crystal lattice destroyed the center of inversion. Such an explanation is not reasonable since not nearly so large an energy shift with change of halide would be expected for internal d transitions (less than 2-kK shift between successive halides is observed for internal d transitions of isoelectronic $PtX_4{}^{2-}$).[17] Thus all of the transitions of Table III appear to be electron-transfer transitions as also concluded by Jørgensen.[17]

It should be noted that the weak shoulders in the spectra of $AuCl_4{}^-$ and $AuBr_4{}^-$ in solution are not due to complexes other than $AuX_4{}^-$. The absorption spectra are the same in various solvents except for very small energy shifts. Addition of excess Cl^- (up to saturated $(C_2H_5)_4NCl$) to an acetonitrile solution of $(C_2H_5)_4NAuCl_4$ causes no change in absorption spectrum. Harris and Reece[23] found that addition of Br^- to a nitromethane solution of $AuBr_4{}^-$ markedly lowers its absorption in the visible region and attributed this to formation of $AuBr_6{}^{3-}$. A similar effect was observed by this author except that the reported[23] shift in the rather broad

(23) C. M. Harris and I. H. Reece, *Nature*, **182**, 1665 (1958).

absorption peak from 394 to 379 mμ was not observed. The nitromethane cutoff occurs in this region and any reference mismatch may cause an apparent shift in a broad peak. When the experiment is done in acetonitrile, the spectrum can be measured to lower wavelength. In freshly prepared $(C_4H_9)_4NBr$-saturated solution the 394-mμ peak is reduced to less than 10% of its value in the absence of excess Br^-, and a strong band develops at 273 mμ. This band has exactly the same position and shape as $Br_3{}^-$ in this solvent, and the molar extinction coefficient is that of $Br_3{}^-$ assuming 1 mol of $Br_3{}^-$ produced per mole of $AuBr_4{}^-$ disappearing. This 273-mμ peak decays slowly with time as does that of $Br_3{}^-$ due to slow reaction with the solvent. The conclusion is that Au(III) is reduced in such solutions in qualitative agreement with results obtained in aqueous solutions,[24,25] and there is no evidence for gold(III) halide complexes beyond $AuX_4{}^-$.

(24) B. I. Peschevitski, V. P. Kazakov, and A. M. Erenburg, *Russ. J. Inorg. Chem.*, **8**, 437 (1963).

(25) V. P. Kazakov and M. V. Konovalova, *ibid.*, **13**, 231 (1968).

Study of the Pentacyanonitrosylchromate Ion. III. Aquation

By D. I. BUSTIN, J. E. EARLEY, and A. A. VLČEK

Aquation of $Cr(CN)_5NO^{3-}$ in mildly acidic solutions yields $Cr(CN)_2(H_2O)_3NO$ which is inert to further aquation. In solutions of pH less than 2, further loss of CN^- occurs. The Cr–NO grouping remains intact until loss of CN^- is complete. The slow step in the initial aquation is the loss of the first CN^-. This step is first order in substrate with a rate constant $k = k'K[H^+]/(1 + K[H^+])$, where K is 9×10^2 M^{-1} and k' is 7×10^{-3} sec^{-1} at 17.5° in 1 M NaCl. For k', $\Delta H^{\ddagger}$ is 19 kcal/mol.

Several studies of the pentacyanonitrosylchromate ion, $Cr(CN)_5NO^{3-}$, have led to the conclusion that this ion may be considered to contain Cr(I).[1] Although the ion is stable in basic or neutral solutions, it undergoes aquation in acidic solution. The ultimate products of this process are familiar Cr(III) species. We have studied the kinetics of the multistep aquation and the nature of intermediates in order to observe the chemical properties of the Cr–NO grouping.

Experimental Section

Reagents and Instruments.—$K_3Cr(CN)_5NO$ was prepared by reduction of K_2CrO_4 by NH_2OH in the presence of KCN[1] and recrystallized three times from water. $NaClO_4$ was prepared by neutralization of $HClO_4$, water was triply distilled from quartz, and other reagents were reagent grade used without further purification.

Spectrophotometric measurements were made using a Cary 14 spectrophotometer and 1- and 5-cm cells. A Sargent XV polarograph and a V-301-Zbrojovka, Brno, polarograph (sensitivity of galvanometer used 3.33×10^{-10} A/mm m) were used for

(1) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 872 (1959).

polarographic studies. The capillary employed had a drop time of 3.4 sec and flow rate of 2.05 mg/sec (in short circuit with sce and 64-cm Hg column). A modified Kalousek polarographic cell was used for measurements. No maximum suppressor was used. Ionic strength for polarographic measurements was generally maintained at 1 M. Potentials were measured and are reported *vs.* the sce.

A Metrohm E-336A potentiograph and Sargent combination electrode were used for pH titrations. A Sargent pH stat with combination electrode was used for kinetic measurements.

Results

Kinetics of Primary Aquation.—Solutions of $Cr(CN)_5NO^{3-}$, containing NaCl as inert electrolyte, were allowed to undergo aquation at various temperatures and at hydrogen ion concentrations controlled by the pH stat. In the course of aquation, 3.00 ± 0.05 hydrogen ions were absorbed per ion. Below pH 2.0 a slower, further absorption of hydrogen ions occurred. Figure 1 shows a logarithmic plot of a typical run. There is definite deviation from linearity at the beginning of the reaction. Similar deviations during the first third of the reaction were present in all runs.

The most probable cause of the curvature shown in Figure 1 is a reaction proceeding in several steps of comparable rates. As will be shown below, aquation proceeds with retention of the Cr–NO bond so that a series of steps like equation 1 is required.
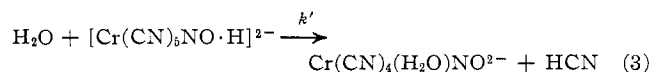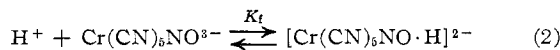
$$Cr(CN)_5NO^{3-} + H_3O^+ \xrightarrow{k_1} Cr(CN)_4(H_2O)NO^{2-} + HCN \quad (1)$$
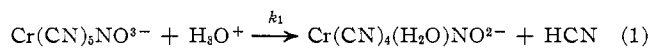
We have used the graphical method of Powell[2] to analyze the data of several runs such as the one shown in Figure 1. The best fit was obtained for the sequence

$$A + H^+ \xrightarrow{k_1} B \qquad B + 2H^+ \xrightarrow{k_2} C$$

where $k_2/k_1 = 2$. The precision of this method is such that we estimate that k_2/k_1 is between 1.8 and 3. The rate of the reaction is therefore primarily limited by the first step, the second and third being faster. The data do not warrant separate definition of the two rate constants for these faster processes. The value of k_1 calculated from the Powell plot corresponded, within 8%, to the limiting slope of the long-time portion of the log curves (*e.g.*, Figure 1). Values of this slope (denoted k) were evaluated for all runs.

Table I shows the variation of k with pH. These data suggest a prior protonation shown by[3]

$$H^+ + Cr(CN)_5NO^{3-} \underset{}{\overset{K_f}{\rightleftarrows}} [Cr(CN)_5NO \cdot H]^{2-} \quad (2)$$

$$H_2O + [Cr(CN)_5NO \cdot H]^{2-} \xrightarrow{k'}$$
$$Cr(CN)_4(H_2O)NO^{2-} + HCN \quad (3)$$

These data are consistent with the rate law

$$k = \frac{k'K_f[H^+]}{1 + K_f[H^+]}$$

where K_f is $(9 \pm 1) \times 10^2 \ M^{-1}$ and k' is $(7 \pm 1) \times 10^{-3}$ sec^{-1} at 17.5°.

TABLE I

VARIATION OF RATE WITH ACIDITY AT 17.5° IN 1 *M* NaCl[a]

pH	10^4k, sec^{-1}	pH	10^4k, sec^{-1}
1.91	62	2.60	48
2.00	58[b]	3.00	33[b]
2.08	62	3.10	29
2.20	60[b]	3.30	21
2.40	55	3.50	15
		4.00	6.5

[a] $[Cr(CN)_5NO^{3-}] = 5–10$ m*M*. [b] Average of two—one in NaCl, one in NaBr.

Table II gives the variation of k with temperature at pH 2 (where $k \approx k'$) and at pH 3.5 (where $k \approx k'K \cdot [H^+]$). The enthalpy of activation corresponding to k'(pH 2) is 19 kcal/mol. The apparent enthalpy of activation at pH 3.5 is 22 kcal/mol, so that reaction 2 appears to be slightly endothermic.

Table III gives the variation of rate with concentration of NaCl at pH 3.00. This effect may be attributed to a change in K_f. Runs in 1 *M* solutions of KBr, KCl, and NaClO$_4$ gave essentially the same results as those in 1 *M* NaCl.

(2) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, p 169.

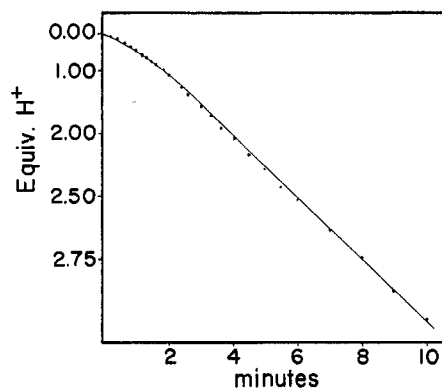(3) The data do not exclude the possibility of a slow irreversible protonation.

Figure 1.—Logarithmic linearization of a typical run at 17.5° and pH 2.3 in 1 *M* NaCl; $[Cr(CN)_5NO^{3-}] = 1.83 \times 10^{-3} \ M$.
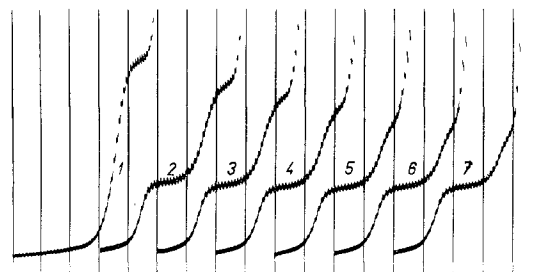

Figure 2.—Time dependence of change of the polarograms of $K_3Cr(CN)_5NO$ and H^+; 213 mV/unit, beginning -0.852 V; sensitivity 1:7; height of Hg head 64 cm; reference electrode sce; temperature 0°; $[Cr(CN)_5NO^{3-}] = 2.43 \times 10^{-4} \ M$: (1) H^+ wave only in 1 *M* NaCl, (2) 30 sec, (3) 210 sec, (4) 390 sec, (5) 580 sec, (6) 685 sec, (7) 930 sec—after addition of $K_3Cr(CN)_5NO$.

TABLE II

VARIATION OF RATE WITH ACIDITY AND TEMPERATURE IN 1 *M* NaCl[a]

pH	Temp, °C	10^4k, sec^{-1}
2.00	17.5	56
2.00	24.0	132
2.00	33.5	340
2.00	43.0	960
3.50	17.5	11
3.50	24.2	32
3.50	33.5	89
3.50	43.0	270

[a] $[Cr(CN)_5NO^{3-}] = 5–10$ m*M*.

Experiments designed to detect the existence of a species such as $HCr(CN)_5NO^{2-}$ by rapid pH titration were unsuccessful since the speed of aquation prevented the measurement of a valid titration curve.

Figure 2 shows a polarographic measurement of the rate of the primary aquation in unbuffered solution. A solution equimolar in H^+ and $Cr(CN)_5NO^{3-}$ gives a polarogram like Figure 2-2. Comparison of polaro-

TABLE III

VARIATION OF RATE WITH NaCl CONCENTRATION[a]

μ, *M*	10^4k, sec^{-1}	μ, *M*	10^4k, sec^{-1}
0.1	50	2.0	27
0.5	42	4.0	12

[a] Conditions: 17.5°, pH 3.00, $[Cr(CN)_5NO^{3-}] = 5–10$ m*M*.
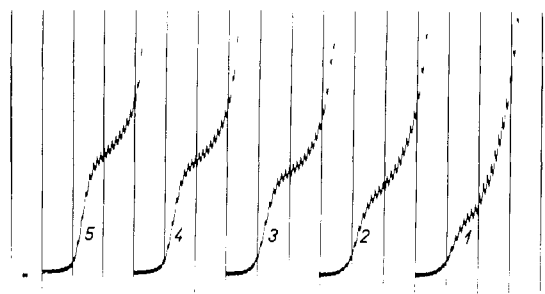
Inorganic Chemistry

Figure 3.—Time dependence of the wave of $K_3Cr(CN)_5NO$ in buffered solutions; 213 mV/unit, beginning -0.95 V; sensitivity 1:70; height of Hg head 64 cm; reference electrode sce; temperature $0°$; pH 1.35; $[K_3Cr(CN)_5NO] = 1.67 \times 10^{-3}$ M: (1) 30 sec, (2) 10 min, (3) 20 min, (4) 30 min, (5) 40 min—after mixing.
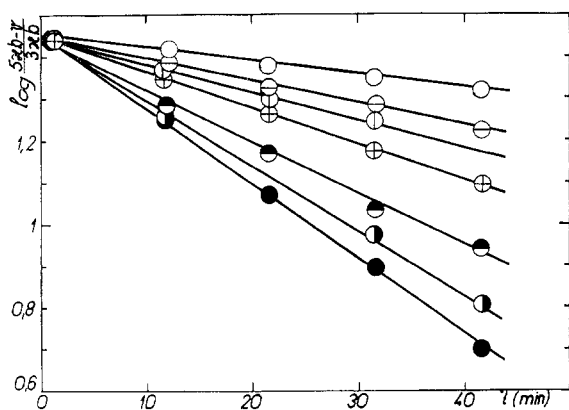

Figure 4.—Logarithmic linearization of time changes of $Cr(CN)_5NO^{3-}$; temperature $0°$: O, pH 1.94; ⊖, pH 1.75; ⊙, pH 1.72; ⊕, pH 1.49; ◓, pH 1.35; ◑, pH 1.23; ●, pH 1.20.

grams 2-1 and 2-2 shows that the wave of H^+ is influenced by $Cr(CN)_5NO^{3-}$ even at zero time. $Cr(CN)_5$-NO^{4-}, the electrode reduction product of $Cr(CN)_5$-NO^{3-}, reacts with and inactivates H^+ in the diffusion layer.[4] As the aquation proceeds, the second wave decreases but the first wave remains quite constant. The decrease of the height of the second wave with time may be used to compute a rough second-order rate constant for the aquation using the stoichiometry measured by the pH stat. The resulting value, converted to a pseudo-first-order constant, is consistent with the data in Table II. The agreement indicates that both methods are measuring the same reaction. The polarographic method would be expected to be relatively less precise than the titrimetric method.

Identification of the Product of Primary Aquation

After completion of the primary aquation, aliquots were removed from the pH stat and made alkaline. Since free CN^- gives rise to an analytically usable anodic polarographic wave due to dissolution of Hg, but CN^- bound to Cr does not, it was possible to determine polarographically that 3 equiv of CN^- was liberated per chromium. The chromium species in the acidic product solution was not absorbed on either Dowex 50-X8 cation-exchange resin (Na^+ form) or

(4) D. I. Bustin and A. A. Vlček, *Collection Czech. Chem. Commun.*, in press.

Dowex 1-X4 resin (Cl^- form). In experiments in which CN^- was removed from the acidic product solution by passing N_2 through the solution, no reduction wave could be observed when the solution had been made basic. If CN^- was not removed before the solution was made basic, a drawn-out cathodic wave near -1.4 V was observed. After the latter solutions had been allowed to stand for several days, the reversible cathode wave at -1.18 V corresponding to $Cr(CN)_5$-NO^{3-} was observed. Addition of excess CN^- caused further, but never complete, regeneration of $Cr(CN)_5$-NO^{3-}. Although a small concentration of $Cr(CN)_6^{3-}$ would have been readily detectable polarographically, none was found even with excess CN^- present.

The results presented above indicate that three CN^- ions, but not the NO group, are lost in the primary aquation and that the product has a zero charge. These observations are consistent with the assignment of $Cr(CN)_2(H_2O)_3NO$ as the major product of the primary aquation.

Further Aquation in Acid Solution

As mentioned previously, a slower further reaction occurs in more acidic solutions. Figure 3 shows a polarographic study of this reaction. Loss of three cyanides per chromium was finished before the second curve of Figure 3 was recorded. The original wave corresponds to a two-electron reduction. As the further aquation proceeds, the current at the plateau increases, approaching that expected for a five-electron reduction.[4] Designating $Cr(CN)_2(H_2O)_3NO$ as D and its concentration as d and the product of the further reaction as F and its concentration as f we may express the current i at the plateau as $i = 2d\varkappa + 5f\varkappa$, where $\varkappa$ is $0.627FD^{1/2}m^{2/3}t_1^{1/2}$ from the Ilkovic equation. Assuming that D and F have the same diffusion coefficient and that the conversion of D to F is a first-order process with rate constant k_4

$$\log \frac{5\varkappa d - 1}{3\varkappa d} = \frac{k_4 t}{2.3} \qquad (4)$$

Figure 4 shows the linear dependence of the left side of eq 4 on time. As shown in Figure 5, $k_4 = k'_4[H^+]$ where k'_4 is 10^{-2} M^{-1} sec^{-1}. The $[H^+]$ dependence suggests that at least one CN^- is lost in the further aquation. Polarographic analysis of product solutions for free CN^- tentatively indicates that both CN^- ions are released. On standing for several weeks, the acidic product solutions eventually are found to contain mostly $Cr(H_2O)_6^{3+}$.

Discussion

In mildly acidic solution aquation of $Cr(CN)_5NO^{3-}$ leads to production of $Cr(CN)_2(H_2O)_3NO$ which is resistant to further aquation. In solutions of pH less than 2, a further reaction producing a second intermediate species, probably $Cr(H_2O)_5NO^+$, takes place. Eventually $Cr(H_2O)_6^{3+}$ is formed, but the Cr-NO grouping remains intact until loss of CN^- is complete.

The aquation of $Cr(CN)_5NO^{3-}$ may be compared with the corresponding reaction of $Cr(CN)_6^{3-}$. The

presence of NO increases the basicity of the ion and increases the rate of loss of CN^-, but the uncharged intermediate has relatively high stability in both systems.[5]

Table IV[6] compares the spectrum of the product of

TABLE IV
POSITIONS (mµ) AND INTENSITIES OF
ABSORPTION BANDS OF Cr–NO SPECIES[a]

Species	λ	ε	λ	ε	λ	ε	λ	ε
$Cr(CN)_5NO^{3-}$	724	14.5	447	127	335	86		
$Cr(CN)_2(H_2O)_3NO$	630	23.6	453	103	358	293	285	247
$Cr(H_2O)_5NO^{2+}$	567	30.6	447	131	390	96	324	101
$Cr(NH_3)_5NO^{2+}$			457	101	348	69	302	157
$Cr(C_2H_5OH)_2NO^{2+}$	570	18	457	61	325	150		

[a] With the exception of $Cr(CN)_2(H_2O)_3NO$, these numbers are taken from ref 6.

the primary aquation, $Cr(CN)_2(H_2O)_3NO$, with ions containing the Cr–NO grouping. It is interesting that each of these species has a band near 450 mµ. The Cr–NO group dominates the MO splitting pattern for one of these species.[7] It seems reasonable to assign the band at 450 mµ to an internal $(d_{xz,yz} \rightarrow *_\pi NO)$ transition of the Cr–NO grouping.

Our present observation of the kinetic inertia of the Cr–NO grouping supplements the previous conclusion[8] that the Cr–NO grouping functions as an electrochemical unit.

After this paper was submitted, an esr study of the aquation of $Cr(CN)_5NO^{3-}$ appeared.[9] The esr study
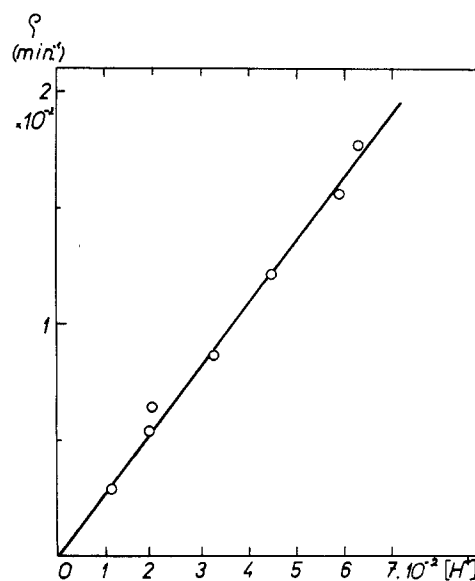

Figure 5.—Dependence of slope of the lines shown in Figure 4 on hydrogen ion concentration.

gives more precise data on the subsequent aquation, but no kinetics on the primary aquation. Our data indicate that the solution resulting from adding an equivalent amount of acid to a solution of $Cr(CN)_5NO^{3-}$ should contain aquated species. This consideration may modify the discussion of some of the esr spectra.

(5) W. B. Schaap and R. Krisnamurthy, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, p 36-O.
(6) W. P. Griffith, *J. Chem. Soc.*, 3286 (1963).
(7) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966).
(8) D. I. Bustin and A. A. Vlček, *Collection Czech. Chem. Commun.*, **32**, 1665 (1967) (paper II in this series).

(9) J. Burgess, B. A. Goodman, and J. B. Raynor, *J. Chem. Soc., A*, 501 (1968).

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Interaction of N,N-Bis(trifluoromethyl)hydroxylamine with Amines

BY GERALD G. FLASKERUD AND JEAN'NE M. SHREEVE

N,N-Bis(trifluoromethyl)hydroxylamine is a very weak acid with a dissociation constant of 1.5×10^{-9} in aqueous solution. It interacts with a variety of simple organic amines to form a series of weakly associated adducts which are liquids or low-melting, sublimable, crystalline solids at room temperature. These adducts are partially dissociated to the parent molecules in the gas phase. Proton nmr spectra, elemental analyses, and mole fraction plots indicate that 1:1 adducts are formed with ammonia, methylamine, dimethylamine, ethylamine, and triethylamine. Trimethylamine and diethylamine form adducts composed of 2 mol of $(CF_3)_2NOH$ per mole of amine.

N,N-Bis(trifluoromethyl)hydroxylamine, $(CF_3)_2N-OH$,[1] is a useful reagent for introducing the N,N-bis(trifluoromethyl)nitroxide group into molecules which contain labile halogens. Also, $(CF_3)_2NOH$ has been found to form an adduct with cesium or potassium fluoride which has been used to prepare a large number

of molecules containing the $(CF_3)_2NO$ moiety.[2-4] It also has been found to react with NaOH in tetrahydrofuran forming the sodium salt, $(CF_3)_2NONa$, which

(1) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1741 (1957).

(2) D. P. Babb and J. M. Shreeve, *Inorg. Chem.*, **6**, 351 (1967).
(3) L. L. Nash, J. J. Conville, D. P. Babb, and J. M. Shreeve, *J. Inorg. Nucl. Chem.*, **30**, 3373 (1968).
(4) J. A. Lott, D. P. Babb, K. E. Pullen, and J. M. Shreeve, *Inorg. Chem.*, **7**, 2593 (1968).