. Chem. Soc.*, **84**, 4256 (1962); *Inorg. Chem.*, **3**, 315 (1964).

(38) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

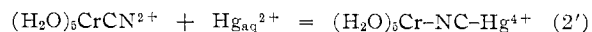
(39) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 343 (1966).

(40) W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *ibid.*, **81**, 2958 (1959).

(41) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5**, 1376 (1966).

ordinate to the softer base site of an ambidentate ligand, the high stability of the cyano dinuclear species is surprising. A species of the structure $(\text{H}_2\text{O})_5\text{Cr-CN-Hg}_{\text{aq}}^{4+}$ would seem to stand little chance of being a stable one, as nitrogen donors generally do not provide especially stable complexes with mercury(II).

We propose that a structural change accompanies formation of the dinuclear complex, as represented by



The proposed internal isomerization of cyanide finds support in the spectral shifts accompanying this reaction [$\lambda_{\text{max}}(\text{CrCN}^{2+})$ 5250 Å, $\lambda_{\text{max}}(\text{Cr-NC-Hg}^{4+})$ 5650 Å], considering that the nitrogen end of cyanide has a smaller ligand field strength than the carbon end.⁴² The spectra of the "supercomplexes" (between $(\text{NH}_3)_5\text{Co-CN}^{2+}$ and Hg^{2+}) found by Siebert³⁸ suggest that a similar rearrangement to form $(\text{NH}_3)_5\text{Co-NC-Hg}^{4+}$ has taken place [$\lambda_{\text{max}}(\text{Co}(\text{NH}_3)_5\text{CN}^{2+})$ 4400 Å, $\lambda_{\text{max}}(\text{Hg}^{2+}$ adduct) 4480 Å]. Support for the postulated internal isomerization comes from our observation⁴³ that the same species, Cr-NC-Hg^{4+} , arises from the reaction of mercury(II) with the isocyano complex, $(\text{H}_2\text{O})_5\text{CrNC}^{2+}$, the latter prepared from the reaction of $(\text{NH}_3)_5\text{CoCN}^{2+}$ with chromium(II).³

A precedent for the proposed linkage isomerization accompanying dinuclear complex formation in eq 2' can be cited. The main products of the reaction of $(\text{H}_2\text{O})\text{Cr-SCN}^{2+}$ and Hg^{2+} were Cr^{3+} and HgSCN^{4+} (eq 21), but an appreciable yield of $(\text{H}_2\text{O})_5\text{Cr-NCS-Hg}^{4+}$ was also formed,⁴⁴ contrary to the original report.³⁹ Further work to verify the proposed structure of Cr-NC-Hg^{4+} is in progress.

(42) D. F. Shriver, S. A. Shriver, and S. A. Anderson, *ibid.*, **4**, 725 (1965).

(43) J. P. Birk and J. H. Espenson, unpublished experiments.

(44) M. Orhanovic and N. Sutin, *J. Am. Chem. Soc.*, **90**, 538 (1968).

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High-Pressure Synthesis of Pyrite-Type Nickel Diphosphide and Nickel Diarsenide

By P. C. DONOHUE, T. A. BITHER, AND H. S. YOUNG

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Synthesis of diphosphide and diarsenide phases of Fe, Co, Ni, Cu, and Pd has been investigated in a high-pressure tetrahedral anvil press at 65 kbars (1100–1400°). Pyrite-type NiP_2 and NiAs_2 compounds with low, nearly temperature-independent resistivity and weak Pauli paramagnetism were formed. The phosphides and arsenides of Fe, Co, Cu, and Pd occurred as the known low-pressure forms. The occurrence of the pyrite structure in the Ni dipnictides and its absence in the others may be explained in terms of stability derived from the electronic configuration of the cation and the high density of the structure.

Introduction

Pyrite-type compounds may be prepared by high-pressure techniques.^{1,2} This discovery has led to a study of the diphosphides and diarsenides of the transition metals Fe, Co, Ni, Cu, and Pd at high

pressure for the purpose of forming new pyrite-type compounds. Except for Co, all of these metals are known to form diphosphides, and their crystal struc-

(1) T. A. Bither, C. T. Prewitt, J. L. Gillson, P. E. Bierstedt, R. B. Flippen, and H. S. Young, *Solid State Commun.*, **4**, 533 (1966).

(2) R. A. Munson, *Inorg. Chem.*, **5**, 1296 (1966).