

H, 4.2. $\nu_{\text{P-H}}$ 2110 cm^{-1} (lit.¹⁷ 2112 cm^{-1}). The ^{19}F nmr spectrum in methylene chloride solution was a 1:1:1:1 quartet ($J = 1.5$ cps) centered at +162 ppm.

$[\text{PtH}(\text{Ph}_3\text{P})_3][\text{BF}_4]$ (0.5 g) in 10 ml of tetrahydrofuran was heated with C_2F_4 (0.5 g) at 90° for 48 hr. The solid slowly dissolved giving a clear yellow solution. After removal of excess C_2F_4 , the THF was evaporated and the residues extracted with small volumes of methanol; 0.1 g (yield 26%) of $[\text{Pt}(\text{Ph}_3\text{P})_2(\text{C}_2\text{F}_4)]$ remained as a white powder which was recrystallized from acetone, mp $208\text{--}209^\circ$ dec (lit.¹⁹ $218\text{--}220^\circ$ dec). *Anal.* Calcd for $\text{C}_{38}\text{H}_{30}\text{F}_4\text{P}_2\text{Pt}$: C, 55.7; H, 3.7. Found: C, 55.7, H, 3.5. The ^{19}F nmr spectrum in methylene chloride solution consisted of a complex resonance

centered at +130 ppm (lit.¹⁹ +131.1 ppm). The infrared spectrum was identical with that of a sample prepared by the method of Green, *et al.*¹⁹

Evaporation of the methanol extract gave 0.35 g of yellow oil which was mainly $[\text{PtH}(\text{Ph}_3\text{P})_3][\text{BF}_4]$. Further separation of products could not be achieved by solubility or chromatographic methods.

When the reaction was repeated with heating for 2 weeks at 90° , the yield was 39%. A third reaction heated at 120° for 48 hr gave a 34% yield, and some $\text{C}_2\text{F}_3\text{H}$ was detected in the excess C_2F_4 . The methanol extract in this last case probably contained other products although some $[\text{PtH}(\text{Ph}_3\text{P})_3][\text{BF}_4]$ was present. Separation of these products was not achieved.

Mechanisms of the Inner-Sphere Electron-Exchange Reactions of Chromium(II) and Aquocyno Complexes of Chromium(III)¹

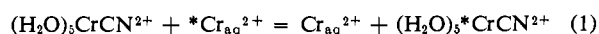
James P. Birk and James H. Espenson

Contribution from the Department of Chemistry and the Institute for Atomic Research, Iowa State University, Ames, Iowa 50010. Received August 28, 1967

Abstract: The kinetics of electron exchange between $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$ was studied in aqueous perchlorate solution. The exchange rate is first order in each chromium species; the second-order rate constant so defined obeys the relation $k_{\text{ex}} = k_1 + k_2/[\text{H}^+]$. The exchange rate was studied at temperatures between 5 and 35° to derive activation parameters. The reactions of Cr^{2+} with *cis*- $(\text{H}_2\text{O})_4\text{Cr}(\text{CN})_2^+$ and 1,2,3- $(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_3$ both produced quantitative yields of $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$. The kinetics of each reaction was studied as a function of $[\text{Cr}^{2+}]$ and $[\text{H}^+]$. Minor spectral discrepancies at some wavelengths indicated the possible presence of a metastable reaction intermediate, but the main reaction of chromium(II) with the cyano complexes followed a mixed second-order rate law, independent of $[\text{H}^+]$. The rate constants are: $\text{Cr}(\text{CN})_2^+$ 4.19 and $\text{Cr}(\text{CN})_3$ 4.56 $\text{M}^{-1}\text{sec}^{-1}$ at 25.0° and unit ionic strength. The mechanisms of the cyanide-bridged exchange reactions are discussed. The principle of microscopic reversibility was applied in considering the possible role of the isocyno complex CrNC^{2+} as an unstable intermediate in the exchange reaction. A comparison is made of the exchange mechanism and linkage isomerization mechanism of cyanide and thiocyanate complexes.

Several studies have been made of Cr(II)–Cr(III) electron-exchange reactions in which ligand X^- in the Cr(III) complex $(\text{H}_2\text{O})_5\text{CrX}^{2+}$ serves as a bridging ligand in an inner-sphere mechanism.^{2–7} The electron-transfer reaction occurring between cyanocobalt(III) complexes and chromium(II)⁸ afforded solutions of the previously unknown^{9,10} monocyanochromium(III) ion, $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$. The role of cyanide ion as a bridging ligand in inner-sphere electron-transfer reactions has been investigated in only a few instances, and it appeared of interest to study the kinetics and mechanism of the

Cr(II)–Cr(III) exchange reaction involving CrCN^{2+} (eq 1).



The cyano complex is the stable C-bonded form, yet it is possible that the electron-exchange reaction occurs *via* the isocyno species, CrNC^{2+} , since CN^- is unsymmetrical and ambidentate. This complex is known⁸ to be a metastable intermediate in the reaction of $\text{L}_5\text{CoCN}^{2+}$ and Cr^{2+} . Since CrNC^{2+} reacts fairly rapidly with chromium(II), it could not exist at high concentrations. It has been possible to apply the principle of microscopic reversibility to two reactions we have studied, the exchange of Cr^{2+} and CrCN^{2+} and the reaction, catalyzed linkage isomerization, of Cr^{2+} and CrNC^{2+} . Consideration of reverse reactions has allowed us to examine the possible role of CrNC^{2+} as an unstable intermediate in the exchange reaction. In addition, the same considerations allow us to learn of the inherent stability of the two bonding modes for cyanide ion by placing a limit on the equilibrium quotient for the transformation $\text{CrNC}^{2+} = \text{CrCN}^{2+}$. Similar studies of exchange³ and isomerization¹¹ have been reported for the thiocyanatochromium(III) complexes, and useful comparisons of mechanism in the two cases can be made.

(11) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).

(1) (a) This work was performed in the Ames Laboratory (Contribution No. 2158) under the auspices of the U. S. Atomic Energy Commission. (b) Based on the Ph.D. thesis of J. P. B., Iowa State University, May 1967.

(2) H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (1954).

(3) D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

(4) R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964).

(5) A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

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

(7) K. A. Schroeder and J. H. Espenson, *J. Am. Chem. Soc.*, **89**, 2548 (1967).

(8) (a) J. P. Birk and J. H. Espenson, *ibid.*, **87**, 3280 (1965); (b) *ibid.*, **90**, 1153 (1968).

(9) Since our original preparation of CrCN^{2+} ,⁹ Schaap and Krishnamurthy¹⁰ have reported preparing the complex from partial aquation of $\text{Cr}(\text{CN})_6^{3-}$.

(10) R. Krishnamurthy and W. B. Schaap, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 36-O.

Experimental Section

Materials. Solutions of monocyanochromium(III) ion were prepared by two methods. In the first procedure excess Cr^{2+} was allowed to react with $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ or $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$.⁸ The excess Cr^{2+} was oxidized to $\text{Cr}_2(\text{OH})_2^{4+}$ by reaction with air, and the complex was placed on a column of Dowex 50 W-X8, 50–100 mesh. The resin was in the Na^+ form and was contained in a jacketed column kept at 0–2° by circulation of ice water. Separation from other species, including Co^{2+} , was accomplished by slow elution with ice-cold 0.99 *F* NaClO_4 –0.01 *F* HClO_4 . The yield of CrCN^{2+} was generally quantitative in the reaction, but only ~40% of the CrCN^{2+} was recovered free of contamination by Co^{2+} . Stock solutions of CrCN^{2+} were frozen and stored at –78°.

The second procedure was based on the stepwise aquation of chromicyanide ion according to procedures devised by Schaap and Krishnamurthy.¹⁰ Solutions of $\text{K}_3\text{Cr}(\text{CN})_6$ were converted to $\text{Cr}(\text{CN})_3$ by allowing them to aquate for 1–2 hr in the presence of ~5 moles of perchloric acid after filtration of the precipitated KClO_4 . The solution was flushed with purified nitrogen, and a small amount of Cr^{2+} was then added. The Cr^{2+} in the sample was oxidized by air after several minutes, and the complex was purified by the ion-exchange procedure outlined above. The second procedure afforded CrCN^{2+} in the best yield and at the highest concentrations.

The identity of CrCN^{2+} was established by analyses for the chromium and cyanide content of a particular sample, by the net charge on the complex, and by the absorption spectrum. Solutions of CrCN^{2+} were analyzed for chromium content by oxidation with peroxide in alkaline solution and measurement of the chromate absorption at 372 nm.¹² Cyanide was analyzed by distilling into NaOH solution the HCN liberated upon heating an acidic solution of CrCN^{2+} . Cyanide so produced was titrated with silver nitrate to a silver iodide end point. The ratio CN^-/Cr found for one preparation was 0.998 ± 0.003 . The complex was readily eluted from cation exchange resin by 1 *F* solutions of HClO_4 or NaClO_4 . The ion-exchange behavior of the complex was typical of other dipositive $\text{Cr}(\text{III})$ complexes of the general formula $(\text{H}_2\text{O})_3\text{CrX}^{2+}$, indicating the cyano complex has a 2+ ionic charge. The absorption spectrum for CrCN^{2+} has maxima at λ 525 nm (ϵ 25.2 $M^{-1} \text{cm}^{-1}$) and 393 (20.0). The position of the low-energy maximum lies toward shorter wavelengths than values for other similar $\text{Cr}(\text{III})$ complexes.¹³ The spectrum is consistent with the known position of CN^- in the spectrochemical and ligand-field series. The absorption spectrum of CrCN^{2+} agrees quite closely with that obtained independently by Krishnamurthy, *et al.*¹⁴

Perchlorate solutions of 1,2,3-triaquotricyanochromium(III) $[(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_3]$ and of *cis*-tetraaquodicyanochromium(III) cation $[(\text{H}_2\text{O})_4\text{Cr}(\text{CN})_2]^+$ were prepared by the procedures of Krishnamurthy and Schaap¹⁰ based on the stepwise acid-catalyzed aquation of hexacyanochromate(III) ion. A fresh solution of $\text{K}_3\text{Cr}(\text{CN})_6$ was mixed with 3 moles of perchloric acid and allowed to stand 1–2 hr. The resulting solution (generally 0.01–0.15 *F* $\text{Cr}(\text{III})$) contained mostly $\text{Cr}(\text{CN})_3$, along with small amounts of other complexes. Precipitated KClO_4 was removed by filtration and the solution was passed through cation-exchange resin (Dowex 50 W-X8, Li^+ form) and then anion-exchange resin (Dowex 1-X8, ClO_4^- form). The resulting solution of $\text{Cr}(\text{CN})_3$, 0.01–0.04 *M*, was flushed with N_2 . The chromium content was analyzed as chromate ion¹² and the Li^+ content by ion-exchange titration. Solutions of *cis*- $\text{Cr}(\text{CN})_2^+$ were prepared using similar procedures but 4 moles of perchloric acid and somewhat longer aquation times. The last remnants of $\text{Cr}(\text{CN})_3$ were rinsed from the cation resin with water, and $\text{Cr}(\text{CN})_2^+$ was eluted with 0.2 *F* lithium perchlorate. The concentrations of $\text{Cr}(\text{CN})_2^+$ so obtained were typically 5×10^{-3} *M*.

Solutions containing these materials were frozen and stored (for periods up to 2 weeks) at –78° without apparent decomposition. The spectra of these complexes were in excellent agreement with published values.¹⁴

The preparation and purification of the other reagents used in these studies were described in the preceding paper.⁸

Exchange Experiments. Exchange reactions of $^*\text{Cr}^{2+}$ with CrCN^{2+} were initiated by the addition of $^*\text{Cr}^{2+}$ solution to a nitro-

gen-flushed solution containing all other reagents and previously brought to constant temperature. The solution was contained in a 150-ml milk dilution bottle capped with a self-sealing Buna-N rubber disk. These reactions were followed typically for 30 min but in some cases for as long as 160 min. Since repeated puncturing of the rubber disk to withdraw samples could cause oxygen leakage, a further precaution was taken. The neck of the bottle was inserted into a large, one-hole rubber stopper, and a glass cylinder was placed over the stopper. The glass cylinder was sealed off except for a nitrogen inlet tube in the side and a small hole, in the top, through which a syringe needle was inserted for withdrawing samples. Aliquots of 1–5 ml, depending on the $^*\text{Cr}^{2+}$ concentration, were withdrawn at appropriate times and quenched by delivery into a small beaker through which a stream of air was bubbled, converting Cr^{2+} to $\text{Cr}_2(\text{OH})_2^{4+}$.¹⁵ The volume of the aliquot quenched was not critical since the specific activity of $\text{Cr}_2(\text{OH})_2^{4+}$ was measured.

The separation of $\text{Cr}_2(\text{OH})_2^{4+}$ from CrCN^{2+} and the determination of the specific activity of $\text{Cr}_2(\text{OH})_2^{4+}$ were carried out as described previously.⁸

Kinetics Experiments. The reactions of Cr^{2+} with $\text{Cr}(\text{CN})_2^+$ and $\text{Cr}(\text{CN})_3$ were studied by conventional spectrophotometric techniques, under nitrogen, in thermostated spectrophotometer cells. This technique was described in detail in the preceding paper.⁸

Results

Kinetics of Exchange of Cr^{2+} and CrCN^{2+} . The rate of an exchange reaction in which no chemical change occurs is given by the McKay equation.¹⁶ In terms of the specific activity of Cr^{2+} , a_t , the relation is given by

$$-d \ln \left[\frac{a_t - a_\infty}{a_0 - a_\infty} \right] = R \frac{[\text{Cr}^{2+}] + [\text{CrCN}^{2+}]}{[\text{Cr}^{2+}][\text{CrCN}^{2+}]} dt \quad (2)$$

eq 2. The rate of the electron exchange reaction R is evaluated from the slope of the logarithmic plot suggested by eq 2. The kinetic data we obtained were in excellent agreement with the McKay equation in all experiments. A nonlinear least-squares computer program was used to fit the specific data to eq 2. This program calculated the value of R , or of $t_{1/2}$, and also the standard deviation of the experimental points from the least-squares line.

The functional dependence of R upon $[\text{Cr}^{2+}]$, $[\text{CrCN}^{2+}]$, and other possible variables was obtained by studying the effect upon R of each of these variables. A typical set of experiments under the conditions of 15.0°, $[\text{H}^+] = 0.0500$ *M*, and unit ionic strength are presented in Table I. These runs cover a range of *ca.*

Table I. Rate Constants for Exchange of Cr^{2+} and CrCN^{2+} ^a

$[\text{CrCN}^{2+}]$, <i>M</i>	$[\text{Cr}^{2+}]$, ^b <i>M</i>	$10^{-2}t_{1/2}$, ^c sec	k_{ex} , ^d $M^{-1} \text{sec}^{-1}$
0.00452	0.0104	11.1 ± 1.4	0.042 ± 0.005
0.00674	0.0152	4.27 ± 0.24	0.074 ± 0.004
0.00689	0.0192	2.88 ± 1.13	0.092 ± 0.036
0.00765	0.0183	3.77 ± 0.39	0.071 ± 0.007
0.00815	0.0135	4.69 ± 0.38	0.068 ± 0.005
0.0104	0.0177	3.90 ± 1.05	0.063 ± 0.017
0.0115	0.0171	4.22 ± 0.70	0.058 ± 0.009
0.0163	0.0166	3.38 ± 0.23	0.062 ± 0.004
0.0265	0.0171	2.90 ± 0.15	0.055 ± 0.003
			$\text{Av}^e k_{\text{ex}} = 0.062 \pm 0.008$

^a Conditions: 15.00°, 0.0500 *M* H^+ , $I = 1.00$ *M*. Ionic strength maintained by addition of lithium perchlorate. ^b $[\text{Cr}^{2+}]$ based on analyses during the runs. ^c Uncertainties in $t_{1/2}$ and k_{ex} represent standard deviations in the least-squares fit of data to the McKay equation. ^d Defined by eq 4. ^e Weighted average, with weight = 1/standard deviation.

(12) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(13) For the $\text{Cr}(\text{III})$ complexes $(\text{H}_2\text{O})_3\text{CrX}$, the long-wavelength λ_{max} is as follows: I^- 650 nm, Br^- 622, Cl^- 609, F^- 595, N_3^- 585, OH^- 574, NCS^- 570, and NH_3 545.

(14) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).

(15) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

(16) H. A. McKay, *Nature*, **142**, 997 (1938).

Table II. Second-Order Rate Constants for Exchange of Cr^{2+} and CrCN^{2+} as a Function of $[\text{H}^+]$ and Temperature^a

$[\text{H}^+], M$	$k_{\text{ex}}, M^{-1} \text{sec}^{-1}{}^b$			
	5.0°	15.0°	25.0°	35.0°
0.0115		0.127 ± 0.005		
0.0157		0.126 ± 0.006		
0.0200	0.0361 ± 0.0020 ^c	0.107 ± 0.008	0.262 ± 0.027	0.453 ± 0.036
0.0500	0.0287 ± 0.0006 ^d	0.062 ± 0.008	0.193 ± 0.018	0.323 ± 0.016
0.100	0.0221 ± 0.0014		0.115 ± 0.010	0.207 ± 0.012
0.200	0.0208 ± 0.0015	0.0607 ± 0.012	0.113 ± 0.006	0.164 ± 0.012 ^e
0.349		0.0560 ± 0.010 ^f	0.081 ± 0.027	

^a The original data are given in ref 1b. ^b The uncertainty given is the standard deviation obtained from the least-squares fit of the data to the McKay equation. ^c 0.0224 $M \text{H}^+$. ^d 0.0487 $M \text{H}^+$. ^e 0.212 $M \text{H}^+$. ^f Excludes one run ($k_{\text{ex}} = 0.072 \pm 0.003$) out of three.

sixfold in $[\text{CrCN}^{2+}]$ and *ca.* twofold in $[\text{Cr}^{2+}]$. The measured half-life for exchange, which has a standard deviation typically about 10%, is tabulated. The rate law for exchange is a simple second-order expression at constant $[\text{H}^+]$ (eq 3). The value of the exchange rate constant k_{ex} is then calculated from the expression given in eq 4. The constancy of k_{ex} within the rather sizable

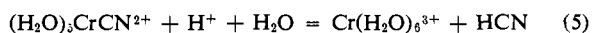
$$R = k_{\text{ex}}[\text{Cr}^{2+}][\text{CrCN}^{2+}] \quad (3)$$

$$k_{\text{ex}} = \frac{\ln 2}{t_{1/2}([\text{CrCN}^{2+}] + [\text{Cr}^{2+}])} \quad (4)$$

experimental uncertainty indicates the correctness of the assumed second-order rate expression. Considering the experiments performed at other hydrogen ion concentrations at 15.0° the concentration of CrCN^{2+} was varied by a factor of 6 and that of Cr^{2+} by a factor of 5 (0.005–0.025 M). At each particular $[\text{H}^+]$ studied, the value of k_{ex} calculated according to eq 4 was constant within experimental error.

Although lithium perchlorate was added to solutions in exchange experiments to maintain constant ionic strength, sodium perchlorate (0–0.9 M , usually <0.3 M) was also present since it was in the stock solution of CrCN^{2+} . The experiments at 15° and 0.05 $M \text{H}^+$ represented the following variations: $0 \leq [\text{Li}^+] \leq 0.80$ and $0 \leq [\text{Na}^+] \leq 0.91 M$. Since the activity coefficient of H^+ is probably more constant in solutions of LiClO_4 than in solutions of NaClO_4 ,¹⁷ and since there was considerable scatter of data at constant $[\text{H}^+]$, values of k_{ex} at 15° and 0.05 $M \text{H}^+$ were treated according to Harned's rule $k_{\text{ex}} = k_0 \exp(\alpha[\text{M}^+])$ to determine whether the exchange rate constant depended on $[\text{Li}^+]$ or $[\text{Na}^+]$. When M^+ was Li^+ , $\alpha = -0.017 \pm 0.25 M^{-1}$, and when M^+ was Na^+ , $\alpha = 0.034 \pm 0.22 M^{-1}$, indicating that such medium effects were not important.¹⁸ Had it been possible to obtain substantially greater precision in values of k_{ex} , an effect might have been noted.

Hydrogen Ion and Temperature Dependences. Exchange experiments were carried out at several hydrogen ion concentrations in the range 0.012–0.35 M at 5–35°. The upper limit of $[\text{H}^+]$ was set by the competing aquation of cyanochromium(III) ion (eq 5), the rate of which increases with $[\text{H}^+]$.¹⁹ As a consequence



of this reaction, exchange experiments were confined to the region $[\text{H}^+] < 0.35 M$.

(17) H. S. Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

(18) J. H. Espenson and D. E. Binau, *Inorg. Chem.*, **5**, 1365 (1966), and references cited therein.

(19) J. P. Birk and J. H. Espenson, to be published.

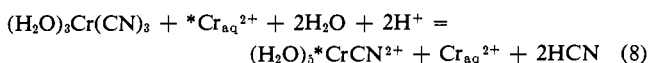
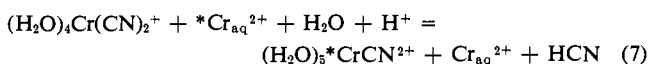
Unlike the results found for most other $\text{Cr(II)}-\text{Cr(III)}$ exchange reactions, the value of k_{ex} exhibited a dependence upon $[\text{H}^+]$. Table II summarizes the values of k_{ex} as a function of $[\text{H}^+]$ and temperature. Plots of $\log k_{\text{ex}}$ vs. $\log [\text{H}^+]$ were not consistent with a single rate term involving an integral power of $[\text{H}^+]$. The slopes of such plots represent the apparent order of the reaction with respect to $[\text{H}^+]$ at that particular $[\text{H}^+]$ and suggested a rate equation consisting of two numerator terms (eq 6). The linearity of plots of k_{ex} vs. $1/[\text{H}^+]$ con-

$$k_{\text{ex}} = k_1 + k_2/[\text{H}^+] \quad (6)$$

firmed the functional dependence in eq 6 and allowed evaluation of k_1 and k_2 . The values are summarized as follows at the four temperatures: $k_1 (M^{-1} \text{sec}^{-1}) = 0.020 \pm 0.001, 0.053 \pm 0.003, 0.077 \pm 0.004,$ and 0.135 ± 0.019 ; $10^3 k_2 (\text{sec}^{-1}) = 0.40 \pm 0.05, 0.89 \pm 0.10, 4.2 \pm 0.2,$ and 7.0 ± 1.0 .

The rate constants were plotted as $\ln(k/T)$ vs. $1/T$; the activation enthalpies are $\Delta H_1^\ddagger = 9.3 \pm 1.1$ and $\Delta H_2^\ddagger = 17.2 \pm 2.8 \text{ kcal mole}^{-1}$. The computed values of ΔS^\ddagger ($\kappa = 1$) are -32 ± 3 and $-8 \pm 8 \text{ eu}$, respectively.

Reactions of Chromium(II) with Dicyano and Tricyano Complexes of Chromium(III). Electron-transfer reactions of two other cyanide complexes were also studied but in considerably less detail than was the simple exchange reaction of the monocyano complex. The complexes studied were *cis*-(H_2O)₄ $\text{Cr}(\text{CN})_2^+$ and 1,2,3-(H_2O)₃ $\text{Cr}(\text{CN})_3$. Both complexes had *cis* configurations of cyanide and were prepared by the stepwise decomposition of chromicyanide ion as described above. Treatment of either of the complexes with catalytic amounts of chromium(II) resulted in formation of quantitative yields of (H_2O)₅ CrCN^{2+} . These reactions are presumably analogous to Cr(II) -catalyzed



aquations of other Cr(III) complexes, notably CrCl_2^{2+} ²⁰ and CrF_2^{2+} ,²¹ and the chromium labeling shown in the equations written here was presumed, but not verified by a tracer study. One might infer from these seemingly simple stoichiometric results that the kinetics would be relatively straightforward. This is not the case, and the details of the reaction kinetics have not been completely resolved. The reactions were studied at 25.0°, with 1.00 M ionic strength maintained by

(20) J. H. Espenson and S. G. Slocum, *Inorg. Chem.*, **6**, 906 (1967).

(21) Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 160 (1959).

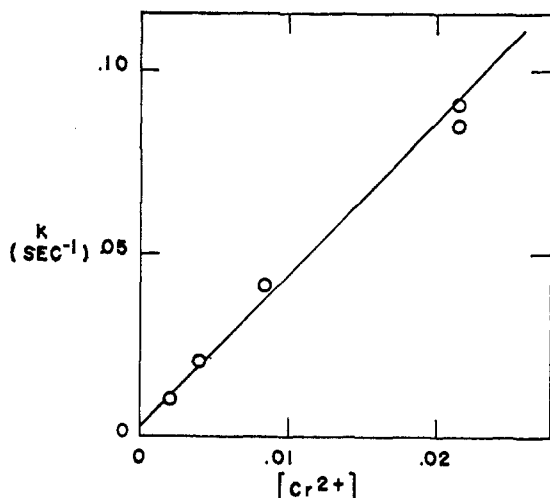


Figure 1. Plots of k vs. $[\text{Cr}^{2+}]$ for the reaction with $\text{cis}-(\text{H}_2\text{O})_4\text{Cr}(\text{CN})_2^+$; see eq 7. Conditions: 25.0° , 1.00 M ionic strength, reaction followed at 460 nm .

lithium perchlorate. First-order kinetics were followed at some wavelengths, especially in the vicinity of the long-wavelength maximum of the reactant complex. At other wavelengths slower subsequent changes, smaller in magnitude, were noted, but the first stage rates were in agreement with those at wavelengths free of this complication. The origin of the slower change is not known. These observations are consistent with the production of one or more intermediates, but the slow stage cannot be attributed to the linkage isomer CrNC^{2+} , which reacts much more rapidly.⁸

The first-order rate constant for the main first-stage reaction of each $\text{Cr}(\text{III})$ complex varied linearly with $[\text{Cr}^{2+}]$, as shown in Figures 1 and 2. The rate constants were independent of $[\text{H}^+]$, and the values for $\text{Cr}(\text{CN})_3$ and $\text{Cr}(\text{CN})_2^+$ were remarkably similar. The first-order rate constants are given by eq 9 and 10.²²

$$\text{Cr}(\text{CN})_2^+: k_{\text{obsd}} = 0.0025 + 4.19 [\text{Cr}^{2+}] \text{ sec}^{-1} \quad (9)$$

$$\text{Cr}(\text{CN})_3: k_{\text{obsd}} = 0.0036 + 4.56 [\text{Cr}^{2+}] \text{ sec}^{-1} \quad (10)$$

It is clear that additional and detailed studies on the stoichiometry, kinetics, and mechanism of these reactions are needed. As noted below, there are many likely intermediates even in a single reaction system.

Interpretation and Discussion

Exchange Reaction of Cr^{2+} and CrCN^{2+} . A number of chromium(III) complexes with the general formula $(\text{H}_2\text{O})_5\text{CrX}^{2+}$ have been found to undergo electron exchange with chromium(II) (eq 1) at a measurable rate. Such exchange reactions do not lead to net chemical change. During the time required for Cr^{2+} - CrCN^{2+} exchange we observed no other reactions, although it has recently been found^{23,24} that two other processes may compete with simple isotopic exchange in some cases. The competing reactions are aquation and chromium(II)-catalyzed aquation. These reactions are generally rather slow, however, and usually become important only after isotopic exchange equilibrium has been established.

(22) The original data are given in ref 1b.

(23) D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, **88**, 3450 (1966).

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

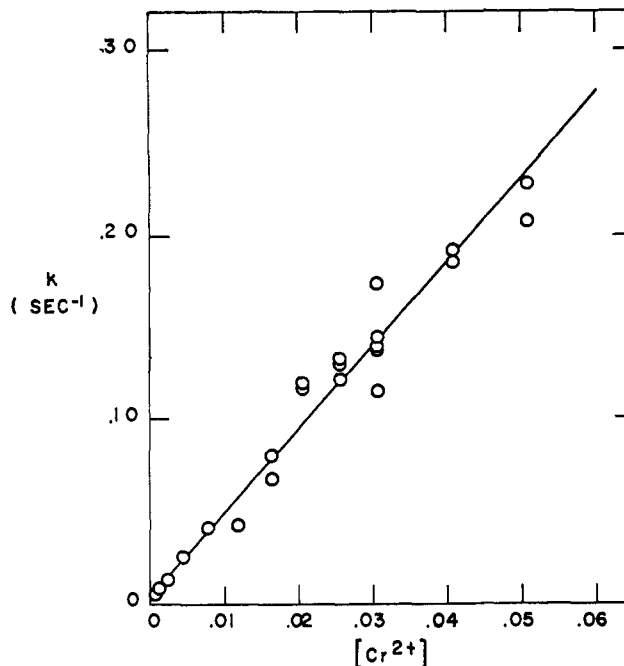


Figure 2. Plots of k vs. $[\text{Cr}^{2+}]$ for the reaction with $1,2,3-(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_3$; see eq 8. Conditions: 25.0° , 1.00 M ionic strength, reaction followed at 440 nm .

It was mentioned above that interference from aquation of CrCN^{2+} could be minimized by restricting exchange experiments to $[\text{H}^+] \leq 0.35\text{ M}$. The second side reaction is the chromium(II)-catalyzed aquation of CrCN^{2+} , whose rate we have measured.¹⁹ The catalysis rate law exhibits an inverse dependence upon $[\text{H}^+]$, and the value of k_c so defined (eq 11) we estimate

$$-d[\text{CrCN}^{2+}]/dt = k_c[\text{CrCN}^{2+}][\text{Cr}^{2+}]/[\text{H}^+] \quad (11)$$

to be $ca. 1 \times 10^{-4}\text{ sec}^{-1}$ at 15° . On this basis one calculates that at $[\text{H}^+] = 0.05\text{ M}$ the half-life for catalyzed aquation will be in the range of 10–17 hr for $0.01 < [\text{Cr}^{2+}] < 0.017\text{ M}$, whereas the exchange data cited in Table I at $[\text{H}^+] = 0.05\text{ M}$ represent values of $t_{1/2}$ in the range of 0.1–0.3 hr. Under the conditions chosen for our study of the kinetics of the exchange reaction, both side reactions proved to be of negligible importance.

An additional point of information concerning the exchange process in question was provided by the periodic sampling and analysis for chromium(II) during the course of each run. The concentrations so determined generally remained constant to within 2% during the course of the exchange. These analyses were carried out primarily to obtain an accurate value for $[\text{Cr}^{2+}]$ needed to define the rate constant in a particular run. They also served to demonstrate that the exchange reaction was not accompanied by side reactions leading to net consumption of chromium(II).

Electron exchange occurs without net loss of cyanide from the primary coordination sphere of $\text{Cr}(\text{III})$. It is clear, on this basis, that cyanide simultaneously coordinates to both chromium atoms in the transition state. Were cyanide not acting as a bridging ligand, net aquation of CrCN^{2+} would have been noted. Since CrCN^{2+} in acid solution is quite unstable with respect to aquation (eq 5), such loss of cyanide, in effect, would have amounted to an irreversible process.

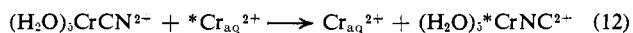
The rate equation for Cr(II)–Cr(III) exchange contains two numerator terms, suggesting a mechanism consisting of two parallel reaction pathways. The first term is independent of $[H^+]$. This pathway appears to be analogous to that for Cr(II)–Cr(III) electron exchange for the Cr(III) complexes $(H_2O)_5CrX^{2+}$ with $X^- = F^-, Cl^-, N_3^-,$ and NCS^- .²⁻⁴ The second term in the rate law varies as $1/[H^+]$. This pattern of $[H^+]$ dependence appears similar to the Cr(II)–Cr(III) exchange processes in the two systems Cr^{2+} – $Cr(H_2O)_6^{3+}$ and Cr^{2+} – $Cr(H_2O)_5NH_3^{3+}$,⁶ where exchange in each case occurs predominantly by rates varying as $1/[H^+]$. In the latter reactions, however, the bridging ligand is presumed to be hydroxide ion,⁶ whereas cyanide is a bridging ligand in the rate term $k' [CrCN^{2+}][Cr^{2+}]/[H^+]$. Thus the reactions of the conjugate bases $Cr(H_2O)_5OH^{2+}$ and $Cr(H_2O)_4(NH_3)OH^{2+}$ follow the pattern of the reactivity shown by the other complexes of Cr(III) with an anion X^- cited above and do not resemble the k_2 pathway for $CrCN^{2+}$.

A single precedent of $1/[H^+]$ rate dependence and X^- transfer in Cr(II)–Cr(III) exchange reactions has been noted in a related reaction. Schroeder and Espenson⁷ have found that the only detectable pathway for Cr(II)–Cr(III) exchange in the system Cr^{2+} – $Cr(H_2O)_5H_2PO_2^{2+}$ shows a rate that varies as $1/[H^+]$. In this system, too, the anionic ligand $H_2PO_2^-$ is transferred, and no net reaction occurs in the time required to establish isotopic equilibrium. The suggestion was made⁷ that this rate behavior for $CrH_2PO_2^{2+}$ can best be explained by invoking a doubly bridged transition state in which both OH^- and $H_2PO_2^-$ act as bridging ligands. This suggestion can be extended to the present $CrCN^{2+}$ reaction as well. The reason that these two complexes follow a pattern of reactivity quite different from most other $(H_2O)_5CrX^{2+}$ complexes is not clear.

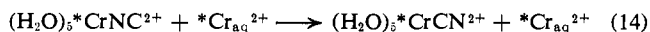
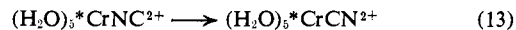
It should be noted, however, that the apparent novelty of the $[H^+]^{-1}$ term in the $CrCN^{2+}$ – Cr^{2+} and $CrH_2PO_2^{2+}$ – Cr^{2+} exchange reactions may be due to the relatively narrow range of $[H^+]$ employed for many other systems. Under the more limited conditions employed in the other reactions,²⁻⁴ the term in question would have been nearly undetectable for $CrCN^{2+}$ as well. For example, the exchange of $CrCN^{2+}$ was studied with $[H^+]$ as low as 0.01 *M*, and in the other reactions $[H^+]$ was generally 0.4–1.0 *M*. Alternatively, the postulated double-bridged mechanism for the $CrCN^{2+}$ – Cr^{2+} exchange by the term proportional to $1/[H^+]$ may offer especial advantages for this particular reaction, and the other reaction rates may be found to remain independent of $[H^+]$ down to quite low values.

In the case of $CrCN^{2+}$, the nonsymmetrical and the ambidentate nature of cyanide ion introduces other complications into a consideration of its reaction mechanism which will be discussed in the following section.

Possible Role of an Isocyano Complex of Cr(III). The isocyanochromium(III) ion is known to be an important metastable intermediate in the reaction of L_5CoCN^{2+} with Cr^{2+} .⁸ One can easily envisage that the same intermediate could be involved in the exchange reaction of $CrCN^{2+}$ and Cr^{2+} . This suggestion is illustrated by the following two-step reaction sequence in which chromium atoms originating in Cr^{2+} are labeled as $*Cr$ for the sake of clarity. In the first step (eq 12) the



isocyano complex is formed. The second step in the exchange is the linkage isomerization reaction, which has been studied independently and which is known to occur by two pathways, a spontaneous reaction (eq 13) and a Cr(II)-catalyzed isomerization (eq 14).^{8b} The



isomerization reactions are substantially faster than the electron-exchange reaction of $CrCN^{2+}$ and Cr^{2+} . Consequently one could not hope to detect $CrNC^{2+}$ were it so formed. On the other hand, application of the principle of microscopic reversibility to reactions 12 and 14, which are the reverse of one another, should enable one to learn more about a possible role of $CrNC^{2+}$ in the isomerization process.

There are two independent pathways for the exchange reaction and apparently only one pathway for the reaction of $CrNC^{2+}$ and Cr^{2+} .⁸ Since the latter reaction is independent of $[H^+]$,⁸ only the exchange rate term $k_1[CrCN^{2+}][Cr^{2+}]$ need be considered in this respect; the term $k_2[CrCN^{2+}][Cr^{2+}]/[H^+]$ is *not* the counterpart of a known rate term for the isomerization and *cannot*, therefore, involve $CrNC^{2+}$ as an intermediate.

The principle of microscopic reversibility requires that a pathway for $CrCN^{2+}$ – Cr^{2+} exchange exists which is the reverse of the Cr^{2+} -catalyzed isomerization; it does not require, however, that this pathway be the sole pathway or even that it contribute a detectable portion of the total exchange. The exchange term under consideration, $k_1[CrCN^{2+}][Cr^{2+}]$, may proceed exclusively through $CrNC^{2+}$, as shown above (remote attack), or a major portion may occur by a direct single-step reaction of Cr^{2+} and $CrCN^{2+}$ (adjacent attack). Since the level of $CrNC^{2+}$ remains negligibly low in an exchange experiment, one can do no more than say that remote attack must make at least a minor contribution, and it very well may make the sole contribution.

On the basis of such arguments based on microscopic reversibility, one can put an upper boundary on the equilibrium quotient for isomerization of $CrNC^{2+}$ to $CrCN^{2+}$. Define $Q_i = [CrCN^{2+}]/[CrNC^{2+}] = k_c/k_1'$, where k_c is the specific rate of the Cr^{2+} -catalyzed isomerization of $CrNC^{2+}$ (eq 14)^{8b} and k_1' is the rate of $CrCN^{2+}$ – Cr^{2+} exchange that proceeds through $CrNC^{2+}$ ($k_1' \leq k_1$). The values at 25° are $k_c = 1.60 M^{-1} sec^{-1}$ ^{8b} and $k_1' \leq 0.077 M^{-1} sec^{-1}$, whence we compute that $Q_i \geq 21$. The greater the fraction of exchange that proceeds by a path other than that involving $CrNC^{2+}$, the larger is Q_i . For the reaction $CrNC^{2+} = CrCN^{2+}$ the value of ΔG° is ≤ -1.8 kcal mole⁻¹.

Reactions of Dicyano and Tricyano Complexes. The two-term rate equations (eq 9 and 10) found for each of these reactions suggest parallel reaction pathways. The small contributions of terms independent of $[Cr^{2+}]$ may correspond to spontaneous aquation. The rate constants for the reactions of the complexes with Cr^{2+} are rather close to one another. The simplest interpretation to be given these rate terms is that they correspond to the rate of Cr(II)–Cr(III) electron transfer through a single bridging cyanide ligand.

The processes appear deceptively simple. Several Cr(III) species are intermediates that may possibly arise in converting the higher complexes to $CrCN^{2+}$, and at least some of them are likely to be important. Among

the species to be considered are the dicyano- and monocyanochromium(III) complexes, both N- and C-bonded and/or mixed, and products of the subsequent reactions of each—spontaneous and catalyzed isomerization and aquation. We have not resolved or identified the secondary absorption changes that were noticeable at wavelengths where the main absorption bands of $\text{Cr}(\text{CN})_3$, $\text{Cr}(\text{CN})_2^+$, and CrCN^{2+} were not too intense. It seems probable that these unaccounted for changes, which were of considerably smaller magnitude, could result from minor amounts of such species. A detailed study of the reactions of $\text{Cr}(\text{CN})_3$ and $\text{Cr}(\text{CN})_2^+$ would be complicated by these features, but they offer intriguing possibilities of reaction mechanisms.

Comparison of Cyanide and Thiocyanate Reactions. Some similar studies have been carried out on the isomeric thiocyanato complexes CrSCN^{2+} and CrNCS^{2+} . The kinetics of the chromium(II)-catalyzed conversion of CrSCN^{2+} to CrNCS^{2+} has been studied,¹¹ as has the slow Cr(II)–Cr(III) electron exchange between CrNCS^{2+} and Cr^{2+} .³ Some of the exchange reaction may proceed by adjacent attack leading directly to CrNCS^{2+} without intervention of CrSCN^{2+} (and, in fact, a major portion may do so). The equilibrium quotient for the conversion CrSCN^{2+} – CrNCS^{2+} is given by k_c/k_{ex}' , where k_c is the rate constant of $\text{CrSCN}^{2+} + \text{Cr}^{2+}$ ($40 \text{ M}^{-1} \text{ sec}^{-1}$)¹¹ and k_{ex}' is the rate constant for remote (S) attack of Cr^{2+} on CrNCS^{2+} . If one assumes all of the exchange proceeds through the linkage isomer, the equilibrium quotient is 3×10^5 , whereas if one assumes the rather arbitrary division of the observed exchange rate into remote and adjacent attack contributions, following Haim and Sutin,¹¹ the value of Q_i so calculated is 1×10^6 . For the same reasons discussed in the case of CN^- , these equilibrium quotients represent lower limits; the true value may be a good deal larger if adjacent attack in the exchange reaction makes a more important contribution than assumed. In any event, a comparison of NCS^- and CN^- leads one to see that the isomerization process is considerably more closely balanced for cyanide ($Q_i \geq 21$) than for thiocyanate ($Q_i \geq 3 \times 10^5$). This is a most remarkable result in that a considerable number of cases have recently been found where, in other complexes, the S-bonded form is the preferred structure, whereas for cyanide only the C-bonded configuration is the more stable in known complexes.²⁵ It must be pointed out, however, that this interpretation of relative isomeric stabilities rests on values of Q_i that are but lower limits. If adjacent attack predominates over remote attack for $\text{CrCN}^{2+} + \text{Cr}^{2+}$, and the reverse holds for $\text{CrNCS}^{2+} + \text{Cr}^{2+}$, then the Q_i values would not show the large difference as computed here. This seems to us less likely, however, and we accept the provisional conclusion that for $\text{Cr}(\text{H}_2\text{O})_5^{3+}$ complexes the two forms of the cyanide complex are more closely balanced than the two forms of the thiocyanate.

Unfortunately, there is at hand no way of measuring the relative importance of adjacent and remote attack

(25) Synthesis of complexes reported to contain N-bonded isocyano ligands has been reported by K. Kuroda and P. S. Gentile [*Inorg. Nucl. Chem. Letters*, 3, 151 (1967)], in work reported subsequent to completion of these studies. The ability to carry out such syntheses is consistent with the small energy difference cited here.

in the exchange reactions of $^*\text{Cr}^{2+}$ with CrNC^{2+} and CrCN^{2+} , so that the point in question cannot be resolved by an experiment on the exchange reaction.

A further remarkable difference was noted between thiocyanate and cyanide in comparing the isomerization and exchange reactions of each. In the case of CrNC^{2+} and Cr^{2+} , k_i was independent of $[\text{H}^+]$ ⁸ (once the acid form CrNCH^{3+} was taken into account), whereas for $\text{CrSCN}^{2+} + \text{Cr}^{2+}$ two rate terms were observed, with the second term showing a dependence upon $1/[\text{H}^+]$.¹¹ On the other hand, the reverse situation held for exchange. In the case of $\text{CrCN}^{2+} + ^*\text{Cr}^{2+}$, $k_{ex} = k_1 + k_2/[\text{H}^+]$, whereas for $\text{CrNCS}^{2+} + \text{Cr}^{2+}$, no H⁺ dependence was sought.³ Since the exchange term for CrCN^{2+} of the form $k_2/[\text{H}^+]$ had no counterpart in linkage isomerization, CrNC^{2+} could not have been involved in the exchange along this pathway, according to the principle of microscopic reversibility (as pointed out earlier). On the other hand, the observation¹¹ that a term proportional to $1/[\text{H}^+]$ makes a substantial contribution to the linkage isomerization reaction of CrSCN^{2+} and Cr^{2+} requires that such a term be important in exchange.^{26–28} The exchange was studied at a single $[\text{H}^+]$,³ and this prediction has yet to be verified. Haim and Sutin¹¹ attribute the $1/[\text{H}^+]$ term in the reaction of CrSCN^{2+} and Cr^{2+} to a doubly bridged transition state made from *cis*- $\text{Cr}(\text{SCN})(\text{OH})^+$ and Cr^{2+} . If one makes the assumption that remote and adjacent attack are equally important in both pathways for isomerization in $\text{CrSCN}^{2+} + \text{Cr}^{2+}$, the predicted value of k_2 in the equation $k_2[\text{CrNCS}^{2+}][^*\text{Cr}^{2+}]/[\text{H}^+]$ is $\sim 7 \times 10^{-6} \text{ sec}^{-1}$. This term should make an easily detected contribution to the exchange rate, carrying 84% of the exchange at $[\text{H}^+] = 0.01 \text{ M}$.

Acknowledgment. We are grateful to Professor W. B. Schaap for making available the details¹⁰ of his preparations of $\text{Cr}(\text{CN})_2^+$ and $\text{Cr}(\text{CN})_3$ prior to publication, to Professor A. F. Voigt for providing the scintillation counter used in this work, and to Professor D. S. Martin for helping us to consider the details of the exchange kinetics.

(26) R. M. Krupka, H. Kaplan, and K. J. Laidler, *Trans. Faraday Soc.*, 62, 2754 (1966).

(27) R. L. Burwell, Jr., and R. G. Pearson, *J. Phys. Chem.*, 70, 300 (1966).

(28) It has been pointed out^{26,27} that incorrect application of the principle of microscopic reversibility to reaction kinetics, especially to exclude possible mechanisms, can lead to false deductions. The arguments for thiocyanate and cyanide must be carefully distinguished; the situation is sufficiently complicated that the following summarizing restatement may provide clarification. The reactions between Cr^{2+} and the unstable forms of the Cr(III) complexes, CrNC^{2+} and CrSCN^{2+} , involve remote attack, since net isomerizations to the stable CrCN^{2+} and CrNCS^{2+} complexes occur. The reverse reactions accomplish isotopic exchange of the stable isomeric complexes and Cr^{2+} . Applying the principle of microscopic reversibility to this situation, we conclude that a pathway for catalyzed isomerization necessarily provides an exchange path, but that the converse does not hold. In the cases at hand, the work of Haim and Sutin,¹¹ which established the isomerization rate term $k[\text{CrSCN}^{2+}][\text{Cr}^{2+}]/[\text{H}^+]$, led to our prediction of a yet undiscovered exchange pathway. The cyanide reactions illustrate clearly that the isotopic exchange mechanism need not be limited to a reaction that is the reverse of ligand isomerization. The over-all exchange rate may contain additional terms, which might have the same kinetic form and thereby be rendered indistinguishable. Such extra terms may contribute a major or a minor part of the over-all exchange process. Given the existence of an exchange term, e.g., $k_2[\text{CrCN}^{2+}][\text{Cr}^{2+}]/[\text{H}^+]$, one cannot conclude that reverse constitutes a pathway for isomerization (and, in fact, the term $[\text{CrNC}^{2+}][\text{Cr}^{2+}]/[\text{H}^+]$ did not make a contribution to isomerization within the precision of our data^{8b}).