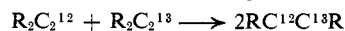


McOmie⁶ suggests that the exchange



may prove successful under the conditions of our experiment for properly selected substituents.

Acknowledgments. Grateful acknowledgment is made for the support of this work by the Atomic Energy Commission under Contract AT(30-1)-3211. We thank Dr. W. F. Wilcox for a helpful discussion of the cyclobutadiene problem.

(6) W. Baker and J. F. W. McOmie, ref. 5, p. 43.

S. H. Bauer, Peter Jeffers

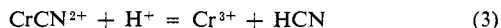
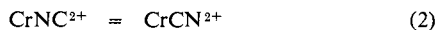
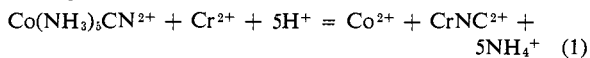
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Kinetics and Mechanisms of the Formation, Isomerization, and Aquation Reactions of the Isomeric Cyanochromium(III) Ions¹

Sir:

This communication describes the results of a kinetic study of the reaction of cyanopentaamminecobalt(III) and chromium(II) ions in acidic perchlorate solution in which a novel intermediate, the nitrogen-bonded isocyanochromium(III) ion, plays an important role. The over-all reaction occurs in three stages, which we interpret (as justified below) as corresponding to the three changes



Since each step is substantially slower than the preceding one, it has been possible to study the three processes in kinetically isolated circumstances. Under typical concentration conditions at 15°, the oxidation-reduction process (eq. 1) is essentially complete within 15–30 sec., the linkage isomerism of cyanide ion (eq. 2) within *ca.* 10 min., and the subsequent aquation (eq. 3) within several hours. It is this fortunate separation of rates which allows us to formulate this relatively detailed description of the reaction.

Oxidation-Reduction Stage. The rate of disappearance of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ was followed spectrophotometrically at its two wave lengths of maximum light absorption, 3270 and 4400 Å. Kinetic runs were carried out over concentration ranges $0.9\text{--}7 \times 10^{-3} M$ in each reactant at 15.0° in 1.00 *F* HClO_4 . The data follow the mixed second-order rate law

$$-d[\text{Co}(\text{NH}_3)_5\text{CN}^{2+}]/dt = k_{ox}[\text{Co}(\text{NH}_3)_5\text{CN}^{2+}][\text{Cr}^{2+}] \quad (4)$$

with $k_{ox} = 61 \pm 6 M^{-1} \text{sec.}^{-1}$.

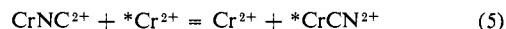
Linkage Isomerization Stage. The primary observations indicating that a second stage of reaction occurs were the continued appreciable changes in absorbance at some wave lengths over a period of several minutes after the primary reaction was essentially complete.²

(1) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 1727.

(2) At some wave lengths (*e.g.*, 3270 Å.), the absorbance falls sharply in the first stage, reaches a minimum, and then slowly rises to a steady value after 8–10 min.; at other wave lengths (*e.g.*, 4400 Å.), an initial sharp decrease in the first stage is noted, and the readings remain essentially constant during the succeeding several minutes; at still other

The data at 5200 Å., where the second stage of reaction exhibits the greatest changes in absorbance, proved the most accurate for kinetic analysis. These data fit a first-order rate equation, $-d \ln (A_\infty - A)/dt = k_i$. The value of k_i so calculated is independent of concentrations of products and of excess reactant, including chromium(II). The average value is $k_i = 9.2 \pm 0.5 \times 10^{-3} \text{sec.}^{-1}$. We postulate that this second stage corresponds to a first-order isomerization reaction (eq. 2) with the associated rate equation $-d[\text{CrNC}^{2+}]/dt = k_i[\text{CrNC}^{2+}]$. The evidence that this reaction is, in fact, the isomerization is summarized in the next section.

The lack of dependence of rate upon the concentration (or presence) of chromium(II) ion leads to the particularly striking conclusion that the isomerization reaction does *not* proceed by involving chromium(II) ion in an electron-transfer process, in which the bridging CN^- ligand becomes bonded to chromium(III) *via* the carbon end (eq. 5). It should be noted also that



Halpern has observed the intermediate species $\text{Co}(\text{CN})_5(\text{NC})^{3-}$ in basic solution.³

Characterization and Identification of the Isomeric Cyanochromium(III) Ions. The identification of the ion CrCN^{2+} is based primarily on three observations: the behavior during ion-exchange elution (related to the net ionic charge), analysis of the cyanide/chromium ratio in the separated complex, and the absorption spectrum. The complex is absorbed onto Dowex 50W-X8 (50–100 mesh) cation resin, and is eluted by concentrations of electrolyte (generally 1 *F* NaClO_4) which will elute other ions of charge +2, including Co^{2+} in these solutions. The complex can be satisfactorily separated from other species, including Co^{2+} , by slow elution with 1 *F* NaClO_4 –0.01 *F* HClO_4 from cation-exchange resin in a water-jacketed column kept at 0°. Analysis of these solutions for the cyanide/chromium ratio led to the value 0.90 in two separate preparations. The spectrum of this ion resembles that of other $\text{Cr}(\text{OH}_2)_5\text{X}^{2+,3+}$ ions, with two peaks of comparable intensity. The absorption maxima occur at 5250 and 3930 Å., shifted more toward higher energies than those of other similar ions.⁴ This is quite reasonable for CrCN^{2+} , since CN^- causes a ligand field splitting considerably higher than other common ligands.

The rapid decomposition ($t_{1/2} = 1.28 \text{min.}$ at 15°) of the precursor of CrCN^{2+} has prevented our determining its composition and structure as firmly as we did for CrCN^{2+} . One indication that the ion is CrNC^{2+} is just that the product of its disappearance is the isomeric CrCN^{2+} ; in addition, it seems a reasonable product of the primary reaction of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ and Cr^{2+} . A less subjective basis for this identification is its absorption spectrum. Extrapolation of the first-order absorbance change in the second stage of wave lengths (*e.g.*, 5200 Å.) the absorbance increases somewhat at the start, then continues to rise quite appreciably, reaching a steady value after 8–10 min. These observations are inconsistent with occurrence of a single reaction.

(3) J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).

(4) The long wave length absorption maxima (Å) of several ions $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+,3+}$, are: X = I⁻, 6500; Cl⁻, 6090; F⁻, 5950; H₂O, 5740; NCS⁻, 5700; NH₃, 5450. This order also represents increasing ligand field strength of X.

reaction to zero time leads, in effect, to a spectrum of this substance (and any excess reactant and Co^{2+}). The necessity for extrapolation and the corrections for other substances contribute some uncertainty, but we are able to fix the long wave length absorption maximum at 5450–5600 Å., which is quite reasonable for the ion CrNC^{2+} .^{5,6}

Aquation of CrCN^{2+} . In acid solution CrCN^{2+} slowly loses cyanide ion; $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ was identified as the product by its absorption spectrum. The rate of this reaction follows the pseudo-first-order rate equation

$$-d[\text{CrCN}^{2+}]/dt = k_{\text{aq}}[\text{CrCN}^{2+}] \quad (6)$$

Experiments performed at 25.0°, $C_{\text{HClO}_4} + C_{\text{NaClO}_4} = 1.00 F$, led to the values $10^4 k_{\text{aq}}$ (sec.⁻¹) = 0.15, 2.7, 3.7 at $C_{\text{HClO}_4} = 0.05, 0.45, 0.85$, respectively, with an rather high uncertainty of ca. 20%. The data appear to correlate with a rate equation involving a term in which $[\text{H}^+]$ appears to a positive power. This situation resembles that found for similar complexes of chromium(III) with strongly basic ligands, e.g., CrF^{2+} and CrN_3^{2+} ,⁸ where the term $k_1[\text{H}^+][\text{CrX}^{2+}]$ provides an important reaction pathway. It is unlikely that for most other complexes CrX^{2+} (e.g., $\text{X} = \text{I}^-, \text{Br}^-, \text{Cl}^-, \text{NCS}^-$)^{7,9-11} where only terms with negative or zero orders with respect to hydrogen ion are found. This behavior has been attributed to the fact that the strongly basic ligand is substantially protonated in the activated complex.^{7,8} The magnitude of ΔH^* and ΔS^* for each path should be particularly revealing in this connection.

We plan to study these processes in more detail, especially with regard to measuring the rate constants more accurately and studying the dependence of these rate constants upon hydrogen ion concentration and temperature. We hope to find conditions under which the isocyanide complex, CrNC^{2+} , can be isolated and characterized more completely.

(5) Shriver, *et al.*, estimate, from spectra of solids containing different CN^- arrangements, that nitrogen-bonded cyanide ion lies between H_2O and NH_3 in ligand field strength, and closer to the latter; our result is consistent with this formulation: D. I. Shriver, S. A. Shriver, and S. A. Anderson, *Inorg. Chem.*, **4**, 725 (1965).

(6) These observations do not exclude the possibility that the second stage of reaction is a first-order decomposition of a dinuclear cobalt-chromium ion, although this appears a less likely interpretation.

(7) T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).

(8) T. W. Swaddle and E. L. King, *ibid.*, **3**, 234 (1964).

(9) J. H. Espenson, *ibid.*, **3**, 968 (1964).

(10) F. A. Guthrie and E. L. King, *ibid.*, **3**, 916 (1964).

(11) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

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An Infrared Investigation of the Magnesium-Adenosine Triphosphate Complex

Sir:

The question of whether or not the Mg^{2+} ion in the Mg^{2+} -ATP complex is coordinated to the adenine moiety is of the greatest interest to biochemists.¹ The only two infrared investigations of this crucial point are in conflict.^{2,3} In the earlier paper, by Epp, *et al.*,²

(1) A. Szent Gyorgyi, "Bioenergetics," Academic Press Inc., New York, N. Y., 1957.

a comparison was made between ATP and Mg^{2+} -ATP spectra using KBr disks pressed from powder obtained by freeze-drying solutions *presumably* of one and the same pH, viz., pH 7. The reported spectra differed in that, in addition to a strong 1640 cm^{-1} band attributed to vibrations characteristic of a nonprotonated adenine moiety, the Mg^{2+} -ATP spectrum also contained a medium intensity band at 1685 cm^{-1} . The presence of this latter band was cited by these authors as evidence that in the Mg^{2+} -ATP complex the Mg^{2+} ion is attached to the adenine moiety and that the positively charged Mg^{2+} ion produces the same effect as a proton on the adenine vibrations.

The more recent investigation of Khalil and Brown³ was carried out in D_2O solution. These authors concluded that when the ratio of the absorbances of the 1630 and 1670 cm^{-1} bands equalled 1.2 a 50% protonation of the adenine moiety was indicated. The Mg^{2+} ion decreased the pD corresponding to this half-protonation to 4.4 from a value of 4.55 in absence of Mg^{2+} . However, they did *not* feel that this small pD lowering was due necessarily to coordination of Mg^{2+} by the adenine moiety, but pointed out that the ionizable adenine proton might simply experience an electrostatic field effect from the Mg^{2+} attached to the triphosphate group.

We have obtained solid-state spectra in the manner described by Epp, *et al.*, but have done so over a pH range of 3–9 by lyophilizing solutions containing equimolar concentrations (0.038 M) of Na_2ATP and MgCl_2 after adjustment to the various pH values with either HCl or NaOH. Two series of experiments, in duplicate, were run. In one series the original solutions contained no KBr, but the lyophilized powders were mixed with KBr powder in preparing the disks. In the second series the solutions contained 3.5% KBr initially. Spectra of ATP in the absence of Mg^{2+} were also obtained over the same pH range, both in the absence and in the presence of KBr initially.

Whether Mg^{2+} was present or absent the spectra show (i) a gradual decrease in the intensity of a 1695 cm^{-1} band simultaneously with a gradual increase of a 1650 cm^{-1} band as the pH of the original solution was raised from 3 to 9; (ii) no 1695 cm^{-1} band above pH 6; and (iii) about equal intensities for the 1695 cm^{-1} band of the pH 3 spectrum and the 1650 cm^{-1} band of the pH 6 spectrum (within about a 10% reproducibility).

These two bands show about equal intensity in the ATP spectra corresponding to pH 4.45 ± 0.15 , whether KBr was absent or present initially. The presence of Mg^{2+} ion caused only a small increase in the pH of equal band intensities, a pH value of 4.65 ± 0.15 being obtained in the absence of KBr and 4.9 ± 0.15 being obtained in the presence of KBr.

These results may appear to be at variance with those of both Epp, *et al.*, and Khalil and Brown. The cause of the discrepancy between our results and those of Epp, *et al.*, seems quite clear. The latter prepared their Mg^{2+} -ATP solution by adding Mg^{2+} ions to an ATP solution which had been adjusted to pH 7. A simple titration shows that such a solution actually has a pH

(2) A. Epp, T. Ramasarma, and L. R. Wetter, *J. Am. Chem. Soc.*, **80**, 724 (1958).

(3) F. L. Khalil and T. L. Brown, *ibid.*, **86**, 5113 (1964).